Day 15

Adsorption and **Catalysis**

Day 15 Outlines ...

- Concept of Surface Chemistry
- Concept of Adsorption
- Factors Affecting Adsorption of Gases on Solids
- Characteristics of Adsorption
- Catalysis
- Characteristics of Catalysis
- Homogeneous and Heterogeneous

Concept of Surface Chemistry

Surface chemistry deals with the phenomenon that occurs at the surface or interfaces. There are several properties of substances, particularly of solids and liquids and solids and gases, which depend upon the nature of the surface of interface.

Concept of Adsorption

Retaining of the molecular species on the surface of the solid is known as adsorption. The solid substance on the surface of which adsorption occurs is called adsorbent. The molecular species that get adsorbed on the solid surface due to intermolecular attractions are called adsorbate.

Rate of adsorption decreases with time whereas rate of absorption remains constant with time.

Positive and Negative Adsorption

If the concentration of an adsorbate at the surface of adsorbent is more than in the bulk of the adjoining phases, it is called **positive adsorption.**

If concentration of an adsorbate at the surface of adsorbent is less than in the bulk of the adjoining phases, it is called **negative adsorption.**

Desorption and Sorption

The removal of the adsorbed substance from a surface is called **desorption**.

Sorption is a process in which adsorption and absorption take place simultaneously and it is difficult to determine the relative extent of adsorption and absorption. *e.g.*, dyes get adsorbed as well as absorbed on the cotton fibres.

Physisorption and Chemisorption

In physisorption, the particles of the adsorbate are held to the surface of the adsorbent by physical forces such as van der Waals' forces while in chemisorption, the molecules of the adsorbate are held to the surface of the adsorbate by chemical bonds.

Comparison between Physisorption and Chemisorption

S.No.	Physisorption	Chemisorption
1.	van der Waals' forces are very weak.	Chemical bonds are quite strong.
2.	It occurs at low temperature.	It occurs at high temperature.
3.	Heat of adsorption is low and it is in the range of 20-40 kJ/mol.	Heat of adsorption is high and it is in the range of 40-400 kJ/mol.
4.	It is reversible process.	It is an irreversible process.
5.	It is an instantaneous process.	It may be rapid or slow.
6.	ΔS is always negative.	ΔS is positive for endothermic process.
7.	In this, multilayer adsorption occurs and thus, adsorbed layer is several molecules thick.	In this, single layer adsorption occurs. Thus, adsorbed layer is only unimolecular in thickness.

- *Chemical adsorption in some cases is endothermic. For example, adsorption of hydrogen on glass surface and adsorption of highly hydrated solutes on solids.*
- *As the particles of the adsorbate are held on surface, ΔH and ΔS both are negative and $\Delta H > T\Delta S$. This is true in beginning. As adsorption proceeds ΔH decreases and $T\Delta S$ increases and ultimately $\Delta H = T\Delta S$ and $\Delta G = 0$. This state is called adsorption equilibrium.*

Factors Affecting Adsorption of Gases on Solids

Adsorption depends upon following number of factors

1. Nature of Adsorbent

A gas is adsorbed in different amounts on different adsorbents. Hydrogen is strongly adsorbed on nickel surface while it is weakly adsorbed on alumina surface under identical conditions.

The adsorption of gases on the surface of metals is called **occlusion**.

2. Nature of Adsorbate

Generally, the more liquefiable a gas is, the more readily will it be adsorbed. Easily liquefiable gases such as NH_3, HCl, Cl_2, SO_2, etc are readily adsorbed than permanent gases, such as O_2, H_2, N_2 etc.

3. Specific Area of Adsorbent

It is the surface area of adsorbent available for adsorption per gram of the adsorbate. The greater the surface area of the solid, the larger would be its adsorbing capacity.

4. Pressure of Gas

At a given temperature, the extent of adsorption will increase with the increase of pressure of the gas.

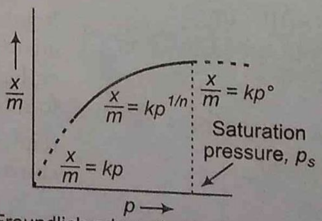
The extent of adsorption is measured as x/m, where m is the mass of adsorbent and x that of adsorbate. At low pressure, x/m varies linearly with p

$$\frac{x}{m} = kp^{1/n}$$

or $$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

At low pressure, $$\frac{x}{m} = kp$$

At high pressure, $$\frac{x}{m} = kp^{\circ}$$



Freundlich adsorption isotherm

This is called **Freundlich adsorption isotherm** at constant temperature.

Langmuir isotherm Freundlich isotherm fails at high pressure and is only for physical adsorption.

Langmuir isotherm is represented as

$$\frac{x}{m} = \frac{ap}{1 + bp} \quad (a \text{ and } b \text{ are constants})$$

At very high pressure, $(bp >> 1)$

$$\frac{x}{m} = \frac{a}{b}$$

At very low pressure, $(bp << 1)$

$$\frac{x}{m} = ap$$

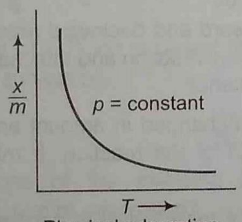
5. **Temperature**

Low temperature value favours the physical adsorption, but on increasing temperature physical adsorption decreases.

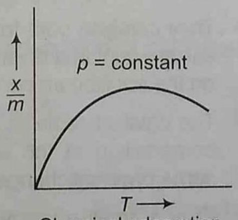
Whereas in case of chemisorption, x/m, initially increases with temperature and then decreases.

The initial increase is due to the fact that chemisorption requires activation energy.

The graph between extent of adsorption $\left(\frac{x}{m}\right)$ and temperature T is called **adsorption isobar**.



Physical adsorption



Chemical adsorption

Adsorption from Solutions

Solids adsorb dissolved substances from solutions. For example, adsorption of colour impurities by activated carbon in decolourising of solutions. Freundlich adsorption isotherm and Langmuir adsorption isotherm are also applicable to adsorptions from solutions.

Freundlich adsorption isotherm,

$$\frac{x}{m} = kC^{1/n} \quad (n > 1)$$

Langmuir adsorption isotherm,

$$\frac{x}{m} = \frac{aC}{(1 + bC)}$$

Langmuir adsorption isotherm is applicable only to chemisorption.

Characteristics of Adsorption

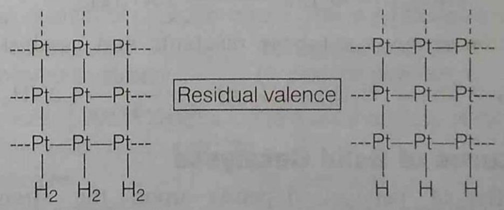
Important characteristics of adsorption are as follows

- **Specificity and Selectivity**
  Adsorption is specific and selective phenomenon, which strictly refers to the existence of a higher concentration of any particular component at the surface of a liquid or a solid phase.
- **Exothermic Process**
  Adsorption is accompanied with decrease in free energy of the system. In adsorption, there is a decrease in entropy of the system.

  As, $\Delta G < 0$ and $\Delta S < 0$,

  Therefore, $\Delta H < 0 \quad (\Delta H = \Delta G + T\Delta S)$

  Hence, the adsorption is associated with decrease in enthalpy of the system. Thus, *adsorption is always an exothermic process.*
- **Residual Valency Bonds**
  The atoms or molecules of a solid surface have unbalanced or residual attractive forces on the surface, which can hold adsorbate particles together. Thus, the adsorbed atoms or molecule can be held on the surface of a metal by physical van der Waals' forces or chemical forces due to residual valence bonds.



Molecular adsorption Atomic adsorption

- **Extent of Adsorption**
  All solids adsorb gases to some extent. Adsorption is not very pronounced unless an adsorbent possesses a large surface area for a given mass. Various types of charcoals, silica gels, metal, etc., are used as adsorbents. Appreciable adsorption also takes place on some smooth surfaces, such as those of platinum and glass. Charcoal and other solids gain increased power of adsorption on heating at low pressure with various gases or in air or vacuum at temperature varying from 350–1000°C. Such treated charcoal is called **activated charcoal** and the process is called **activation**. On activation
  - the hydrocarbons and other impurities are removed from charcoal. the surface area may increase due to chemical interaction with the oxidising agent which is used as **activator.**
  - the degree of unsaturation of the surface atoms may be increased.

Catalysis

The catalyst change the rate of reaction by providing an alternate path of different activation energy. This phenomenon is known as ***catalysis****.*

Promoters and Inhibitors

Promoters are the substances which can increase the efficiency of a catalyst. These are also known as coenzymes or activators. Inhibitors are the substances which can make the catalyst inactive. *e.g.*, Mg^{2+} acts as activators for many enzymes while $C_2O_4^{2-}$ and F^- act as inhibitors as they form complex with Mg^{2+}.

- *The catalytic poisoning is specific in nature. It is of two types; temporary poisoning and permanent poisoning.*
- *In former case, catalyst surface is regenerated by scratching the surface while in later catalyst surface is regenerated by chemical treatment.*

Homogeneous and Heterogeneous Catalysis

In homogeneous catalysis, reactants and catalyst should be in same phase.

e.g., $$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

In heterogeneous catalysis reactants and catalyst are in different phase. $N_2(g) + 3H_2(g) \xrightarrow[\text{divided Fe}(s)]{\text{Finely}} 2NH_3(g)$

Features of Solid Catalysts

Activity of catalyst depends upon the strength of chemisorption to a large extent.

Selectivity means a given substance can act as catalyst only in a particular reaction and not for all reactions. For example,

(i) $CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$

(ii) $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

(iii) $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH(g)$

Enzyme Catalysis

Enzymes are biochemical catalysts. They are proteins and extremely specific in nature. For example,

$$NH_2CONH_2 + H_2O \xrightarrow{\text{Urease}} 2NH_3 + 2CO_2$$

Common steps for all enzyme catalysed reactions are

(i) $E + S \rightleftharpoons ES$ (fast, reversible)

(ii) $ES \longrightarrow E + P$ (slow, rate determining)

Autocatalysis

The phenomenon in which one of the products formed during the reaction acts as catalyst for the reaction. For example,

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

In this reaction Mn^{2+} ions act as autocatalyst.

Induced Catalysis

In this type of catalysis, one reaction influences the rate of other reaction which does not occur under ordinary condition. For example, the reduction of $HgCl_2$ by oxalic acid is slow but becomes faster if reduction is made in mixture of $KMnO_4$ and $HgCl_2$; where both are reduced. Reduction of $KMnO_4$ thus induces the reduction of $HgCl_2$.

Characteristics of Catalysts

Some important characteristics of catalysts are discussed below

- They become temporarily involved in a reaction, providing an alternative reaction path of lower activation energy than that for the uncatalysed reaction.
- They catalyse both forward and backward reactions to the same extent in a reversible reaction and thus have no effect on the equilibrium constant.
- The catalyst remains unchanged in amount and chemical composition at the end of the reaction. It may undergo some physical change.
- Only a small quantity of the catalyst is generally needed. One mole of colloidal platinum in 10^8 L can catalyse decomposition of H_2O_2.
- In certain reactions, the rate of the reaction is dependent on the concentration of the catalyst. *e.g.*, Rate of inversion of cane sugar is dependent on the concentration of H^+ used as catalyst.
- Rate of the reaction in certain heterogeneous reaction varies with surface area of the catalyst. Hence, finely divided metals are preferred in the form of catalyst.
- The catalyst does not initiate the reaction and are specific in their action. *e.g.*, starting from H_2 and CO, 3 different products are possible using different catalysts as

$$CO(g) + 3H_2(g) \xrightarrow{NI} CH_4(g) + H_2O(g)$$

$$CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH(g)$$

$$CO(g) + H_2(g) \xrightarrow[250°C]{Cu} HCHO$$

Practice Zone

DAY
15

1. The Langmuir adsorption isotherm is deduced using the assumption
   (a) the adsorption takes place in multilayer
   (b) the adsorbed molecules interact with each other
   (c) the adsorption sites are equivalent in their ability to absorb the particles
   (d) the heat of adsorption varies with coverage.

2. The minimum energy level necessary to permit a reaction to occur is
   (a) internal energy
   (b) threshold energy
   (c) activation energy
   (d) free energy

3. In Zeigler Natta polymerisation of ethylene, the active species is
   (a) $AlCl_3$
   (b) Et_3Al
   (c) CH_2CH_2
   (d) Ti^{3+}

4. Lake test of Al^{3+} ion is based on adsorption of blue litmus on solid surface of
   (a) Al
   (b) $Al(OH)_3$
   (c) Al_2O_3
   (d) $AlCl_3$

5. Which one of the following is not applicable to the phenomenon of adsorption? **[NCERT Exemplar]**
   (a) $\Delta H > 0$
   (b) $\Delta G < 0$
   (c) $\Delta S < 0$
   (d) $\Delta H < 0$

6. Physical adsorption becomes appreciable at
   (a) high temperature
   (b) room temperature
   (c) low temperature
   (d) None of the above

7. $KClO_3$ on heating decomposes into KCl and O_2. If some MnO_2 is added the reaction goes much faster because
   (a) MnO_2 decomposes to give oxygen
   (b) MnO_2 acts as catalyst
   (c) MnO_2 provides heat by reacting
   (d) MnO_2 provides better contact

8. The efficiency of an enzyme in catalysing a reaction is due to its capacity
   (a) to form an enzyme substrate complex
   (b) to decrease the bond energies of the substrate molecule
   (c) to change the shape of the substrate molecule
   (d) None of the above

9. Zeolites
   (a) are microporous alumino silicates
   (b) have general formula $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot mH_2O$
   (c) have pore sizes between 260 pm to 740 pm
   (d) All of the above

10. Following reaction is catalysed by $Br^-(aq)$

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

   This is an example of
   (a) homogeneous catalysis
   (b) heterogeneous catalysis
   (c) Both (a) and (b)
   (d) None of these

11. The decomposition of H_2O_2 may be checked by adding small quantity of phosphoric acid. This is an example of
   (a) neutralisation
   (b) negative catalysis
   (c) positive catalysis
   (d) catalytic poisoning

12. The void space in zeolites forms more than 50% of the total volume which is occupied by
   (a) silicates
   (b) aluminates
   (c) water molecules
   (d) Na^+, Mg^{2+} and Ca^{2+} ions

13. H_2O_2 can be prevented from decomposition in presence of
   (a) glycerine
   (b) acetanilide
   (c) Both (a) and (b)
   (d) None of these

14. When a litmus solution is shaken with a piece of charcoal
   (a) it is decolourised
   (b) it turns red to blue
   (c) it turns blue to red
   (d) None of these

15. 50 mL of 1 M oxalic acid (molar mass = 126) is shaken with 0.5 g of wood charcoal. The final concentration of the solution after adsorption is 0.5 M. What is the amount of oxalic acid adsorbed per gram of carbon?
   (a) 3.15
   (b) 1.575
   (c) 6.30
   (d) 12.60

16. Surface area per gram of the adsorbent is called
   (a) molar surface area
   (b) normal surface area
   (c) specific surface area
   (d) equivalent surface area

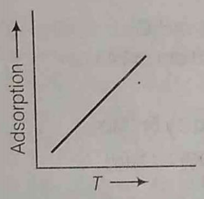
17. In the Freundlich adsorption equation $x/m = kp^{1/n}$, the value of n is

(a) always greater than one
(b) always smaller than one
(c) always equal to one
(d) greater than one at low temperature and smaller than one at high temperature.

18. Who got the Nobel Prize for the study of catalytic reactions?

(a) Landsberger
(b) Dalton
(c) Berzelius
(d) van't Hoff

19. Following is the variation of physical adsorption with temperature

(a)


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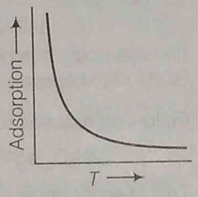

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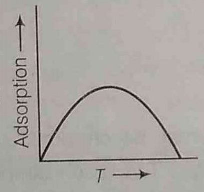

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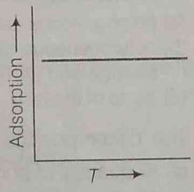


20. In the stoichiometry of natural faujasite a zeolite with formula $Na_x[(AlO_2)_{56}(SiO_2)_{136}] \cdot 250H_2O$, the value of x is

(a) 12
(b) 56
(c) 136
(d) 256

21. Soaking of water by a sponge is an example of

(a) simple adsorption
(b) physical adsorption
(c) chemisorption
(d) absorption

22. The volume of the gases H_2, CH_4, CO_2 and NH_3 adsorbed by 1 of activated charcoal at 298 K are in order

(a) $H_2 > CO_2 > CH_4 > NH_3$
(b) $H_2 > CH_4 > CO_2 > NH_3$
(c) $NH_3 > CO_2 > CH_4 > H_2$
(d) $NH_3 > CH_4 > CO_2 > H_2$

23. Amount of gas adsorbed per gram of adsorbent increases with pressure, but after certain limit is reached, adsorption becomes constant. It is due to

(a) multilayers are formed
(b) desorption takes place
(c) temperature is increased
(d) absorption also starts

24. In which of the following reactions heterogenous catalysis is involved?

(i) $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$
(ii) $2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$
(iii) $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$
(iv) $CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl\ (l)} CH_3COOH(aq) + CH_3OH(aq)$

[NCERT Exemplar]

(a) (ii), (iii)
(b) (ii), (iii) and (iv)
(c) (i), (ii) and (iii)
(d) (iv)

25. It is instructed that automobiles with catalytic converter must use unleaded gasolines because

(a) leaded gasolines may give more fumes
(b) surface of the catalyst is rendered ineffective by adsorption of lead
(c) automobiles with catalytic converter cannot run on leaded gasolines
(d) unleaded gasoline is cheaper

26. Surface of the eye is protected from bacterial infection by enzyme

(a) carbonic anhydrase
(b) urease
(c) lysozyme
(d) zymase

27. Which of the following statements is incorrect?

(a) Catalysts only accelerate the rate of chemical equation
(b) Catalysts connot start a chemical reaction
(c) Catalysts can retard the rate of a chemical reaction
(d) Catalysts can expedite and retard the rate of a chemical reaction

28. Which one of the following is an example of homogeneous catalysis?

(a) Acid hydroysis of methyl acetate
(b) Catalytic conversion of water gas to methanol
(c) Catalytic conversion of SO_2 to SO_3 in contact process
(d) Haber process of synthesis of ammonia

29. Which of the following small sized elements can replace the silicon and aluminium in the frame work at zeolites?

(a) Boron
(b) Magnesium
(c) Phosphorus
(d) All of these

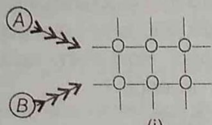
30. Which of the following assumptions is not correct about Langmuir adsorption isotherm?

(a) The solid surface is homogeneous and has a fixed number of adsorption sites
(b) Every adsorption site is equivalent
(c) The adsorbed layer is not uniform all over the adsorbent
(d) The adsorbed gas behaves ideally in the vapour phase

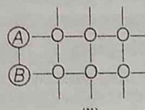
31. Which statement about enzymes is not correct?
(a) Enzymes are in colloidal state.
(b) Enzymes are catalysts.
(c) Enzymes can catalyse any reaction.
(d) Urease is an enzyme.

32. The catalyst, which is a zeolite, can convert alcohol to various types of gasoline (petrol) by shape selective catalysis is
(a) erionite (b) ZSM-5 (c) gemelinite (d) fanzasite

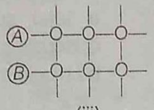
33. Arrange the following diagrams in correct sequence of steps involved in the mechanism of catalysis, in accordance with modern adsorption theory



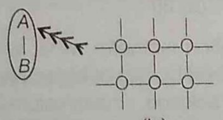
(i)



(ii)



(iii)



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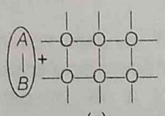


(v)

[NCERT Exemplar]

(a) (i) → (ii) → (iii) → (iv) → (v) (b) (i) → (iii) → (ii) → (iv) → (v)
(c) (i) → (iii) → (ii) → (v) → (iv) (d) (i) → (ii) → (iii) → (v) → (iv)

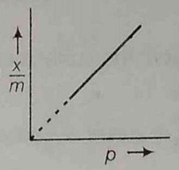
Directions (Q. Nos. 34 to 36) *Adsorption is specific and selective phenomenon, which strictly refers to the existence of a higher concentration of any particular component at the surface of a liquid or a solid phase. Adsorption may be physisorption or chemisorption. Adsorption is spontaneous and is accompanied with decrease in free energy of the system.*

It is always an exothermic process. Physical adsorption is reversible, not very specific, multilayer, appreciable only at low temperature and involves physical forces. Chemisorption is irreversible, appreciable at high temperature, specific, unilayer and involves transfer of electrons between gas and solid.

34. Which of the following statements is false?
(a) Adsorption may be monolayer or multilayer
(b) Increase of pressure increases the amount of adsorption
(c) Increase of temperature may decrease the amount of adsorption
(d) Particle size of adsorbent will not affect the amount of adsorption

35. Adsorption is a surface phenomenon because
(a) adsorbent has large surface area
(b) chemical compounds formed are not on the surface of adsorbent
(c) only the surfaces of the adsorbent have unutilised valencies
(d) None of the above

36. Which of the following is an adsorption isotherm?

(a)


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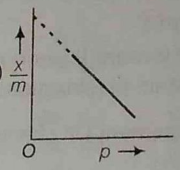

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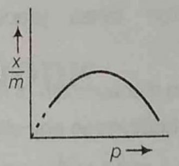

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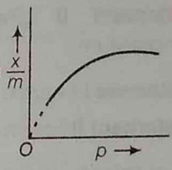

Directions (Q. Nos. 37 and 38) *Enzymes are complex, biological, nitrogenous, macromolecules derived from living organisms and thus, phenomenon is also named as biological or biochemical catalysis. Enzyme catalysed reactions are highly specific, normally hydrolytic and takes place with evolution of gases. Rate of enzyme catalysed reactions depends upon concentration of enzyme. Favourable range of pH is 5 to 7 and optimum temperature is nearly 30°C for enzyme catalysed reactions.*

37. Select the incorrect statement.
(a) The rate of enzyme catalysed reaction also depends upon enzyme concentration
(b) The rate of enzyme catalysed reaction depends upon ionic strength
(c) The rate of enzyme catalysed reaction first increases with temperature and then decreases after attaining optimum temperature
(d) The increase in activity of protein as enzyme is due to denaturation

38. Organic catalysts differ from inorganic catalysts
(a) by acting at very high temperature
(b) by acting at low temperature
(c) being used up
(d) being proteinous in nature

Directions (Q. Nos. 39 to 42) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*
(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

39. **Statement I** Zeolites are water softener as well as catalyst.
Statement II The catalytic action of zeolites is based upon their shape selectivity.

40. **Statement I** The molecules on the surface have higher energy.

Statement II During adsorption, the surface of solid is in a state of relaxation.

41. **Statement I** In chemisorption, all gases are adsorbed on all sides.

Statement II Chemisorption takes place at low temperature.

42. **Statement I** Enzyme catalysed reactions are of first order.

Statement II Enzyme never undergoes any change.

43. 1g of charcoal adsorbs 100 mL of 0.5 M CH_3COOH to form a monolayer, and thereby the molarity of CH_3COOH reduces to 0.49 M. What is the surface area of charcoal used by each molecule of acetic acid?

[Surface area of charcoal = $3.01 \times 10^2\ m^2/g$]

(a) $6.02 \times 10^{-20}\ m^2$
(b) $5.00 \times 10^{-19}\ m^2$
(c) $3.01 \times 10^{-2}\ m^2$
(d) $2.00 \times 10^{-19}\ m^2$

44. In an adsorption experiment, a graph between log x/m *versus* log p was found to be linear with a slope of 45°. The intercept on the log x/m axis was found to be 0.3010. The amount of the gas adsorbed per gram of charcoal under a pressure of 0.5 atm will be

(a) 1.0 g
(b) 0.5 g
(c) 2.0 g
(d) 2.5 g

45. The following data were obtained for the adsorption of CO on 3 g of charcoal at 0°C.

Pressure, p(mm)	180	540
Volume of gas adsorbed x (cc)	16.5	38.1

The values of constants k and n used in Freundlich equation will be respectively

(a) $\bar{1}.0188$, 1.31
(b) 0.1044 $cm^3 g^{-1}$, 1.31
(c) − 0.9812 $cm^3 g^{-1}$, 1.31
(d) − 0.9812 $cm^3 g^{-1}$, log3

46. It is said that finely divided catalyst has greater catalytic activity than solid in compact form. For a catalysed reaction, a total surface area of 6291456 cm^2 is required for adsorption of gaseous reactants. How many splits should be made of cube exactly 1 cm in length?

(a) 5
(b) 10
(c) 15
(d) 20

47. Applying Freundlich adsorption isotherm, what will be the amount of acetic acid adsorbed by 1kg of blood charcoal at 25°C from a 5% vinegar solution (mass/volume) if the concentration is expressed in molarity (mol dm^{-3}) and x/m is mass of the solute adsorbed per gram of adsorbent.

[Given, $k = 0.160$, and $n = 2.32$]

(a) 0.1481 g
(b) 148.1 g
(c) 0.837 g
(d) 14.81 g

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48. According to Freundlich adsorption isotherm which of the following is correct? **[AIEEE 2012]**

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

(b) $\frac{x}{m} \propto p^1$

(c) $\frac{x}{m} \propto p^{1/n}$

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

49. Which of the following statements is incorrect regarding physisorptions? **[AIEEE 2009]**

(a) It occurs because of van der Waals' forces
(b) More easily liquefiable gases are adsorbed readily
(c) Under high pressure it results into multi molecular layer on adsorbent surface
(d) Enthalpy of adsorption ($\Delta H_{adsorption}$) is slow and positive

50. In Langmuir's model of adsorption of a gas on a solid surface **[AIEEE 2006]**

(a) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered
(b) the adsorption at a single site on the surface may involve multiple molecules at the same time
(c) the mass of gas striking a given area of surface is proportional to the pressure of the gas
(d) the mass of gas striking a given area of surface is independent of the pressure of the gas

51. Rate of physisorption increases with **[IIT JEE 2003]**

(a) decrease in temperature
(b) increase in temperature
(c) decrease in pressure
(d) decrease in surface area

52. Which one of the following characteristics is not correct for physical adsorption? **[AIEEE 2003]**

(a) Adsorption on solids is reversible
(b) Adsorption increases with increase in temperature
(c) Adsorption is spontaneous
(d) Both enthalpy and entropy of adsorption are negative

Answers

1. (c)	**2.** (b)	**3.** (d)	**4.** (b)	**5.** (a)	**6.** (c)	**7.** (b)	**8.** (a)	**9.** (d)	**10.** (a)
11. (b)	**12.** (c)	**13.** (c)	**14.** (a)	**15.** (c)	**16.** (c)	**17.** (a)	**18.** (c)	**19.** (b)	**20.** (b)
21. (d)	**22.** (c)	**23.** (a)	**24.** (a)	**25.** (b)	**26.** (c)	**27.** (a)	**28.** (a)	**29.** (d)	**30.** (c)
31. (c)	**32.** (b)	**33.** (b)	**34.** (d)	**35.** (c)	**36.** (d)	**37.** (d)	**38.** (d)	**39.** (a)	**40.** (c)
41. (c)	**42.** (c)	**43.** (b)	**44.** (a)	**45.** (b)	**46.** (d)	**47.** (b)	**48.** (d)	**49.** (d)	**50.** (c)
51. (a)	**52.** (b)								

Hints & Solutions

1. The Langmuir adsorption is based on chemisorption.

2. Threshold energy level is the minimum energy barrier required to be crossed to bring in a chemical change.

3. $(C_2H_5)_3Al + TiCl_4 \longrightarrow$ Active species. Ti^{3+} has one active site vacant and thus accommodate one alkyl group. (as $(C_2H_5)_3Al$ reduces $TiCl_4$ to $TiCl_3$).

4. $Al(OH)_3$.

5. For the phenomenon of adsorption ΔH must be less than zero.

6. Physical adsorption occurs at low temperature.

7. MnO_2 increases the rate of decomposition of $KClO_3$.

8. Enzyme + substrate $\longrightarrow$ [Complex intermediate] $\longrightarrow$ Product + Enzyme

9. All are the facts about zeolites.

10. $2H_2O_2(aq) \xrightarrow{Br^-(aq)} 2H_2O(l) + O_2(g)$

This is an example of homogeneous catalysis.

11. If the addition of a substance decreases the rate of reaction, the process is called negative catalysis.

12. More than 50% of the total volume of the void space in zeolite is occupied by water molecules.

13. Glycerine and actanilide both prevent the decomposition of H_2O_2.

14. Charcoal decolourise the litmus solution.

15. 50 mL of 1 M oxalic acid = 50 millimol = 0.050 mol

$= 0.050 \times 126\ g = 6.3\ g$

50 mL of 0.5 M oxalic acid = 3.15 g

Adsorbed oxalic acid = 6.3 − 3.15 = 3.15 g on 0.5 g charcoal

Amount of oxalic acid adsorbed per gram of charcoal

$$= \frac{3.15}{0.5} = 6.3$$

16. Specific surface area is the surface area per gram of the adsorbent.

17. In Freundlich adsorption isotherm, $n > 1$.

18. Berzelius introduced the terms catalyst and catalysis. He got the Nobel prize for the study of catalytic reactions.

19. Adsorption of gases decreases with increase in temperature.

20. The formula of a zeolite is

$$M_{x/n}\ [(AlO_2)_x \cdot (SiO_2)_y] \cdot mH_2O$$

21. Soaking of water by a sponge is an example of absorption.

22. ∵ The higher the critical temperature, the more is the ease of liquefaction of a gas and greater is the amount of gas adsorbed.

23. Langmuir showed that at low pressure, the physically adsorbed gas forms only one molecule thick layer. However, above a certain pressure, multimolecular thick layer is formed.

24. In heterogeneous catalysis, reactants and catalysts are in different phase. Only (ii) and (iii) reactions have different phase.

25. Surface of catalyst is rendered ineffective by adsorption of lead.

26. Lysozyme helps in protection of eyes from bacterial infection.

27. Catalysts can accelerate as well as retard the rate of a chemical reaction. However, they never initiate a chemical reaction.

28. In acid hydrolysis of methyl acetate, the reactants as well as the catalyst are in same phase, *i.e*,, aqueous. So, it is an example of homogeneous catalysis.

29. B, Mg and P can replace the Si and Al in the frame work at zeolites.

30. Langmuir adsorption isotherm is based upon the fats that every adsorption site is equilvernt and the binding ability of particles does not depend on nearby sites.

31. Enzymes are specific in nature.

32. ZSM-5 is a shape selective catalyst that catalyses the conversion of alcohols to various gasoline.

33. (i) → (iii) → (ii) → (iv) → (v)

34. Physisorption is multilayer while chemisorption is monolayer. Extent of adsorption is affected by pressure, temperature and particle size of adsorbent all.

35. Adsorption is a surface phenomenon because unutilised valencies are present only at the surface.

36. At low pressure, $\frac{x}{m} = kp$ and

at high pressure, $\frac{x}{m} = k$ (*i.e.*, constant)

37. Denaturation means biologically inactive protein.

38. Almost all organic catalysts are proteinous in nature.

39. Zealots are water softener as well as shape relative catalyst.

42. The rate of enzyme catalysed reactions change from first order to zero order as the concentration of substrate is increased.

43. 100 mL of 0.5 M CH_3COOH contains $CH_3COOH = 0.05$ mol

After adsorption, CH_3COOH remained = 0.049 mol

$\therefore$ Acetic acid adsorbed = 0.001 mol = 6.02×10^{20} molecules

$\therefore$ Surface area of charcoal adsorbed by each molecule

$$= \frac{3.01 \times 10^2 m^2}{6.02 \times 10^{20}} = 5 \times 10^{-19} m^2$$

44. According to Freundlich equation

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

$$\because \quad \text{Slope} = \frac{1}{n} = \tan\theta = \tan 45° = 1$$

$$\therefore \quad n = 1$$

$$\log k = 0.3010$$

or $\quad k = \text{antilog } 0.3010 = 2$

At $p = 0.5$ atm, $\quad \frac{x}{m} = kp^{1/n} = 2 \times (0.5)^1 = 1.0$ g

45. As Freundlich adsorption equation is

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

Substituting the values of two given sets, we get

Ist set $\quad \log \frac{16.5}{3} = \log k + \frac{1}{n} \log 180 \quad \ldots \text{(i)}$

IInd set $\quad \log \frac{38.1}{3} = \log k + \frac{1}{n} \log 540 \quad \ldots \text{(ii)}$

Subtracting Eq. (i) from, we get Eq. (ii)

$$\log \frac{38.1}{16.5} = \frac{1}{n} \log \frac{540}{180}$$

or $\quad \log 2.3091 = \frac{1}{n} \log 3 \quad$ or $\quad n = \frac{0.4771}{0.3634} \quad$ or $\quad n = 1.31$

By Eq (i)

and $\quad \log 5.5 = \log k + \frac{1}{1.31} \log 180$

or $\quad 0.7404 = \log k + \frac{1}{1.31}(2.2553) = \log k + 1.7216$

or $\quad \log k = -0.9812 = \bar{1}.0188 = 0.1044 \text{ cm}^3 \text{g}^{-1}$

46. Total surface area of six faces of a cube = $6 \times (1 \times 1) = 6 \text{ cm}^2$

General formula of surface area on n splits (cube) is

$$= 8^n \times 6 \times \left(\frac{1}{2}\right)^{2n} = 2^n \times 6$$

$$2^n \times 6 = 6291456 \text{ cm}^2$$

$$n = 20$$

Thus, total splits are to be made of a cube of 1 cm length.

47. Freundlich adsorption isotherm for solutions is

$$\frac{x}{m} = kC^{1/n}$$

$\because$ 5% vinegar = 5 g acetic acid in 100 mL solution

$\therefore$ 5g acetic acid = $\frac{5}{60}$ mol

and 100 mL of solution contains acetic acid

$$= \frac{5}{60} \times \frac{1}{100} \times 1000 = 0.837 \text{ mol}$$

or $\quad C = 0.837 \text{ mol L}^{-1}$

Substituting the values in Eq. (i), we get

$$\frac{x}{m} = 0.160 \times (0.837)^{1/2.32}$$

$$\therefore \quad \log \frac{x}{m} = \log(0.160) + \frac{1}{2.32}(\log 0.837)$$

$$= -0.7959 + 0.435(-0.0773)$$

$$= -0.8292 = (\bar{1}.1708)$$

$$\therefore \quad \frac{x}{m} = \text{Antilog}(\bar{1}.1708) = 0.1481 \text{g (g charcoal}^{-1})$$

$\therefore$ Amount absorbed by 1 kg (1000 g) of charcoal = 148.1 g

48. By Freundlich adsorption isotherm

$\frac{x}{m} = kp^{1/n}$ (in between low and high pressure)

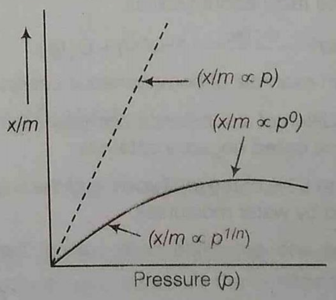
When $n = 1$,

$\frac{x}{m} \propto p^1$ (in lower pressure range)

when n is large, $\quad \frac{x}{m} = k$ (independent of pressure)

Thus, $\quad \frac{x}{m} \propto p^0$

(in high pressure range when saturation point is reached)



49. Adsorpiton is an exothermic process *i.e.*, energy is released against van der Waals' force of attraction (physisorptions). Hence, ΔH is always negative.

50. The adsorption of a gas is directly proportional to the pressure of the gas.

51. The physical adsorption is an exothermic process, so on the basis of Le-Chatelier's principle increasing temperature is favourable towards a direction in which heat is absorbed, so the rate of physisorption increases with decrease in temperature.

52. As temperature increases desorption increases. Adsorbent + Adsorbate $\rightleftharpoons$ Adsorbed state + ΔE

Adsorption is exothermic process (forward direction), desorption is endothermic process (backward direction).

According to Le-Chatelier's principle increase in temperature favours endothermic process.

Day 16

Colloidal State

Day 16 Outlines ...

- Concept of Colloidal State
- Types of Solutions
- Classification of Colloids
- Preparation of Lyophobic Solution
- Purification of Colloidal Solutions
- Properties of Colloidal Solutions
- Emulsions

Concept of Colloidal State

A substance is said to be in the colloidal state, when it is dispersed in another medium in form of very small particular having diameter between 10^{-4} *to* 10^{-7} *cm.*

Types of Solutions

Depending upon the size of dispersed particles, there are three different types of solutions *viz*, **true solutions**, **suspensions** and **colloidal solutions.**

In true solutions, the dispersed particles are present as single molecules or ions. The size of the dispersed particles is less than 1 nm. True solutions are homogeneous.

In colloidal solution, the size of dispersed particles is 1 to 100 nm. Colloidal solutions are heterogeneous. In suspension, the size of dispersed particles is more than 100 nm. Suspensions are also heterogeneous.

Dispersed Phase *and* Dispersion Medium

The colloidal system is made of two phases

(i) the substance distributed as the colloidal particles, called the **dispersed phase**.

(ii) the phase in which the colloidal particles are scattered, called **dispersion medium**.

The dispersed phase or dispersion medium can be a gas, liquid or solid. There are eight types of colloidal system. *These are as follows*

S. No.	Colloidal system	Dispersed phase	Dispersion medium	Examples
1.	Foam	Gas	Liquid	Soda water, froth, shaving cream
2.	Solid foam	Gas	Solid	Foam rubber, cork
3.	Aerosol	Liquid	Gas	Fog, mist, clouds
4.	Emulsion	Liquid	Liquid	Milk, hair cream
5.	Solid emulsion (gel)	Liquid	Solid	Butter, cheese
6.	Aerosol of solids	Solid	Gas	Dust in air, smoke
7.	Sol	Solid	Liquid	Paint, ink, colloidal gold,
8.	Solid sol	Solid	Solid	Ruby glass, some gem stones, alloys, rock salt

Classification of Colloids

Colloids can be classified in a number of ways based upon some of their important characteristics as given below

Based upon Appearance

1. The colloidal systems, in which the dispersion medium is a liquid or gas, are called **sols**. They are called **hydrosols** or **aquasols**, if the dispersion medium is water. When the dispersion medium is alcohol or benzene, they are accordingly called **alcosols** or **benzosol**.
2. The colloidal systems, in which the dispersion medium is gas are called **aerosols**.

Based upon Charge

The colloids can be classified into positive or negative colloids according to the charge present on the dispersed phase particles.

Based on Affinity of Phase

1. **Lyophilic colloids** represent such colloidal systems in which the particles of dispersed phase have great affinity for the dispersion medium.

   These are reversible colloids, e.g., gum, gelatin, rubber, proteins etc.
2. **Lyophobic colloids** represent such colloidal systems in which particles of the dispersed phase have no affinity for the dispersion medium.

   These are irreversible. e.g., soils of metals and their insoluble compounds like sulphides and oxides.

   If water is the dispersion medium, the terms used are **hydrophilic** and **hydrophobic colloids.**

➧ Lyophobic colloids are less stable due to the presence of electric charge on their particles. On the otherhand, lyophilic colloids are stable due to their presence of charge as well as their extensive solvation.

Based on Molecular Size

1. **Multimolecular colloids**, are the colloids in which colloidal particles consist of aggregate of atoms or small molecules with diameter less than 10^{-9} m or 1 nm. *e.g.*, a sol of gold, a sol of sulphur.
2. **Macromolecular colloids** are the colloids in which colloidal particles themselves are large molecules.
3. **Associated colloids** or **micelles** are the substances which behave as normal electrolytes at low concentration but as colloids at higher concentration. This is because at higher concentration, they form associated particles called micelles. *e.g.*, soap and synthetic detergents.

   The concentration above which micelle formation occurs, is called **CMC (critical micelle concentration)** and the temperature above which micelle formation occurs is called **Kraft temperature**.

- *In polydisperse colloids, the colloidal particles are of different sizes while in monodisperse collids, all the colloidal particles are more or-less of identical size.*
- *The colligative properties of colloidal systems are low due to aggregation. Hence, all colloidal solutions exhibit very low osmotic pressure, very small elevation in boiling point and depression in freezing point.*

Preparation of Lyophobic Solution

Lyophilic colloids may be prepared by simply warming the solid with the liquid dispersion medium. On the other hand, lyophobic colloids have to be prepared by special methods.

Substances are converted into colloidal solutions by the following two methods

Dispersion Methods

These methods involve the breaking of bigger particles to the size of colloidal particles. The various dispersion methods are

(i) **Electrodisintegration methods (Bredig's arc method)**, by this method colloidal solutions of metals like gold, silver etc., are obtained.

(ii) **Peptisation** involves the conversion of freshly prepared precipitate into colloidal solution by adding suitable electrolyte. The suitable electrolyte is known as peptising agent. *e.g.*,

$$\underset{\text{fresh ppt.}}{Fe(OH)_3} + \underset{\text{electrolyte}}{FeCl_3} \longrightarrow \underset{\text{colloid}}{[Fe(OH)_3Fe]^{3+}} + 3Cl^-$$

Condensation or Chemical Methods

These methods involve the growing of size of the dispersed phase or the size of colloidal particles.

(i) **By double decomposition**

$$As_2O_3 + 3H_2S \longrightarrow \underset{\text{colloidal solution}}{As_2S_3} + 3H_2O$$

(ii) **By hydrolysis**

$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{colloidal solution}}{Fe(OH)_3} + 3HCl$$

(iii) **By oxidation**

$$H_2S + 2HNO_3 \longrightarrow 2H_2O + 2NO_2 + \underset{\text{colloidal}}{S}$$

In periodic precipitation, precipitation reaction is carried out in gel medium. As a result of this, rings or layers of precipitates are formed at definite intervals.

Purification of Colloidal Solutions

The following methods are commonly used to purify the colloids

- **Dialysis** It is the process of removing small molecules or ions from a soil by diffusion through a semipermeable membrane.

  In this process, impure colloidal solution is placed in a bag of semipermeable membrane, dipping in water, the ions diffuse through membrane. Ferric hydroxide sol can be purified by this method.
- **Electrodialysis** If dialysis is carried out under the influence of electric field, it is called electrodialysis. This speeds up the migration of ions to the opposite electrodes.
- **Ultrafiltration** Separation of sol particles from the liquid medium and electrolytes by filtration through an ultrafilter is called **ultrafiltration**.
- **Ultra-Centrifugation** In ultra-centrifuge, the colloidal particles settle down at the bottom and impurities remain in the solution.

Properties of Colloidal Solutions

The important properties of the colloidal solutions are given below.

Brownian Movement

Colloidal particles are always in a state of rapid random motion, which is termed as Brownian movement.

Tyndall Effect

When a strong and converging beam of light is passed through a colloidal solution, its path becomes visible due to scattering of light by particles. It is called Tyndall effect.

Electrophoresis

The phenomenon, involving the migration of colloidal particles under the influence of electric field towards the oppositely charged electrode, is called electrophoresis.

- *Sedimentation potential or Dorn effect is the reverse of electrophoresis. It is set up when a particle is forced to move in a resting liquid.*
- *Electrophoretic mobility of colloidal particles is the distance travelled by particles in one second under a potential gradient in one volt per cm. Since, different colloids have different mobilities, so the method is used for separation of proteins, nucleic acids, polysaccharides etc.*

Coagulation or Flocculation

The precipitation of particles of the dispersed phase in a sol is known as **coagulation**.

The minimum amount of an electrolyte required to cause precipitation of one litre of a colloidal solution is called coagulation value or flocculation value. The reciprocal of coagulation value is regarded as the coagulating power.

Hardy-Schulze rule

Higher the valency of the active ion, the greater will be its power to precipitate the sol.

e.g., order of coagulating power is

$$Al^{3+} > Ba^{2+} > Na^+$$

$$PO_4^{3-} > SO_4^{2-} > Cl^-$$

Protective Action of Lyophilic Colloids

As lyophobic sols are unstable (*e.g.*, Au, Ag) and get easily precipitated, the addition of lyophilic colloids like gums, soaps etc makes it difficult. The process is known as **protection** and the lyophilic colloids are termed as **protective colloids.**

Gold Number

It is the minimum weight (in mg) which must be added to 10 mL of standard red gold sol so that no coagulation of it takes place when 1 mL of 10% NaCl solution is rapidly added to it.

Emulsions

These are the colloidal solutions of two immiscible liquids in which the liquids act as the dispersed phase as well as the dispersion medium.

Types of Emulsions

There are two types of emulsions

- **Oil in water type** *e.g.*, milk in which tiny droplets of liquid fat are dispersed in water.
- **Water in oil type** *e.g.*, stiff greases, in which water being dispersed in lubricating oil.

Emulsifying Agents

During the preparation of emulsion, a small amount of some substances such as soap, gum, agar and protein etc are added to stabilise the emulsion. These substances are known as emulsifying agents.

Breaking of Emulsions

Emulsions can be broken into constituent liquids by heating, freezing, centrifuging or chemical destruction of emulsifying agent.

- *Surfactants are the substances which get preferentially absorbed at the air-water, oil-water and solid-water interfaces.*
- $C_{15}H_{31}COO^-Na^+$ *is anionic surfactant* $C_{18}H_{37}NH_3^+Cl^-$ *is cationic surfactant* $C_nH_{2n+1}(OCH_2CH_2)_xOH$ *is non-ionic surfactant.*

Practice Zone

DAY 16

1. Separation of colloidal particles from those of molecular dimensions by means of electric current is known as

(a) electrosmosis
(b) electrophoresis
(c) electrodialysis
(d) electrolysis

2. The Brownian movement is due to

(a) enthalpy change during the formation of colloids
(b) attractive force between the colloidal particles and the molecules of dispersion medium
(c) the impact of molecules of the dispersion medium on the colloidal particles
(d) the movement of positively charged colloidal particles to negatively charged particle

3. Gold number is the index for

(a) protective power of lyophilic colloid
(b) purity of gold
(c) metallic gold
(d) electroplated gold

4. Which of the following process is responsible for the formation of delta at a place where rivers meet the sea? **[NCERT Exemplar]**

(a) Emulsification
(b) Colloidal formation
(c) Coagulation
(d) Peptisation

5. The critical micelle concentration (CMC) is

(a) the concentration at which micellisation starts
(b) the concentration at which the true solution is formed
(c) the concentration at which one molar electrolyte is present per 1000 g of the solution
(d) the concentration at which $\Delta H = 0$

6. Which type of molecules form micelles?

(a) Non-polar molecules
(b) Polar molecules
(c) Surfactant molecules
(d) Salt of weak acid and weak base

7. Fog is a colloidal solution of

(a) liquid particles dispersed in a gas
(b) gaseous particles dispersed in a liquid
(c) solid particles dispersed in a liquid
(d) solid particles dispersed in a gas

8. A gel is

(a) a liquid mass of a lyophilic sol in which all the dispersion medium has penetrated into the sol particles
(b) like an emulsion which is stabilised by adding emulsifying agent
(c) a semirigid mass of a lyophobic sol in which all the dispersion medium has penetrated into the sol particles
(d) a semirigid mass of a lyophilic sol in which the dispersion medium has penetrated into the sol particles

9. Addition of lyophilic solution to the emulsion, forms

(a) a protective film around the dispersed phase
(b) a protective film around the dispersion medium
(c) an aerosol
(d) true solution

10. During the micelle formation

(a) $\Delta H = +\text{ve} \quad \Delta S = +\text{ve}$
(b) $\Delta H = -\text{ve} \quad \Delta S = -\text{ve}$
(c) $\Delta H = -\text{ve} \quad \Delta S = +\text{ve}$
(d) $\Delta H = +\text{ve} \quad \Delta S = -\text{ve}$

11. Micelles form only

(a) below the critical micelle concentration (CMC) and below the Kraft temperature (T_k).
(b) above CMC and below the T_k
(c) above the CMC and above the T_k
(d) below the CMC and above the T_k

12. Micelles are

(a) emulsion cum gel
(b) associated colloids
(c) adsorbed catalysis
(d) ideal solutions

13. Which of the following ions have minimum value of flocculating power?

(a) PO_4^{3-}
(b) SO_4^{2-}
(c) SO_3^{2-}
(d) NO_3^-

14. The isoelectric point of a colloidally dispersed material is the pH value at which

(a) the dispersed phase migrate in an electric field
(b) the dispersed phase does not migrate in an electric field
(c) the dispersed phase has pH equal to 7
(d) the dispersed phase has pH equal to zero

15. Which of the following statements is incorrect?
(a) Emulsions are prepared by shaking two liquid components, say oil and water and adding some emulsifying agent
(b) Water in oil emulsions are formed when the emulsifying agent at the interface is chiefly in the water phase
(c) Water in oil emulsions are formed when the emulsifying agent at the interface is chiefly in the oil phase
(d) Gems and gels mixed together to give emulsions

16. Blue colour of sky and red colour of sunsets are due to
(a) scattering of light from the sun
(b) scattering of light from particles of dust in the atmosphere
(c) refraction of blue light by impurities in sea water
(d) scattering of light due to ozone layer

17. The arsenious sol is negatively charged, the maximum power of precipitating it, is in
(a) Na_2SO_4 (b) Na_3PO_4 (c) $AlCl_3$ (d) $Mg(NO_3)_2$

18. Which of the following statements is correct for Tyndall effect?
(a) Scattering and polarising of light by small suspended particles is called Tyndall effect
(b) Tyndall effect of colloidal particles is due to dispersion of light
(c) Tyndall effect is due to refraction of light
(d) *Zig*-zag motion of suspended particles

19. In a coagulating experiment, 5 mL of As_2S_3 is mixed with distilled water and 0.2 M solution of an electrolyte *AB*, so that the total volume is 20 mL. All solutions containing 5.4 mL of *AB* coagulate within 2 min. The flocculation value of *AB* (in millimol) is
(a) 5 (b) 50
(c) 54 (d) None of these

20. Milk is an emulsion in which
(a) a liquid is dispersed in a liquid
(b) a solid is dispersed in a liquid
(c) a gas is dispersed in a liquid
(d) lactose is dispersed in a liquid

21. Lyophilic solutions are more stable than lyophobic solutions because
(a) the colloidal particles have positive charge
(b) the colloidal particles have negative charge
(c) the colloidal particles are solvated
(d) there is strong electrostatic repulsions between the negatively charged colloidal particles

22. Hardy-Schulze law states that
(a) larger the charge on the coagulating ions, greater is its coagulating power, having opposite sign of solution
(b) solution must have zero gold number
(c) disperse phase and dispersion medium must be of the same sign
(d) micelles coagulate in presence of surfactants

23. Peptisation involves
(a) precipitation of colloidal particles
(b) disintegration of colloidal aggregates
(c) evaporation of dispersion medium
(d) impact of molecules of the dispersion medium on the colloidal particles

24. A freshly prepared $Fe(OH)_3$ precipitate is peptised by adding $FeCl_3$ solution. The charge on the colloidal particles is due to preferential adsorption of
(a) Br^- ion (b) Fe^{3+} ion (c) OH^- ion (d) Ba^{2+} ion

25. Which of the following is not the property of hydrophilic solutions?
(a) High concentration of dispersed phase can be easily obtained
(b) Coagulation is reversible
(c) Viscosity and surface tension are nearly the same as that of water
(d) The charge of the particles depends on the pH of the medium and it may be positive, negative or zero

26. The values of colligative properties of colloidal solution are of small order in comparison to those shown by true solutions of same concentration because of colloidal particles **[NCERT Exemplar]**
(a) exhibit enormous surface area
(b) remain suspended in the dispersion medium
(c) form lyophilic colloids
d) are comparatively less in number

27. Tanning of leather is
(a) colouring of leather by chemicals
(b) drying process to make the leather hard
(c) polishing of leather to make its look attractive
(d) coagulative hardening of the leather by chemicals

28. Which of the following will show Tyndall effect? **[NCERT fExemplar]**
(a) Aqueous solution of soap below critical micelle concentration
(b) Aqueous solution of soap above critical micelle concentration
(c) Aqueous solution of sodium chloride
(d) Aqueous solution of sugar

29. When dilute aqueous solution of $AgNO_3$ (excess) is added to KI solution, positively charged sol particles of AgI are formed due to adsorption of ion
(a) K^+ (b) Ag^+ (c) I^- (d) NO_3^-

30. Which one is hydrophobic in nature?
(a) Gelatin (b) Sulphur (c) Starch (d) Protein

31. Cod liver oil is
(a) fat dispersed in water (b) water dispersed in fat
(c) water dispersed in oil (d) fat dispersed in fat

32. The spontaneous outcome of internal liquid from gels is called

(a) synersis
(b) thixotropy
(c) swelling
(d) None of these

Directions (Q. Nos. 33 to 35) *If a pair of immiscible liquids such as olive oil and water are mixed and shaken vigorously, a dispersion of very fine droplets of one liquid in the other will result. Such a dispersion is termed as emulsion.*

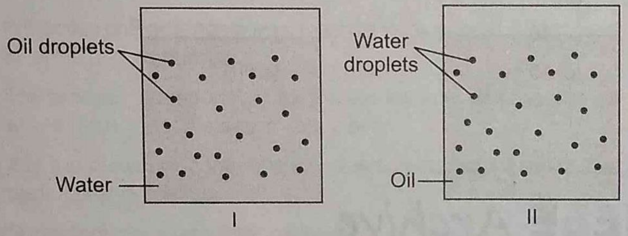
One of the components in emulsion is water and the other one is an oily substance immiscible in water.

Emulsion droplets are bigger than sol particles (≈ 10^{-6} m) and can be seen under an ordinary microscope or sometimes even with a magnifying glass.

Emulsions resemble lyophobic sols in some of the properties.

Emulsion can be identified by dye test.

33. In the following emulsions :



(a) I is of oil in water type and II is of water in oil type
(b) I is of water in oil type and II is of oil in water type
(c) Both are of oil in water type
(d) Both are of water in oil type

34. An oil soluble dye is shaken with the given emulsion under study. We observe that whole background appears coloured. This indicates that emulsion is

(a) water in oil type
(b) oil in water type
(c) liquid under study is pure oil
(d) liquid under study is pure water

35. An oil soluble dye is shaken with the given emulsion under study. We observe coloured drops when seen under microscope. Thus, emulsion is

(a) water in oil type
(b) oil in water
(c) liquid under study is pure oil
(d) liquid under study is pure water

Directions (Q. Nos. 36 and 37) *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.*

Critical micelle concentration (CMC) is the lowest concentration at which micelle formation appears. CMC increases with the total surfactant concentration. At concentration higher than CMC, they form extended parallel sheets known as ***lamellar micelles*** *which resemble biological membranes.*

In concentrated solutions, micelles take the form of long cylinders packed in hexagonal arrays and are called ***lytotropic mesomorphs****.*

In an aqueous solution (polar medium), the polar groups point towards the periphery and the hydrophobic hydrocarbon chains point towards the centre forming the core of the micelle.

Micelles from the ionic surfactants can be formed only above a certain temperature called the ***Kraft temperature.*** *They are capable of forming ions.*

Molecules of soaps and detergents consist of lyophilic as well as lyophobic parts which associate together to form micelles.

Micelles may contain as many as 100 molecules or more.

36. Select the incorrect statement(s).

(a) Surface active agents like soaps and synthetic detergents are micelles
(b) Soaps are emulsifying agents
(c) $C_{17}H_{35}$ (hydrocarbon part) and —COO^- (carboxylate) part of stearate ion ($C_{17}H_{35}COO^-$) both are hydrophobic
(d) All of the above are incorrect statements

37. Cleansing action of soap occurs because

(a) oil and grease can be adsorbed into the hydrophobic centres of soap micelles and washed away
(b) oil and grease can be adsorbed into hydrophilic centres of soap micelles and washed away
(c) oil and grease can be adsorbed into both hydrophilic and hydrophobic centres but not washed away
(d) cleansing action is not related to micelles

Directions (Q. Nos. 38 to 41) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

38. Statement I Micelles are formed by surfactant molecules above the critical micellar concentration (CMC).

Statement II The conductivity of a solution having surfactant molecules decreases sharply at the CMC.

39. Statement I A colloid gets coagulated by addition of an electrolyte.

Statement II The rate of coagulation depends on the magnitude and sign of the charge of the coagulant ion.

40. **Statement I** Colloidal AgI is prepared by adding $AgNO_3$ in slight excess to KI solution. When subjected to an electric field, the colloidal particles migrate to the anode.

Statement II Colloidal particles adsorb ions and thus, become electrically charged.

41. **Statement I** Proteins, starch and gum rubber are lyophilic colloids.

Statement II They have strong interaction with the dispersion medium.

42. When 6.0×10^{-5} g of a protective colloid was added to 20 mL of a standard gold sol, the precipitation of later was just prevented on addition of 1 mL of 10% NaCl solution. The gold number of the protective colloid is

(a) 3 (b) 3×10^{-5} (c) 0.06 (d) 0.03

43. The colloidal sol formed from SnO_2 in acidic and basic medium are respectively

(a) $[SnO_2]SnO_3^{2-} : 2\,Na^+$ and $[SnO_2]Sn^{4+} : 4Cl^-$

(b) $[SnO_2]Sn^{4+}$ and $[SnO_2]SnO_3^{2-} : 2Na^+$

(c) positively and negatively charged

(d) $[SnO_2]SnO_3^{2-} : 2Na^+$ in both the mediums

44. When 9.0 mL of arsenious sulphide sol and 1.0 mL of 0.1 M $BaCl_2$ are mixed, turbidity due to precipitation just appears after 2 h. The effective ion and its coagulating value are respectively.

(a) Cl^-, 10 millimol L^{-1} (b) Cl^-, 20 millimol L^{-1}

(c) Ba^{2+}, 10 millimol L^{-1} (d) Ba^{2+}, 20 millimol L^{-1}

45. The coagulation values of $AlCl_3$ and NaCl are 0.093 and 52 respectively. The ratio of coagulating powers of both will be

(a) 0.093 : 1 (b) 52 : 1

(c) 559 : 1 (d) 1.788 : 1

46. A particle of radius 1 cm is broken to form colloidal particles of radius 1000 Å. The number of colloidal particles produced are

(a) 10^{15} (b) 6.023×10^{23}

(c) 10^{12} (d) 10^{10}

JEE Main & AIEEE Archive

47. The coagulating power of electrolytes having ions Na^+, Al^{3+} and Ba^{2+} for arsenic sulphide solution increases in the order **[JEE Main 2013]**

(a) $Na^+ < Ba^{2+} < Al^{3+}$ (b) $Ba^{2+} < Na^+ < Al^{3+}$

(c) $Al^{3+} < Na^+ < Ba^{2+}$ (d) $Al^{3+} < Ba^{2+} < Na^+$

48. The migration of dispersion medium under the influence of an electric potential is called **[JEE Main Online 2013]**

(a) cataphoresis (b) electroosmosis

(b) electrophoresis (d) gas dispersed in solid

49. Smoke is an example of **[JEE Main Online 2013]**

(a) solid dispersed in solid (b) gas dispersed in liquid

(c) solid dispersed in gas (d) gas dispersed in solid

50. Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is **[AIEEE 2008]**

(a) $D < A < C < B$ (b) $C < B < D < A$

(c) $A < C < B < D$ (d) $B < D < A < C$

51. Among the following the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions, is **[IIT JEE 2008]**

(a) $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ (b) $CH_3(CH_2)_{11}OSO_3^-Na^+$

(c) $CH_3(CH_2)_6COO^-Na^+$ (d) $CH_3(CH_2)_{11}N^+(CH_3)_3Br^-$

52. Lyophilic sols are **[IIT JEE 2005]**

(a) irreversible sols

(b) prepared from inorganic compounds

(c) coagulated by adding electrolytes

(d) self-stabilising

53. The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectively. Which of the following statements is not correct? **[AIEEE 2005]**

(a) Coagulation in both sols can be brought about by electrophoresis

(b) Mixing the sols has no effect

(c) Sodium sulphate solution causes coagulation in both sols

(d) Magnesium chloride solution coagulates, the gold sol more readily than the iron (III) hydroxide sol

54. The volume of a colloidal particle, V_C as compared to the volume of a solute particle in a true solution V_S, could be **[AIEEE 2005]**

(a) $\frac{V_C}{V_S} \approx 10^3$ (b) $\frac{V_C}{V_S} \approx 10^{-3}$

(c) $\frac{V_C}{V_S} \approx 10^{23}$ (d) $\frac{V_C}{V_S} \approx 1$

Answers

1. (b)	**2.** (c)	**3.** (a)	**4.** (c)	**5.** (a)	**6.** (c)	**7.** (a)	**8.** (d)	**9.** (a)	**10.** (c)
11. (c)	**12.** (b)	**13.** (a)	**14.** (b)	**15.** (d)	**16.** (b)	**17.** (c)	**18.** (a)	**19.** (c)	**20.** (a)
21. (c)	**22.** (a)	**23.** (b)	**24.** (b)	**25.** (c)	**26.** (d)	**27.** (d)	**28.** (b)	**29.** (b)	**30.** (b)
31. (c)	**32.** (a)	**33.** (a)	**34.** (a)	**35.** (b)	**36.** (c)	**37.** (a)	**38.** (b)	**39.** (b)	**40.** (a)
41. (a)	**42.** (d)	**43.** (c)	**44.** (c)	**45.** (c)	**46.** (a)	**47.** (a)	**48.** (b)	**49.** (c)	**50.** (c)
51. (a)	**52.** (d)	**53.** (b)	**54.** (a)						

Hints & Solutions

1. In electrophoresis charged sol particles move towards opposite electrodes.

2. Brownian movement is *zig-zag* motion of suspended particles.

3. Protective character of various lyophilic substances is expressed in terms of gold number.

4. The process is responsible for the fromation of delta at a place where rivers meet the sea is coagulation.

5. It is the minimum concentration at which surfactant molecules undergo aggregation.

6. Surfactant molecules form micelles.

7. Fog is liquid dispersed in gas, a class of colloidal system.

8. A gel is liquid dispersion in solid. *e.g.* cheese.

9. Surface phase reaction takes place.

10. ΔH = negative, ΔS = positive

11. Micelle formation takes place above a particular temperature, called Kraft temperature (T_k) and above a particular concentration, called Critical Micelle Concentration (CMC).

12. Micelles are associated colloids.

13. PO_4^{3-} have minimum value of flocculating power.

14. The hydrogen ion concentration at which the colloidal particles have neither positive nor negative charge is known as isoelectric point. Therefore, at isoelectric point particles do not migrate under the influence of electric field.

15. Gems are solid and gels are semisolid. This mixture will not form emulsion.

16. It is due to scattering of light from particles of dust in the atmosphere.

17. Due to greater charge on Al, $AlCl_3$ has maximum power of precipitating arsenious sol.

18. When a beam of light is passed through a colloidal solution, its path becomes visible. This is known as Tyndall effect.

19. Flocculation value is the amount of electrolyte, in millimoles required to bring about complete coagulation of one litre of colloidal solution.

Amount of *AB* in 5.4 mL of 0.2 M *AB*

$$= \frac{5.4 \times 0.2}{1000} = 1.08 \times 10^{-3} \text{ mol}$$

20 mL of As_2S_3 requires *AB* for coagulation $= 1.08 \times 10^{-3}$ mol

1000 mL of As_2S_3 requires *AB* (*i.e.*, flocculation value)

$$= \frac{1.08 \times 10^{-3}}{20} \times 1000 = 0.054 \text{ mol} = 54 \text{ millimol}$$

20. Milk—liquid (fat) is dispersed in liquid (water).

21. Lyophilic colloids are more stable due to solvation.

22. Definition of Hardy-Schulze law.

23. Peptisation involves disintegration of colloidal aggregates.

24. Solution particle adsorbs common ion present in the medium.

25. Viscosity is higher than that of dispersion medium (water) while surface tension is usually lower than that of dispersion medium (water).

26. The values of colligative properties of colloidal solution are of small order in comparison to these shown by true solutions of same concentration because of colloidal particles are comparatively less in number.

27. Definition of tanning of leather.

28. Aqueous solution of soap above critical micelle concentration show Tyndall effect.

29. Sol particles possess the tendency to adsorb preferentially the common ion present in solution.

30. Inorganic sols are usually hydrophobic in nature.

31. It is water dispersed in oil type emulsion.

32. It is a property of gel.

33. In the given emulsions, I is oil in water type and II is water in oil type.

34. Whole background appears coloured in case of water in oil type emulsion as dye is oil soluble.

35. When oil soluble dye is shaken with oil in water type emulsion, coloured drops are observed.

36. —COO^- (carboxylate part)–hydrophilic, $C_{17}H_{35}$ (hydrocarbon part)–hydrophobic.

37. Oil and grease (dirt) can be adsorbed into the hydrophobic centres of soap micelles (hydrocarbon part). The carboxylate part of soap or detergent molecule is hydrophilic, therefore when we rinse the clothes with water, oil and grease particles trapped by micelles are washed away.

38. At a certain concentration surfactant molecules start to aggregate and form micelle, the concentration is called critical micellisation concentration (CMC).

Aggregation of surfactant molecules (ions; $RCOO^-$) *i.e.*, micelle formation cause effective fall in number of free ions to conduct electricity, thus conductivity decreases at CMC.

39. Coagulation of sols by addition of electrolytes is explained by Hardy-Schulze rule. For positive sol, negative ion of electrolyte is the effective ion while for negative sol, positive ion of electrolyte is the effective ion. Greater is the valency of effective ion, more is its coagulating power and more is the coagulating power, lesser is the coagulation value.

40. Colloidal particles are electrically charged, hence they move towards oppositely charged electrode on applying electric field.

41. Dispersion of starch, gum rubber and proteins in water form lyophilic sols.

42. The protective colloid added to 20 mL of gold sol to completely prevent coagulation by 1 mL of 10% NaCl solution $= 6.0 \times 10^{-5}$g $= 6.0 \times 10^{-2}$mg

Hence, the protective colloid required to be added to 10 mL of gold sol to completely prevent coagulation by 1 mL of 10% solution $= \frac{6.0 \times 10^{-2} \times 10}{20} = 0.03$ mg

Hence, Gold number = 0.03

43. In acidic medium, Sn^{4+} ion is formed which is preferentially adsorbed on SnO_2 giving positively charged colloidal sol.

$$SnO_2 + Sn^{4+} \longrightarrow \underset{\text{positively charged}}{[SnO_2]Sn^{4+} : 4Cl^-}$$

In basic medium, SnO_3^{2-} is formed which is preferentially adsorbed on SnO_2, giving negatively charged colloidal sol.

$$SnO_2 + SnO_3^{2-} \longrightarrow \underset{\text{negatively charged}}{[SnO_2]SnO_3^{2-} : 2Na^+}$$

44. As_2S_3 sol in negatively charged due to preferential adsorption of S^{2-} ions by As_2S_3 particles. Hence, cation of largest valency (*i.e.*, Ba^{2+}) would be most effective in causing coagulation of the sol.

$$\text{Moles of } Ba^{2+} = \frac{1.0 \times 0.1}{1000} = 1.0 \times 10^{-4} \text{ mol}$$

10 mL (9.0 mL of As_2S_3 and 1.0 mL $BaCl_2$) of As_2S_3 requires $BaCl_2$ for coagulation $= 1.0 \times 10^{-4}$ mol 1000 mL of As_2S_3 requires $BaCl_2$ for coagulation (*i.e.*, coagulation value)

$$= \frac{1.0 \times 10^{-4} \times 1000}{10} = 1.0 \times 10^{-2} \text{ mol L}^{-1}$$

$$= 10 \text{ millimol L}^{-1}$$

45. As coagulating power is inversely proportional to coagulation value, the ratio of their coagulating powers will be

$$\frac{\text{Coagulating power of } AlCl_3}{\text{Coagulating power of NaCl}}$$

$$= \frac{\text{Coagulation value of NaCl}}{\text{Coagulation value of } AlCl_3} = \frac{52}{0.093} = 559 : 1$$

46. Volume of a particle with radius 1 cm $= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi \text{cm}^3$

The particle is broken into colloidal particle of radius 1000Å *i.e.*, 10^{-5} cm

$$\text{Hence, volume of the particle} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \pi \times (10^{-5})^3$$

$$= \frac{4}{3}\pi \times 10^{-15} \text{ cm}^3$$

$$\text{Hence, number of colloidal particles} = \frac{\frac{4}{3}\pi \text{ cm}^3}{\frac{4}{3}\pi \times 10^{-15} \text{cm}^3} = 10^{15}$$

47. Al_2S_3 is an anionic sol (negative sol) hence coagulation will depend upon coagulating power of cation, which is directly proportional to the valency of cation (Hardy-Schulze rule).

48. Electroosmotic flow is caused by the coulomb force induced by an electric field on net mobile electric charge in a solution. When an electric field is applied to the fluid, the net charge in the electrical double layer (a layer of mobile ions forms in the region near the interface) is induced to move by the resulting coulomb force.

49. Smoke is a colloid in which dispersed phase is solid and dispersion medium is gas or in other words, in smoke, a solid is dispersed in gas.

50. Higher the gold number, less will be the protective power of colloid.

51.

	Sodium dodecyl sulphate (SDS)	Hexadecyltrimethyl ammonium bromide (CTAB)
CMC (mm)	> – 10	1

52. Lyophilic sols are self stabilising because these sols are reversible and are highly hydrated in the solution.

53. Mixing the soles together can cause coagulation, since, the charges are neutralised.

54. Size of colloidal particles = 1 to 100 nm (say 10 nm)

$$V_C = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(10)^3$$

Size of true solution particles ≈ 1 nm

$$V_S = \frac{4}{3}\pi(1)^3$$

Thus, $\frac{V_C}{V_S} = 10^3$

Unit Test 3

(Physical Chemistry-II)

DAY
17

1. The cell, $Zn|Zn^{2+}(1M)||Cu^{2+}(1M)|\ Cu\,(E^\circ_{cell} = 1.10\ V)$, was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is

(a) antilog (24.08) (b) 37.3
(c) $10^{37.\ 3}$ (d) 9.65×10^4

2. The molar conductivities Λ°_{NaOAc} and Λ°_{HCl} at infinite dilution in water at 25°C are 91.0 and 426.2 S cm^2/mol respectively. To calculate Λ°_{HOAc}, the additional value required is

(a) $\Lambda^\circ_{H_2O}$ (b) Λ°_{KCl}
(c) Λ°_{HOAc} (d) Λ°_{NaCl}

3. Given the data at 25°C,

$$Ag + I^- \rightarrow AgI + e^-; E^\circ = 0.152\ V$$

$$Ag \rightarrow Ag^+ + e^-; E^\circ = -0.800\ V$$

What is the value of log K_{sp} for AgI ?

$$\left(2.303\,\frac{RT}{F} = 0.059\ V\right)$$

(a) – 8.12 (b) – 8.612 (c) – 37.83 (d) – 16.13

4. The highest electrical conductivity from the following aqueous solution is of

(a) 0.1 M difluoroacetic acid (b) 0.1 M fluoroacetic acid
(c) 0.1 M chloroacetic acid (d) 0.1 M acetic acid

5. When a certain conductivity cell was filled with 0.01 M solution of KCl, it had a resistance of 160 ohm at 25°C and when filled with 0.005 M NaOH, it had a resistance of 190 ohm. If specific resistance of KCl solution is, 700 ohm-cm, specific conductance (ohm^{-1} cm^{-1}) of NaOH solution is

(a) 0.00120 (b) 0.00170 (c) 0.00180 (d) 0.00190

6. In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to

(a) generate heat
(b) create potential difference between the two electrodes
(c) produce water of high purity
(d) remove adsorbed oxygen from electrode surfaces

7. The $E^\circ_{M^{3+}/M^{2+}}$, values for Cr, Mn, Fe and Co are – 0.41, + 1.57, + 0.77 and + 1.97 V respectively. For which one of these metals the change in oxidation state from + 2 to + 3 is easiest?

(a) Cr (b) Mn
(c) Fe (d) Co

8. Consider the following E° values

$$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77\ V$$

$$E^\circ_{Sn^{2+}/Sn} = -0.14\ V$$

Under standard conditions the potential for the reaction

$Sn\,(s) + 2Fe^{3+}\,(aq) \longrightarrow 2Fe^{2+}(aq) + Sn^{2+}(aq)$ is

(a) 1.68 V (b) 1.40 V
(c) 0.91 V (d) 0.63 V

9. In a cell that utilises the reaction,

$$Zn\,(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

addition of H_2SO_4 to cathode compartment will

(a) lower the E and shift equilibrium to the left
(b) lower the E and shift the equilibrium to the right
(c) increase the E and shift the equilibrium to right
(d) increase the E and shift the equilibrium to the left

10. Consider the following reactions at 1100°C

(I) $2C + O_2 \longrightarrow 2CO, \Delta G^\circ = -460\ kJ\ mol^{-1}$

(II) $2Zn + O_2 \longrightarrow 2ZnO, \Delta G^\circ = -360\ kJ\ mol^{-1}$

Based on these, select the correct alternate.

(a) Zinc can be oxidised by CO
(b) Zinc oxide can be reduced by carbon
(c) Both (a) and (b)
(d) None of the above

11. Consider the reaction, $2A + B \longrightarrow$ products, when concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is

(a) L mol^{-1} s^{-1} (b) no unit
(c) mol L^{-1} s^{-1} (d) s^{-1}

12. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will

(a) remain unchanged (b) triple
(c) increase by a factor of 4 (d) double

13. $t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to $3/4$ of its initial value. If the rate constant for a first order reaction is k, the $t_{1/4}$ can be written as

(a) $0.75/k$ (b) $0.69/k$ (c) $0.29/k$ (d) $0.10/k$

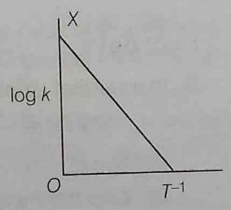
14. Consider an endothermic reaction, $X \longrightarrow Y$ with the activation energies E_b and E_f for the backward and forward reactions respectively. In general,

(a) there is no definite relation between E_b and E_f
(b) $E_b = E_f$
(c) $E_b > E_f$
(d) $E_b < E_f$

15. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 min. The time taken for the concentration to change from 0.1 M to 0.025 M is

(a) 30 min (b) 15 min (c) 7.5 min (d) 60 min

16. Graph between $\log k$ and $\frac{1}{T}$ (k is rate constant in s^{-1} and T is the temperature in K is a straight line. If $OX = 5$ and slope of the line $= -\frac{1}{2.303}$ then E_a is



(a) 2.303×2 cal (b) $\frac{2}{2.303}$ cal
(c) 2 cal (d) None of these

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

(a) $\frac{1}{2^{m+n}}$ (b) $(m+n)$ (c) $(n-m)$ (d) $2^{(n-m)}$

18. Half-life period of second order is

(a) proportional to initial concentration of reactants
(b) independent of initial concentration of reactants
(c) inversely proportional to initial concentration of reactants
(d) None of the above

19. The average molecular weight of colloidal particles is determined by

(a) Tyndall effect
(b) Osmotic pressure measurement
(c) Victor Meyer's method
(d) None of the above

20. Blood contains

(a) positively charged particles (b) negatively charged particles
(c) neutral particles (d) Any of the above

21. When light is incidented on a colloidal solution,

(a) it is absorbed partially (b) it is absorbed completely
(c) it is scattered (d) it passes undeviated

22. When a sulphur sol is evaporated sulphur is obtained. On mixing with water sulphur sol is not formed. The sol is

(a) lyophilic (b) reversible
(c) hydrophobic (d) hydrophilic

23. Compared to common colloidal sol, micelles have

(a) higher colligative property (b) lower colligative property
(c) same colligative property (d) None of these

24. The process of removing dissolved impurities from a colloidal system, by means of diffusion through suitable membrane under the influence of an electric field is called

(a) electro-osmosis (b) electrodialysis
(c) electrophoresis (d) peptisation

25. Silt in water is

(a) gel (b) sol (c) aerosol (d) foam

26. Mayonnaise represents

(a) sol (b) an aerosol (c) a foam (d) an emulsion

27. If dilute HCl is added to a precipitate of stannic oxide,

(a) $SnCl_2$ and $SnCl_4$ are formed
(b) $Sn(OH)_2$ is formed
(c) a stable sol of stannic oxide is formed
(d) Sn_2O_3 is formed

28. Select the incorrect statement.

(a) Physical adsorption is reversible while chemical is irreversible
(b) High pressure favours physical adsorption while low pressure favours chemical adsorption
(c) Physical adsorption is not specific while chemical is highly specific
(d) High activation energy is involved in chemical adsorption.

29. Hemidialysis is used to

(a) separate colloidal sol from water
(b) separate charged and uncharged particles
(c) cleanse the blood of patients whose kidneys have malfunctioned
(d) None of the above

30. In multimolecular colloidal sols, atoms or molecules are held together by

(a) H-bonding (b) van der Waals' forces
(c) ionic bonding (d) polar covalent bonding

31. SnO_2 is taken in basic medium and current is passed. Colloidal sol migrates towards

(a) anode (b) cathode
(c) Both (a) and (b) (d) None of these

32. [AgI] I^- colloidal sol can be coagulated by the addition of a suitable cation. 1 mole of [AgI] I^- requires mole of $AgNO_3$, $Pb(NO_3)_2$ and $Fe(NO_3)_3$ as

(a) 1, 1, 1 (b) 1, 2, 3] (c) $1, \frac{1}{2}, \frac{1}{3}$ (d) 6, 3, 2

33. Protective sols are

(a) lyophilic (b) lyophobic
(c) Both (a) and (b) (d) None of these

34. Select the correct statements.

(a) Emulsifiers stabilise the emulsion.
(b) Soaps, detergents, long chain sulphonic acids and lyophilic colloids are emulsifiers.
(c) Cleansing action of soap is due to the formation of emulsions.
(d) All of the above are correct statements

35. Milk is an emulsion of fat dispersed in water. It is stabilised by

(a) casein—a lyophilic colloidal sol
(b) casein—a lyophobic colloidal sol
(c) lactose—a lyophilic colloidal sol
(d) lactose—a lyophobic colloidal sol

36. $KMnO_4$ reacts with oxalic acid as

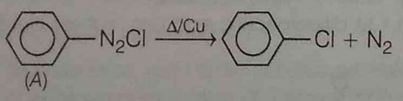
$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

Hence, 50 mL of 0.04 $KMnO_4$ in acidic medium is chemically equivalent to

(a) 100 mL of 0.1 M $H_2C_2O_4$ (b) 50 mL of 0. 2 M $H_2C_2O_4$
(c) 50 mL of 0.1 M $H_2C_2O_4$ (d) 25 mL of 0.1 M $H_2C_2O_4$

37. Given that $E^\circ_{Cu^{2+}/Cu} = 0.34$ V; $E^\circ_{Ag^+/Ag} = 0.80$ V; $E^\circ_{Mg^{2+}/Mg} = 2.37$ V and $E^\circ_{Al^{3+}/Al} = -1.66$ V in which of the following cells the standard free energy decrease is maximum ?

(a) $Mg|Mg^{2+}(1M)||Cu^{2+}(1\ M)|Cu$
(b) $Mg\ |Mg^{2+}(1\ M)||Ag^+\ (1\ M)|Ag$
(c) $Ag\ |Ag^+(1\ M)||Al^{3+}\ (1\ M)|Al$
(d) $Cu\ |Cu^{2+}(1\ M)||Ag^+\ (1\ M)|Ag$

38. 

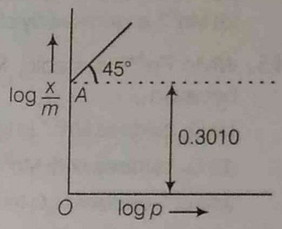
Half-life is independent of conc. of *A*. After 10 minutes volume of N_2 gas is 10 L and after complete reaction 50 L Hence, rate constart is

(a) $\frac{2.303}{10}\log 5$ min (b) $\frac{2.303}{10}\log 1.25\ min^{-1}$
(c) $\frac{2.303}{10}\log 2\ min^{-1}$ (d) $\frac{2.303}{10}\log 4\ min^{-1}$

39. Gold number of haemoglobin is 0.03. Hence, 100 mL of gold sol will require haemoglobin so that gold is not coagulated by 10 ml of 10% NaCl sol

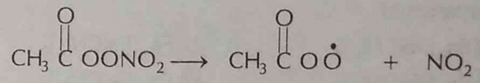
(a) 0.03 mg (b) 30 mg (c) 0.30 mg (d) 3 mg

40. Graph between $\log\left(\frac{x}{m}\right)$ and $\log p$ is a straight line at angle 45° with intercept *OA* as shown. Hence, $\left(\frac{x}{m}\right)$ at a pressure of 0.2 atm is



(a) 0.2 (b) 0.4 (c) 0.6 (d) 0.8

Directions (Q. Nos. 41 to 43) *Peroxyacetylnitrate (PAN) is an air pollutant, produced in photochemical smog by the reaction of hydrocarbons, oxides of nitrogen and sunlight. It dissociates as*



$$CH_3\overset{O}{\overset{\|}{C}}OONO_2 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}O\dot{O} + NO_2$$

PAN peroxyacetyl radical

A sample of polluted air is analysed for its PAN content which is reported as molecules PAN per litre of air at 25°C.

Time (min)	Molecules × 10^{-14} / L air
0.0	5.0
10.0	4.0
20.0	3.2
30.0	2.6
40.0	2.1
50.0	1.7
60.0	1.3

41. Determine the order of the PAN decomposition reaction.

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

42. Rate constant of the reaction is

(a) 0.0231 min^{-1} (b) 0.009 min^{-1}
(c) 0.0231 L mol^{-1} min^{-1} (d) 0.009 L mol^{-1} min^{-1}

43. Half-life of the reaction is

(a) 10 min (b) 20 min (c) 30 min (d) 60 min

Directions (Q. Nos. 44 to 46) *Redox reaction play a pivotal role in chemistry and biology. The values of standard redox potential (E°) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniell cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their E° (V with respect to normal hydrogen electrode) values.*

$I_2 + 2e^- \longrightarrow 2I^-$;	$E^\circ = 0.54$
$Cl_2 + 2e^- \longrightarrow 2Cl^-$;	$E^\circ = 1.36$
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$;	$E^\circ = 1.50$
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$;	$E^\circ = 0.77$
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$;	$E^\circ = 1.23$

44. Among the following, identify the correct statement.

(a) chloride ion is oxidised by O_2
(b) Fe^{2+} is oxidised by iodine
(c) iodide ion is oxidised by chlorine
(d) Mn^{2+} is oxidised by chlorine

45. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because

(a) O_2 oxidises Mn^{2+} to Mn^{3+}
(b) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(c) Fe^{3+} oxidises H_2O to O_2
(d) Mn^{3+} oxidises H_2O to O_2

46. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of

(a) $Fe_4[Fe(CN)_6]_3$
(b) $Fe_3[Fe(CN)_6]_2$
(c) $Fe_4[Fe(CN)_6]_2$
(d) $Fe_3[Fe(CN)_6]_3$

Directions (Q. Nos. 47 to 50) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

47. Statement I Reaction of white phosphorus with NaOH (*aq*) gives PH_3.

Statement II The reaction is disproportionation of P in alkaline medium.

48. Statement I If two half reactions with electrode potential $E_1°$ and $E_2°$ gives a third half reaction,

$$\Delta G_3° = \Delta G_1° + \Delta G_2°$$

Statement II $E_3° = E_1° + E_2°$

49. Statement I Larger is the activation energy, lesser is the effect of a given temperature rise on rate constant, k.

Statement II $k = Ae^{-E_a/RT}$

50. Statement I The conversion of a fresh precipitate into a colloidal state by the action of solute or solvent is called **peptisation**.

Statement II Peptisation is a property of colloidal state.

Answer *with* Solutions

1. *(c)* Cell is completely discharged, it means equilibrium gets established, $E_{cell} = 0$

$$Zn \mid Zn^{2+}(1\,M) \parallel Cu^{2+}(1\,M) \mid Cu$$

Cell reaction : $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

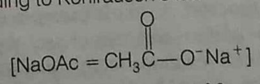
We know,

$$E_{cell} = E°_{cell} - \frac{0.0591}{n} \log K_{eq}$$

$$E°_{cell} = -\frac{0.0591}{2} \log K_{eq} \quad \text{or} \quad 1.10 = \frac{0.0591}{2} \log K_{eq}$$

$$K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \text{antilog}\,\frac{2.20}{0.0591} = \text{antilog } 37.3$$

2. *(d)* According to Kohlrausch's law



$$[NaOAc = CH_3\overset{\overset{O}{\|}}{C}{-}O^-Na^+]$$

$$\Lambda°_{CH_3COOH} = \lambda°_{CH_3COO^-} + \lambda°_{H^+} \quad \text{...(i)}$$

$$\Lambda°_{HCl} = \lambda°_{H^+} + \lambda°_{Cl^-} \quad \text{...(ii)}$$

$$\Lambda°_{CH_3COONa} = \lambda°_{CH_3COO^-} + \lambda°_{Na^+} \quad \text{...(iii)}$$

Thus, after adding Eqs (ii) and (iii) if $\lambda°_{Na^+}$ and $\lambda°_{Cl^-}$ are subtracted, we can obtained the value of $\Lambda°_{HOAc}$. Thus, additional value required is $\Lambda°_{NaCl}$.

3. *(d)* $AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$; $E° = -0.152$

$$Ag(s) \rightarrow Ag^+ + e^-;\ E° = -0.8$$

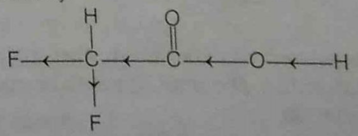
$$AgI(s) \rightarrow Ag^+ + I^-;\ E° = -0.952$$

$$E°_{cell} = \frac{0.059}{n} \log K_{sp}$$

$$-0.952 = \frac{0.059}{1} \log K_{sp}$$

$$\log K_{sp} = \frac{0.952}{0.059} = -16.135$$

4. *(a)* Fluoro group causes negative inductive effect increasing ionisation, thus 0.1 M difluoroacetic acid has highest electrical conductivity.



5. *(a)* Resistance = specific resistance × cell constant

$$R_{(KCl)} = (\rho)_{KCl} \times \text{cell constant}$$

$$R_{(NaOH)} = (\rho)_{NaOH} \times \text{cell constant}$$

$$\frac{(R)_{KCl}}{(R)_{NaOH}} = \frac{(\rho)_{KCl}}{(\rho)_{NaOH}}$$

$$\frac{160}{190}=\frac{700}{(\rho)_{NaOH}}$$

$$(\rho)_{NaOH}=831.25 \text{ ohm cm}$$

specific conductance, $\kappa_{(NaOH)}=\frac{1}{831.25}=1.20\times10^{-3}\ \text{ohm}^{-1}\text{cm}^{-1}$

6. *(b)* Any cell (like fuel cell), works when potential difference is developed.

7. *(a)*

$$E^\circ_{Cr^{3+}/Cr^{2+}}=-0.41\text{ V}$$
$$E^\circ_{Mn^{3+}/Mn^{2+}}=+1.57\text{ V}$$
$$E^\circ_{Fe^{3+}/Fe^{2+}}=+0.77\text{ V}$$
$$E^\circ_{Co^{3+}/Co^{2+}}=+1.97\text{ V}$$

More negative value of E°_{red} indicates better reducing agent, thus easily oxidised. Thus, oxidation of Cr^{2+} to Cr^{3+} is easiest.

8. *(c)* $Sn(s)+2Fe^{3+}(aq)\longrightarrow 2Fe^{2+}(aq)+Sn^{2+}(aq)$

$$E^\circ_{cell}=E^\circ_{ox}+E^\circ_{red}=E^\circ_{Sn/Sn^{2+}}+E^\circ_{Fe^{3+}/Fe^{2+}}$$

Given, $E^\circ_{Sn^{2+}/Sn}=-0.14\text{ V}$

$\therefore$ $E^\circ_{Sn/Sn^{2+}}=+0.14\text{ V}$

$E^\circ_{Fe^{3+}/Fe^{2+}}=0.77\text{ V}$

$\therefore$ $E^\circ_{cell}=0.14+0.77=0.91\text{ V}$

9. *(c)* $Zn(s)+2H^+(aq)\longrightarrow Zn^{2+}(aq)+H_2(g)$

Reaction quotient, $Q=\frac{[Zn^{2+}]}{[H^+]^2}$

Corresponding cell is

$$\underset{\text{anode}}{\overset{\ominus}{Zn\mid Zn^{2+}(C_1)}}\ \|\ \underset{\text{cathode}}{\overset{\oplus}{H^+(aq)\mid Pt(H_2)}}$$

and
$$E_{cell}=E^\circ_{cell}-\frac{0.0591}{2}\log K$$
$$=E^\circ_{cell}-\frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[H^+]^2}$$
$$=E^\circ_{cell}+\frac{0.0591}{2}\log\frac{[H^+]^2}{[Zn^{2+}]}$$

If H_2SO_4 is added to cathodic compartment (towards reactant side), Q decreases (due to increase in H^+).

Hence, equilibrium is displaced towards right and E_{cell} increases.

10. *(b)* $ZnO+C\longrightarrow Zn+CO$, $\Delta G^\circ=-ve$.

Hence, this is spontaneous.

11. *(a)* $2A+B\rightarrow$ products

$[B]$ is doubled, half-life did not change. Half-life is independent of change in concentration of reactant for first order reactions, *i.e.*, First order *wrt* to B

When $[A]$ is doubled, rate increases by two times

$\Rightarrow$ First order *w.r.t* A

Hence, net order of reaction = 1 + 1 = 2

Unit for the rate constant $=\text{conc}^{(1-n)}t^{-1}=(\text{mol L}^{-1})^{-1}.\text{s}^{-1}$

$=\text{L}\cdot\text{mol}^{-1}\text{s}^{-1}$

12. *(c)* Given,

$$r\propto[CO]^2$$
$$r'\propto[2CO]^2$$
$$r'\propto 4\,[CO]^2$$

Hence, $\frac{r'}{r}=\frac{4[CO]^2}{[CO]^2};\ r'=4r$

13. *(c)* $A\longrightarrow$ Product

	A	Product
Initially	a	0
After time t	$(a-x)$	x
After $t_{1/4}$	$\left(a-\frac{a}{4}\right)$	$\frac{a}{4}$

For first order kinetics,

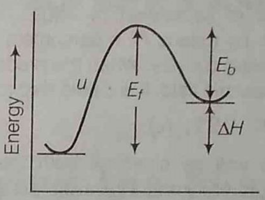
$$k=\frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

$$\therefore\quad k=\frac{2.303}{t_{1/4}}\log\left(\frac{a}{3a/4}\right)$$

$$t_{1/4}=\frac{2.303\log\frac{4}{3}}{k}=\frac{0.29}{k}$$

14. *(d)* $X\rightarrow Y$ is an endothermic reaction,

$\Delta H=+ve$



E_b = energy of activation of backward reaction

E_f = energy of activation of forward reaction

ΔH = heat of reaction

Thus, $E_f=E_b+\Delta H$

Thus, $E_f>E_b$

15. *(a)* Order = 1

Concentration changes from 0.8 M to 0.4 M (50%) in 15 min, thus half-life = 15 min = T_{50}

A change from 0.1 M to 0.025 M is 75% and for first order reaction

$$T_{75}=2\times T_{50}=2\times15=30\text{ min}\quad\text{or}\quad T_{50}=15\text{ min}$$

$$k=\frac{2.303\log2}{T_{50}}=\frac{2.303\log2}{15}$$

$$a=0.1\text{ M}$$
$$(a-x)=0.025\text{ M}$$

For first order :

$$k=\frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$
$$\frac{2.303\log2}{15}=\frac{2.303}{t}\log\frac{0.1}{0.025}=\frac{2.303}{t}\log4$$
$$\therefore\quad\frac{2.303\log2}{15}=\frac{2\times2.303\log2}{t};\ t=30\text{ min}$$

16. *(c)* $\log_{10} = \log_{10} A - \dfrac{E_a}{2.303\,RT}$

$$\text{Slope} = -\frac{E_a}{2.303\,R} = -\frac{1}{2.303}$$

$$\therefore \quad E_a = R = 2 \text{ cal}$$

17. *(d)* Rate becomes x^y times, if concentration is made x times of a reactant giving y^{th} order reaction.

$$\text{Rate} = k[A]^n[B]^m$$

Concentration of A is doubled, hence $x = 2$, $y = n$ and rate becomes $= 2^n$ times

Concentration of B is halved, hence $x = 1/2$, $y = m$ and rate becomes $= \left(\dfrac{1}{2}\right)^m$ times

Net rate becomes $= (2)^n \left(\dfrac{1}{2}\right)^m$ times $= (2)^{n-m}$ times

18. *(c)* $t_{1/2} \propto \dfrac{1}{(a)^{n-1}}$ for second order, $n = 2$, $t_{1/2} \propto \dfrac{1}{a}$

19. *(b)* The osmotic pressure measurement gives the molecular mass of aggregated molecule.

20. *(b)** **21.** *(c)* **22.** *(c)* **23.** *(b)*

24. *(b)* The process of separation of soluble impurities from a colloidal solution by means of a parchment paper (a suitable membrane) is called dialysis. When the process is done under the influence of electric field, it is called electrodialysis.

25. *(b)* **26.** *(d)* **27.** *(c)*

28. *(b)* Physical as well as chemical both the adsorptions are favoured by high pressure. However, the difference is that decrease in pressure causes desorption in case of physical adsorption but not in the case of chemical adsorption.

29. *(c)* Hemidialysis is used to cleanse the blood of patients having malfunctioned kidneys.

30. *(b)* van der Waals' forces.

31. *(a)* In alkaline medium SnO_2 is converted into negatively charged colloidal sol.

$$SnO_2 + 2OH^- \longrightarrow SnO_3{}^{2-} + H_2O$$

$$SnO_2 + SnO_3{}^{2-} \longrightarrow \underbrace{[SnO_2]\,SnO_3^{2-}}_{\text{anion migrate to anode}}$$

32. *(c)* $\underset{1\text{ mol}}{[AgI]I^-} + \underset{1\text{ mol}}{AgNO_3} \longrightarrow AgI + AgI + NO_3^-$

$$\underset{\substack{2\text{ mol}\\1\text{ mol}}}{2[AgI]I^-} + \underset{\substack{1\text{ mol}\\1/2\text{ mol}}}{Pb(NO_3)_2} \longrightarrow 2AgI\downarrow + PbI_2\downarrow + 2NO_3{}^-$$

33. *(a)* **34.** *(d)* **35.** *(a)*

36. *(c)* Eq. mass of $MnO_4{}^- = \dfrac{\text{molar mass}}{7-2} = \dfrac{\text{molar mass}}{5}$

$$\text{Eq. mass of } C_2O_4{}^{2-} = \frac{\text{molar mass}}{2[4-3]} = \frac{\text{molar mass}}{2}$$

$$\text{Meq. of } KMnO_4 = 50 \times 5 \times 0.04 = 10$$
$$= \text{Meq. of } H_2C_2O_4 = 50 \times 2 \times 0.1 = 10$$

37. *(b)* $-\Delta G° = nFE°_{cell}$

38. *(b)* T_{50} is independent of conc of A. Hence, the reaction is of first order.

$$A \longrightarrow N_2\,(g)$$

At $t = 0$, a 0

At time t, $(a - x)$ $x = 10$ L [after 10 min]

At complete reaction $(a - a)$ $a = 50$ L

$\therefore$ $(a - x) = 40$ L

$\therefore$ $k = \dfrac{2.303}{10} \log \dfrac{50}{40} = \dfrac{2.303}{10} \log 1.25 \text{ min}^{-1}$

39. *(c)* Gold number of haemoglobin = 0.03

10mL of gold sol requires haemoglobin to prevent coagulation = 0.03 mg

100 mL of gold sol will require haemoglobin to prevent coagulation = 0.3 mg

40. *(b)* By Freundlich adsorption isotherm $\left[\dfrac{x}{m}\right] = k(p)^{1/n}$

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

Compare with $y = mx + c$

$\therefore$ slope $= \tan\theta = \tan 45° = 1$

$\therefore$ $\dfrac{1}{n} = 1$, $\therefore$ $n = 1$

and $\log k = 0.3010 = \log 2$

$$\log\left[\frac{x}{m}\right] = \log(0.2) + \log 2 = \log 0.4 \;\therefore\; \left[\frac{x}{m}\right] = 0.4$$

41. *(b)* From the table (given), we observe that concentration changes to 50% in 30 min and further 50% in 30 min (total 60 min). Thus, half-life period is independent of concentration, hence, it is first order reaction.

42. *(a)* $k = \dfrac{0.693}{T_{50}}$ (for first order) $= \dfrac{0.693}{30} = 0.0231 \text{ min}^{-1}$

43. *(c)* $t_{1/2} = \dfrac{0.693}{k} = 0.693/0.0231 = 30$ min

44. *(c)* $2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-$

$$E°_{cell} = 1.36 - 0.54 = 0.82 \text{ V}$$

$E°_{cell}$ is positive. Thus, cell reaction is feasible.

45. *(d)* $[Mn^{3+} + e^- \longrightarrow Mn^{2+}] \times 4$

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$$
$$4Mn^{3+} + 2H_2O \longrightarrow 4Mn^{2+} + 4H^+ + O_2$$
$$E°_{cell} = 1.50 - 1.23 = 0.27 \text{ V}$$

$E°_{cell}$ is positive *i.e.*, the process is spontaneous.

46. *(a)*

$$Na + C + N \longrightarrow \underset{\text{[sodium extract]}}{NaCN}$$
$$Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$$
$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \longrightarrow \underset{\text{Prussian blue ppt.}}{Fe_4[Fe(CN)_6]_3}$$

47. *(a)* **48.** *(c)* **49.** *(d)* **50.** *(c)*

Day 18

Classification and **Periodicity of Elements**

Day 18 Outlines ...

- Laws for Classifying the Elements
- Present Form of Periodic Table
- Classification of Elements into Groups and Periods
- Periodic Properties

Laws for Classifying the Elements

Many attempts were made to classify the known elements from time to time. These are

(i) Proust hypothesis
(ii) Dobereiner triad law
(iii) Newlands octave law
(iv) Lother Meyer's curve
(v) Mendeleef periodic law (1869) *The properties of elements are periodic functions of their atomic weights.*
(vi) Modern periodic law (given by Moseley) *The physical and chemical properties of elements are periodic functions of their atomic numbers.*

Present Form of Periodic Table

The modern Periodic Table was further modified to extended form or long form of Periodic Table. It is the present form of Periodic Table.

This modification was not done by a single person, but it incorporates the modifications by many scientists especially Rang, Werner, Bohr, Bury etc.

- This table is also called Bohr's Periodic Table and just graphical representation of **Aaufbau principle**.
- In this table, elements are arranged in **increasing order** of atomic number (Z) (same as that seen in modern Periodic Table). The isotops are all grouped together as they have the same atomic number.

s-Block Elements

p-Block Elements

Group 1 IA ← New Notation, CAS Version → 17 VIIA, 18 0 (zero)

Key to Chart

STATE	
Gas	G
Liquid	L
Solid	S
Not found in nature	X

G 8 → Atomic number
O → Symbol
Oxygen → Name
15.9994 → Atomic mass

d-Block Elements

Period	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 0 (zero)
1	1 G H Hydrogen 1.008																1 G H Hydrogen 1.008	2 G He Helium 4.003
2	3 S Li Lithium 6.941	4 S Be Beryllium 9.0121											5 S B Boron 10.811	6 S C Carbon 12.011	7 G N Nitrogen 14.007	8 G O Oxygen 15.999	9 G F Fluorine 18.998	10 G Ne Neon 20.180
3	11 S Na Sodium 22.999	12 S Mg Magnesium 24.305											13 S Al Aluminium 26.982	14 S Si Silicon 28.086	15 S P Phosphorus 30.914	16 S S Sulphur 32.066	17 G Cl Chlorine 35.453	18 G Ar Argon 39.948
4	19 S K Potassium 39.098	20 S Ca Calcium 40.078	21 S Sc Scandium 44.956	22 S Ti Titanium 47.867	23 S V Vanadium 50.942	24 S Cr Chromium 51.996	25 S Mn Mangansese 54.938	26 S Fe Iron 55.845	27 S Co Cobalt 58.933	28 S Ni Nickel 58.693	29 S Cu Copper 63.546	30 S Zn Zinc 65.39	31 S Ga Gallium 69.723	32 S Ge Germanium 72.61	33 S As Arsenic 74.922	34 S Se Selenium 78.96	35 L Br Bromine 79.904	36 G Kr Krypton 83.30
5	37 S Rb Rubidium 85.468	38 S Sr Strontium 87.62	39 S Y Yttrium 89.906	40 S Zr Zirconium 91.224	41 S Nb Niobium 92.906	42 S Mo Molybedenum 95.94	43 X Tc Technetium (98)	44 S Ru Ruthenium 101.07	45 S Rh Rhodium 102.906	46 S Pd Palladium 106.42	47 S Ag Silver 107.868	48 S Cd Cadmium 112.411	49 S In Indium 114.818	50 S Sn Tin 118.710	51 S Sb Antimony 121.760	52 S Te Tellurium 177.60	53 S I Iodine 126.904	54 G Xe Xenon 131.29
6	55 S Cs Cesium 132.905	56 S Ba Barium 137.327	57 S La Lanthanum 138.906	72 S Hf Hafnium 178.49	73 S Ta Tantalum 180.948	74 S W Tungsten 183.84	75 S Re Rhenium 186.207	76 S Os Osmium 190.23	77 S Ir Indium 192.217	78 S Pt Platinum 195.078	79 S Au Gold 196.967	80 L Hg Mercury 200.59	81 S Tl Thallium 204.383	82 S Pb Lead 207.2	83 S Bi Bismuth 208.980	84 S Po Polonium (209)	85 S At Astatine (210)	86 G Rn Radon (222)
7	87 S Fr Francium (223)	88 S Ra Radium (226)	89 S Ac Actinium (227)	104 X Rf Rutherfordium (261)	105 X Db Dubnium (262)	106 X Sg Seaborgium (263)	107 X Bh Bohrium (262)	108 X Hs Hassium (265)	109 X Mt Meitnerium (266)	110 X Ds Darmstadtium (269)	111 X Rg Rontgenium (272)	112 X Uub Ununbium (227)	113 X Uut Ununtrium (284)	114 X Uuq Ununquadium (289)	115 X Uup Ununpentium (228)	116 X Uuh Ununhexium (292)	117	118 X Uuo Ununoctium (294)

f-Block Elements

*Lanthanides	58 S Ce Cerium 140.116	59 S Pr Praseodymium 140.908	60 S Nd Neodymium 144.908	61 X Pm Promethium (145)	62 S Sm Samarium 150.36	63 S Eu Europium 151.964	64 S Gd Gadolinium 157.25	65 S Tb Terbium 158.925	66 S Dy Dysprosium 162.50	67 S Ho Holmium 164.930	68 S Er Erbium 167.26	69 S Tm Thulium 168.934	70 S Yb Ytterbium 173.04	71 S Lu Lutetium 174.967
**Actinides	90 S Th Thorium 232.038	91 S Pa Protactinium 231.036	92 S U Uranium 238.029	93 S Np Neptunium (237)	94 S Pu Plutonium (244)	95 X Am Americium (243)	96 X Cm Curium (247)	97 X Bk Berkelium (247)	98 X Cf Californium (251)	99 X Es Einsteinium (252)	100 X Fm Fermium (257)	101 X Md Mendelevium (258)	102 X No Nobelium (259)	103 X Lr Lawrencium (262)

☐ Metals
☐ Metalloids
☐ Non-metals

- The table contains **7 periods** (representing 7 orbits) and **18 groups** (1-18). The concept of subgroup A and B is removed and groups are given no. 1 to 18. The name of zero group is changed to group 18.

A new period begins with the occupency of new energy shell (principal quantum number) by the first electron. Thus, a period begins with the element having ns^1 configuration ($n = 1, 2, 3, \ldots$ for 1st, 2nd and 3rd period respectively).

Classification of Elements into Groups and Periods

Total number of groups (vertical columns) = 18

Total number of periods (horizontal columns) = 7

Depending upon the orbital in which last electron enters, the elements are classified as

s-Block Elements

- I and II group elements belong to this block and the last electron enters in *s*-orbital.
- General configuration is ns^{1-2}.

p-Block Elements

- Last electron enters in *p*-orbital.
- General configuration is ns^2, np^{1-6}.
- Groups 13th to 18th excluding He, belongs to this group.

Diagonal relationship The first member of each group of *s* and *p*-block elements shows different characteristics from the rest of the members of the same group. However, the first three elements of second period (Li, Be, B) show diagonal similarity with elements (Mg, Al, Si) of third period placed on the right hand side. This is called diagonal relationship.

$$\begin{tikzcd}[row sep=small, column sep=small]
\text{2nd Period} & \text{Li} \arrow[dr] & \text{Be} \arrow[dr] & \text{B} \arrow[dr] & \text{C} \\
\text{3rd Period} & \text{Na} & \text{Mg} & \text{Al} & \text{Si}
\end{tikzcd}$$

s and p-block elements are known as representative elements.

d-Block or Transition Elements

- General configuration is $ns^{1-2}\,(n-1)d^{1-10}$.
- Last electron enters in *d*-orbital.
- Two outermost shells are incomplete.
- 10 groups → from 3rd to 12th.
- Four series $3d, 4d, 5d, 6d$.

f-Block or Inner-Transition Elements

- General configuration $ns^2(n-1)d^{0-1}(n-2)f.^{1-14}$
- Last electron enters in *f*-orbital.
- Two series $4f$ (lanthanoids) and $5f$ (actinoids).
- Also known as rare earth elements.

Elements 113 and 115 Discovered

Two super heavy elements, element 113 and element 115, have been discovered by scientists. The team observed atomic decay patterns or chains, that confirm the existence of these elements. In these decay chains, element 113 is produced *via* the alpha decay of element 115.

Periodic Properties

The elements in the periodic table are arranged in order of increasing atomic number. All of these elements display several other trends and we can use the periodic law and table formation to predict their chemical, physical and atomic properties.

1. Atomic Size or Atomic Radius

Left to right size of atom decreases; down the group size increases.

(i) Ionic radius Distance of the outermost shell of an ion from its nucleus.

(ii) Covalent radius

(a) In homodiatomic molecule, $(A-A)$

$$r = \frac{d_{A-A}}{2}$$

d_{A-A} = bond length in molecule

(b) In heterodiatomic molecule $(A-B)$:

- When $(\chi_A - \chi_B)$ is very small :

$$d_{A-B} = r_A + r_B$$

d_{A-B} = bond length

r_A and r_B = covalent radii of A and B respectively

χ_A and χ_B = electronegativities of A and B

- When $(\chi_A - \chi_B)$ is considerable

$$d_{A-B} = r_A + r_B - 0.09\,(\chi_A - \chi_B)$$

(iii) Metallic radius, $r' = \dfrac{d}{2}$

$r' >$ actual size of atom

(iii) **van der Waals' radius**, $r_1 = \frac{d}{2}$

[illegible] actual size of atom

Covalent radius < Metallic radius

< van der Waals' radius

At the end of the period, atomic radii of inert gases are exceptionally higher because they do not form molecule and their radii are simply van der Waals' radii.

- *Atomic radii of inert gases are exceptionally higher because their radii are simple van der Waals' radii.*
- *Cs is the largest in size. Its size is approximately 4.4 times to that of H atom.*

2. Ionisation Enthalpy

It is the energy required when an electron is removed from an isolated gaseous atom.

Generally left to right in periods IE increases; down the group it decreases but half-filled orbitals and fully-filled orbitals are stable form and have high IE.

Various factors with which ionisation energy varies are

(i) Atomic size : varies inversely

(ii) Screening effect : varies inversely

(iii) Nuclear charge : varies directly

(iv) Helium has the highest IE_1 while Cs has the lowest.

(v) IE values of inert gases are exceptionally higher due to stable configuration.

Screening Effect

Shielding (or screening effect) is the repulsion of valence electrons by the electrons in penultimate shell to reduce effective nuclear charge.

$$Z_{eff} = Z - \sigma$$

where, Z = atomic number, σ = shielding constant

σ = [0.35 × number of electrons in n^{th} shell excluding last (valence) electron] + [0.85 × number of electrons in $(n-1)^{th}$ shell] + [1.0 × number of electrons in inner shell]

3. Electron Gain Enthalpy

It is the energy released when an electron is added in an isolated gaseous atom.

Chlorine has the highest electron affinity but oxidising power of fluorine is larger than chlorine.

Various factors affecting electron gain enthalpy are

(i) Atomic size : varies inversely

(ii) Nuclear charge : varies directly

(iii) Configuration : Half-filled orbitals and fully-filled orbitals are stable form, therefore electron gain enthalpy will be low or even sometimes energy is required rather than getting released.

Exception Cl > F (electron gain enthalpy)

S > O

F and O atoms have small size and high charge density, therefore have lower electron gain enthalpy.

4. Electronegativity

It is the tendency to attract the shared pair of electrons. F is the most electronegative element while Cs is the least.

Difference in the electronegativities of two atoms (A and B),

$$\chi_A - \chi_B = 0.208 \sqrt{\Delta}$$

where, Δ = actual bond energy − energy for 100% covalent bond.

$$\therefore \quad \Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$$

Here, E_{A-B} = dissociation enthalpy of $A-B$ (kcal mol^{-1})

E_{A-A} = dissociation enthalpy of $A-A$ (kcal mol^{-1})

E_{B-B} = dissociation enthalpy of $B-B$ (kcal mol^{-1})

Mulliken's approach :

$$\chi_M = \frac{IE + EA}{2}$$

Mulliken values are ≈2.8 times greater than Pauling values

$$\chi_p = \frac{IE + EA}{5.6}$$

or $$\chi_p = 0.336 [\chi_M - 0.615]$$

unit of electronegativity = eV

For noble gases, its value is taken as zero.

Decreasing order of electronegativity

$$F > O > Cl \approx N > Br > S \approx C > I > H$$

In periods : left to right electronegativity increases.

In groups : down the group electronegativity decreases.

sp hybridised carbon is more electronegative than a sp^2 hybridised carbon, which in turn is more electronegative than a sp^3 hybridised carbon.

5. Valency

The valency of an element is related to the electronic configuration of its atom and usually determined by electrons present in valence shell (outer shell).

Variation of valency in a period Valency of the elements with respect to hydrogen increases from 1 to 4 up to 14th group and then decreases to 1.

For example,

$$NaH, CaH_2, AlH_3, SiH_4, PH_3, H_2S, HCl.$$

But valency of the elements with respect to oxygen increases from one to seven along a period.

For example,

$$Na_2O, CaO, Al_2O_3, SiO_2, P_4O_{10}, SO_3, Cl_2O_7$$

Variation of valency in a group All elements in a group have the same valency as they have same number of electrons in their outer shell.

p-block elements show variable valency on account of inert pair effect.

Term **oxidation state** is also being used for caralence, which indicates the actual charge on atom in that particular molecule. It follows the same trend along period or group as valency.

Tin has maximum number of isotopes. (10 in number) and Os has the highest oxidation state or valency (+8).

Variation of valency in transition elements

Transition metals and inner-transition metals show variable valency of 1, 2 or 3 as they use electrons from outer as well as penultimate or inner-penultimate shell.

6. Chemical Reactivity

Reactivity of metals increases with decrease in Ionisation energy, electronegativity and increase in atomic radii and electropositive character.

Reactivity of non-metals increases with increase in electronegativity and electron gain enthalpy and decreases with increase in atomic radii.

Variation in a group

On moving down the group, reactivity of metals increases while for non-metals it decreases.

Variation in a period

Reactivity of metals decreases while reactivity of non-metals increases across the period.

Some Points to Remember

- Alkali metals are most reactive, strongest reducing agent and have lowest ionisation enthalpy.
- Hydrogen is the lightest element and lithium is the lightest metal.
- Liquid metal is Hg.
- Diamond is the hardest natural substance.
- Halogens are most reactive, strongest oxidising agent and have higher ionisation enthalpy.
- Metallic character increases down the group.
- Basic strength of the oxides or hydroxides increases down the group.
- The reducing character of the elements increases down the group.
- The oxidising character of the element decreases down the group.
- Nomenclature of elements with atomic numbers > 100.
- Almost all metallic oxides are basic but ZnO and Al_2O_3 are amphoteric. Similarly non-metallic oxides are acidic but CO, N_2O and NO are neutral. Cl_2O_7 is the most acidic oxide.
- Li metal has minimum density while iridium (Ir) metal has maximum density.
- Tungsten metal has highest melting point while non-metal with the highest melting point is carbon (diamond).

Notation for IUPAC Nomenclature of Elements

S.No.	Digit	Name	Abbreviation
1.	0	nil	n
2.	1	un	u
3.	2	bi	b
4.	3	tri	t
5.	4	quad	q
6.	5	pent	p
7.	6	hex	h
8.	7	sept	s
9.	8	oct	o
10.	9	enn	e

To write the name of any element with atomic number more than 100, write the name of each number from the table followed by "ium".

Atomic no.	Name
101	un-nilunium 1 0 1
109	un-nil-ennium 1 0 9

Practice Zone

DAY 18

1. The electronic configuration of an element is $1s^2 2s^2 2p^6$, $3s^2$ $3p^3$. The atomic number and the group number of the element 'X' which is just below the above element in the periodic table are respectively

(a) 23 and 5
(b) 23 and 15
(c) 33 and 15
(d) 33 and 5

2. A sudden jump between the values of second and third ionisation energy will be associated with the electronic configuration

(a) $1s^2, 2s^2\ 2p^6, 3s^1$
(b) $1s^2, 2s^2\ 2p^6, 3s^2 3p^1$
(c) $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6$
(d) $1s^2, 2s^2\ 2p^6, 3s^2$

3. Atomic radii of fluorine and neon (in Å) are respectively given by

(a) 0.72, 1.60
(b) 1.60, 1.60
(c) 0.72, 0.72
(d) None of these

4. The first ionisation potential of Na, Mg, Al and Si are in the order

(a) Na $<$ Mg $>$ Al $<$ Si
(b) Na $>$ Mg $>$ Al $>$ Si
(c) Na $<$ Mg $<$ Al $>$ Si
(d) Na $>$ Mg $>$ Al $<$ Si

5. The outermost electronic configuration of the most electronegative element is

(a) ns^2np^3
(b) ns^2np^4
(c) ns^2np^5
(d) ns^2np^6

6. Which one of the following is correct order of increase of size ?

(a) $Mg < Na^+ < F^- < Al$
(b) $Na^+ < Al < Mg < F^-$
(c) $Na^+ < F^- < Al < Mg$
(d) $Na^+ < F^- < Mg < Al$

7. Which element was named as eka-silicon in Mendeleef classification of elements?

(a) Germanium
(b) Gallium
(c) Thallium
(d) Selenium

8. Which of the following electronic configurations would exhibit the lowest ionisation energy ?

(a) $1s^2$
(b) $1s^2, 2s^2 2p^2$
(c) $1s^2, 2s^2 2p^6$
(d) $1s^2, 2s^2 2p^6, 3s^1$

9. The statement that is not correct for the periodic classification of elements, is

(a) the properties of the elements are the periodic function of their atomic number
(b) non-metallic elements are lesser in number than metallic elements
(c) the first ionisation energies of elements along a period do not vary in a regular manner with increase in atomic number
(d) for transition elements the *d* subshells are filled with electrons monotonically with increase in atomic numbers

10. Which one of the following is smallest in size?

(a) N^{3-}
(b) O^{2-}
(c) F^-
(d) Na^+

11. A coinage metal has

(a) two electrons in valence shell
(b) eight electrons in the penultimate shell
(c) eighteen electrons in the penultimate shell
(d) eight electrons in the outermost shell

12. The correct order of second ionisation potential of carbon, nitrogen, oxygen and fluorine is

(a) C $>$ N $>$ O $>$ F
(b) O $>$ N $>$ F $>$ C
(c) O $>$ F $>$ N $>$ C
(d) F $>$ O $>$ N $>$ C

13. The incorrect statements among the following is

(a) the first ionisation potential of Al is less than the first ionisation potential of Mg
(b) the second ionisation potential of Mg is greater than the second ionisation potential of Na
(c) the first ionisation potential of Na is less than the first ionisation potential of Mg
(d) the third ionisation potential of Mg is greater than the third ionisation potential of Al

14. The bond between atoms of two elements with atomic number 37 and 53 is

(a) electrovalent
(b) covalent
(c) coordinate
(d) metallic

15. Ionic radii of

(a) $Ti^{4+} < Mn^{2+}$
(b) $_{35}Cl^- < _{37}Cl^-$
(c) $K^+ > Cl^-$
(d) $P^{3+} > P^{5+}$

16. The correct order of radii is

(a) $N < Be < B$
(b) $F^- < O^{2-} < N^{3-}$
(c) $N < Li < K$
(d) $Fe^{3+} < Fe^{2+} < Fe^{4+}$

17. The formation of the oxide ion, O^{2-} (*g*) from oxygen atom requires first an exothermic and then an endothermic step as shown below

$$O(g) + e^- \rightarrow O^-(g);\ \Delta H^\ominus = -141 \text{ kJ mol}^{-1}$$

$$O^-(g) + e^- \rightarrow O^{2-}(g);\ \Delta H^\ominus = +780 \text{ kJ mol}^{-1}$$

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, **[NCERT Exemplar]**

(a) oxygen is more electronegative
(b) addition of electron in oxygen results in larger size of the ion
(c) electron repulsion outweights the stability gained by achieving noble gas configuration
(d) O^- ion has comparatively smaller size than oxygen atom

18. Which pair of elements has same chemical properties?

(a) 13, 22
(b) 3, 11
(c) 4, 24
(d) 2, 4

19. How many Cs atoms can be converted to Cs^+ ion by 1 Joule energy if IE_1 for Cs is 376 kJ mol^{-1} ?

(a) 1.60×10^{23}
(b) 1.60×10^{15}
(c) 1.60×10^{18}
(d) 16.0×10^{26}

20. Chloride ion and potassium ion are isoelectronic, then

(a) their sizes are same
(b) Cl^- ion is bigger than K^+ ion
(c) K^+ ion is relatively bigger
(d) their sizes depend on other cation and anion

21. Identify the least stable ion amongst the following.

(a) Li^-
(b) Be^-
(c) B^-
(d) C^-

22. Electronegativity of F on Pauling scale is 4.0. What will be its value on Mulliken scale ?

(a) 10.0
(b) 11.2
(c) 8.54
(d) 16.0

23. Which one of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of the given atomic species ?

(a) $Cl < F < S < O$
(b) $O < S < F < Cl$
(c) $S < O < Cl < F$
(d) $F < Cl < O < S$

24. Two elements whose electronegativities are 1.2 and 3.0, the bond formed between them would be

(a) ionic
(b) covalent
(c) coordinate
(d) metallic

25. How many joules of energy must be absorbed to convert Li to Li^+, all the atoms present in 1.00 mg of gaseous Li? IE_1 of Li is 520.3 kJ mol^{-1} (Li = 7).

(a) 0.00743 kJ
(b) 0.520 kJ
(c) 520 kJ
(d) 0.0743 kJ

26. Which of the following series of elements have nearly the same atomic radii?

(a) F, Cl, Br, I
(b) Na, K, Rb, Cs
(c) Li, Be, B, C
(d) Fe, Co, Ni, Cu

27. Electronic configurations of four elements *A*, *B*, *C* and *D* are given below, **[NCERT Exemplar]**

(A) $1s^2 2s^2 2p^6$
(B) $1s^2 2s^2 2p^4$
(C) $1s^2 2s^2 2p^6 3s^1$
(D) $1s^2 2s^2 2p^5$

Which of the following is the correct order of increasing tendency to gain electron?

(a) $A < C < B < D$
(b) $A < B < C < D$
(c) $D < B < C < A$
(d) $D < A < B < C$

Directions (Q. Nos. 28 to 30) *The IE_1 and IE_2 in kJ mol^{-1} of a few elements are given below*

Element	IE_1	IE_2
A	2372	5251
B	520	7300
C	900	1760
D	1680	3380

Based on the above information, answer the following questions

28. Which of the above elements is likely to be a reactive metal ?

(a) *A*
(b) *B*
(c) *C*
(d) *D*

29. Which represents a noble gas ?

(a) *A*
(b) *B*
(c) *C*
(d) *D*

30. Which of the above elements forms a stable binary halide of the formula MX_2 ?

(a) *A*
(b) *B*
(c) *C*
(d) *D*

Directions (Q. Nos. 31 and 32) *The heats of formation (ΔH_f°) of the oxides of third period, sodium to chlorine, are in kJ mol^{-1}*

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
−416	−602	−1676	−911	−2984	−395	+ 250

31. Which oxide has maximum negative heat of formation per oxygen atom?

(a) P_4O_{10}
(b) Al_2O_3
(c) Na_2O
(d) MgO

32. Most stable and least stable oxides are

(a) P_4O_{10}, Cl_2O_7
(b) Na_2O, Cl_2O_7
(c) MgO, Cl_2O_7
(d) Cl_2O_7, MgO

Directions *(Q. Nos. 33 to 36) Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

33. **Statement I** Cesium and fluorine both reacts violently.
Statement II Cesium is most electropositive and fluorine is most electronegative.

34. **Statement I** Scandium ($Z = 21$) is placed in d-block element.
Statement II Last filling electron goes into $3d$ orbit.

35. **Statement I** The atomic radii of the elements of the oxygen family are smaller than the atomic radii of the corresponding elements of the nitrogen family.
Statement II The members of the oxygen family are more electronegative and thus, have lower values of nuclear charge than those of the nitrogen family.

36. **Statement I** Fluorine has a less negative electron affinity than chlorine.
Statement II There is relatively greater effectiveness of $2p$ electrons in the small fluorine atom to repel the additional electron entering the atom than to $3p$ electrons in the larger Cl atom.

37. The IE values of $Al(g) \longrightarrow Al^{+} + e^{-}$ is 577.5 kJ mol^{-1} and ΔH for $Al(g) \longrightarrow Al^{3+}(g) + 3e^{-}$ is 5140 kJ mol^{-1}.
If the ratio of second and third IE is 2 : 3, the values of IE_2 and IE_3 are respectively
(a) 1825 and 2737.5 kJ mol^{-1} (b) 182.5 and 273.75 kJ mol^{-1}
(c) 1825 and 2700 J mol^{-1} (d) 2737.5 and 1825 kJ mol^{-1}

38. How many Cl atoms can you ionise in the process $Cl \longrightarrow Cl^{+} + \bar{e}$, by the energy liberated for the process $Cl + \bar{e} \longrightarrow Cl^{-}$ for Avogadro's number of atoms?
[Given IE = 12.967 and EA = −3.61 eV]
(a) 16.75×10^{23} Cl atoms (b) 1.675×10^{18} Cl atoms
(c) 1.675×10^{32} Cl atoms (d) 1.675×10^{23} Cl atoms

39. What will be the electronegativity of carbon at Pauling scale?
Given that $E_{H-H} = 104.2$ kcal mol^{-1}, $E_{C-C} = 83.1$ kcal mol^{-1}

$$E_{C-H} = 98.8 \text{ kcal mol}^{-1}$$

[Electronegativity of hydrogen = 2.1]
(a) 0.498 (b) 0.598 (c) 2.134 (d) 2.598

40. Ionisation potential and electron affinity of fluorine are 17.42 and 3.45 eV respectively. What will be the ratio of electronegativity of fluorine on Mulliken scale and Pauling scale ?
(a) 2.80 : 1 (b) 1.80 : 1 (c) 2.40 : 1 (d) 4.20 : 1

41. An extra electron is added at the periphery of nitrogen atom in the formation of anion. What will be the ratio of effective nuclear charge of nitrogen atom and nitrogen anion ?
(a) 2.09 : 1 (b) 0.09 : 1 (c) 3.09 : 1 (d) 1.09 : 1

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42. The element with which of the following outer electron configuration may exhibit the largest number of oxidation states in its compounds **[JEE Main Online 2013]**
(a) $3d^5 4s^2$ (b) $3d^8 4s^2$
(c) $3d^7 4s^2$ (d) $3d^6 4s^2$

43. Which is the correct order of second ionization potential of C, N, O and F in the following? **[JEE Main Online 2013]**
(a) O > N > F > C
(b) O > F > N > C
(c) F > O > N > C
(d) C > N > O > F

44. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^{+} will be **[IIT JEE-Main 2013]**
(a) − 5.1 eV (b) − 10.2 eV
(c) + 2.55 eV (d) − 2.55 eV

45. Which of the following represents the correct order of increasing first ionisation enthalpy for Ca, Ba, S, Se and Ar? **[IIT JEE-Main 2013]**
(a) S < Se < Ca < Ba < Ar (b) Ba < Ca < Se < S < Ar
(c) Ca < Ba < S < Se < Ar (d) Ca < S < Ba < Se < Ar

46. The increasing order of the ionic radii of the given isoelectronic species is **[AIEEE 2012]**
(a) $Cl^{-}, Ca^{2+}, K^{+}, S^{2-}$ (b) $S^{2-}, Cl^{-}, Ca^{2+}, K^{+}$
(c) $Ca^{2+}, K^{+}, Cl^{-}, S^{2-}$ (d) $K^{+}, S^{2-}, Ca^{2+}, Cl^{-}$

47. Which one of the following orders present the correct sequence of the increasing basic nature of the given oxides? **[AIEEE 2011]**
(a) $Al_2O_3 < MgO < Na_2O < K_2O$
(b) $MgO < K_2O < Al_2O_3 < Na_2O$
(c) $Na_2O < K_2O < MgO < Al_2O_3$
(d) $K_2O < Na_2O < Al_2O_3 < MgO$

48. The correct sequence which shows decreasing order of the ionic radii of the elements is **[AIEEE 2010]**

(a) $Al^{3+} > Mg^{2+} > Na^{+} > F^{-} > O^{2-}$
(b) $Na^{+} > Mg^{2+} > Al^{3+} > O^{2-} > F^{-}$
(c) $Na^{+} > F^{-} > Mg^{2+} > O^{2-} > Al^{3+}$
(d) $O^{2-} > F^{-} > Na^{+} > Mg^{2+} > Al^{3+}$

49. The charge/size ratio of a cation determines its polarising power. Which one of the following sequences represents the increasing order of the polarising power of the cationic species, K^{+}, Ca^{2+}, Mg^{2+}, Be^{2+}? **[AIEEE 2007]**

(a) $Mg^{2+} < Be^{2+} < K^{+} < Ca^{2+}$
(b) $Be^{2+} < K^{+} < Ca^{2+} < Mg^{2+}$
(c) $K^{+} < Ca^{2+} < Mg^{2+} < Be^{2+}$
(d) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^{+}$

50. The ionic mobility of alkali metal ions in aqueous solution is maximum for **[AIEEE 2006]**

(a) K^{+} (b) Rb^{+}
(c) Li^{+} (d) Na^{+}

51. The increasing order of the first ionisation enthalpies of the elements B, P, S, and F (lowest first) is **[AIEEE 2006]**

(a) F < S < P < B (b) P < S < B < F
(c) B < P < S < F (d) B < S < P < F

52. In which of the following arrangements the order is not according to the property indicated against it ? [AIEEE [illegible]]

(a) Li < Na < K < Rb : increasing metallic radius.
(b) I < Br < F < Cl : increasing electron gain enthalpy (with negative sign)
(c) B < C < N < O : increasing first ionisation enthalpy
(d) $Al^{3+} < Mg^{2+} < Na^{+} < F^{-}$: increasing ionic size

53. Based on lattice energy and other considerations which one of the following alkali metal chlorides is expected to have the highest melting point ? [AIEEE [illegible]]

(a) RbCl (b) KCl (c) NaCl (d) LiCl

54. Which among the following factors is the most important in making fluorine the strongest oxidising agent ? [AIEEE [illegible]]

(a) Electron affinity (b) Ionisation enthalpy
(c) Hydration enthalpy (d) Bond dissociation energy

55. The atomic numbers of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe) are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionisation enthalpy ? [AIEEE [illegible]]

(a) V (b) Cr (c) Mn (d) Fe

56. Identify the correct order of solubility in aqueous medium. [AIEEE [illegible]]

(a) $CuS > ZnS > Na_2S$ (b) $ZnS > Na_2S > CuS$
(c) $Na_2S > CuS > ZnS$ (d) $Na_2S > ZnS > CuS$

Answers

1. (c)	**2.** (d)	**3.** (a)	**4.** (a)	**5.** (c)	**6.** (b)	**7.** (a)	**8.** (d)	**9.** (d)	**10.** (d)
11. (c)	**12.** (c)	**13.** (b)	**14.** (a)	**15.** (d)	**16.** (b)	**17.** (c)	**18.** (b)	**19.** (c)	**20.** (b)
21. (b)	**22.** (b)	**23.** (b)	**24.** (a)	**25.** (d)	**26.** (d)	**27.** (a)	**28.** (b)	**29.** (a)	**30.** (c)
31. (d)	**32.** (b)	**33.** (a)	**34.** (a)	**35.** (c)	**36.** (a)	**37.** (a)	**38.** (d)	**39.** (d)	**40.** (a)
41. (d)	**42.** (a)	**43.** (b)	**44.** (a)	**45.** (b)	**46.** (c)	**47.** (a)	**48.** (d)	**49.** (c)	[illegible]
51. (d)	**52.** (c)	**53.** (c)	**54.** (c)	**55.** (b)	**56.** (d)				

Hints & Solutions

1. Atomic number of the given element = 15

Group number = 10 + 5 (valence electron) = 15
Period = 3
Atomic number of the element just below = 33

2. The jump in ionisation energy is noticed during successive removal of electron when valence shell changes.

3. Atomic radii of neon being van der Waals' radius is higher than that of fluorine which is infact covalent radius.

4. IE_1 of Mg is higher than that of Na because of increased nuclear charge and also that of Al because in Mg a 3*s* electron (more stable) has to be removed while in Al it is the 3*p* electron.

The IE_1 of Si is, however, higher than those of Mg and Al because of increased nuclear charge. Thus, the overall order is Na < Mg > Al < Si.

5. ns^2np^5 configuration represents the most electronegative element as after gaining one electron it becomes more stable (inert gas configuration). [electronegativity is the tendency of attracting electron]

6. Na^{+} and F^{-} ions are isoelectronic, therefore, F^{-} has the largest and Na^{+} has the lowest size. Further, Al with higher nuclear charge has lower size than Mg. Thus, the overall order is

$$Na^{+} < Al < Mg < F^{-}$$

7. Germanium was called eka-silicon in Mendeleef's time.

8. Bigger the size of the atom, smaller will be its IE.

9. For transition elements, *d*-subshells are not filled with electrons monotonically (one at a time) because of extra stability of d^5 and d^{10} configuration. Besides these, there are many other exceptions also, *e.g.*, Nb, Mo, Ru, Rh, Pb, etc.

10. As the nuclear charge increases atomic size decreases (in case of isoelectronic species).

11.
$$\text{Cu} = [\text{Ar}]\ 3d^{10}, 4s^1$$
$$\text{Ag} = [\text{Kr}]\ 4d^{10}, 5s^1$$
$$\text{Au} = [\text{Xe}]\ 5d^{10}, 6s^1$$

12. After the removal of an electron from C, N, O and F, their electronic configurations are :

$$C^+ (1s^2, 2s^2 2p^1)$$
$$N^+ (1s^2, 2s^2\ 2p^2)$$
$$O^+ (1s^2, 2s^2 2p_x^1 2p_y^1 2p_z^1)$$
and $$F^+ (1s^2, 2s^2 2p_x^2 2p_y^1 2p_z^1)$$

Since O^+ gives a stable electronic configuration with exactly half filled 2*p*-subshell.

$\therefore$ IE_2 of O is higher than that of F. The IE_2 of C because of the larger size is lower than that of N. Thus, the overall order is $O > F > N > C$.

13. IE_2 of Mg is lower than that of Na because in case of Mg^{2+}, 3s electron has to be removed while in case of Na^+, an electron from the stable inert gas configuration (neon) has to be removed.

14. Atomic number 37 = Rb

Atomic number 53 = I

The bond between alkali metals and halogens is electrovalent.

15. P^{5+} has more effective nuclear charge than P^{3+} and is smaller in size than P^{3+}.

16. Among the isoelectronic species, the size increases as the negative charge increases.

17. The process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon because electron repulsion outweights the stability gained by achieving noble gas configuration.

18. The pair which belongs to same group *i.e.*, in which both the elements have same outer electronic configuration has same chemical properties.

$$3 \Rightarrow 1s^2, 2s^1$$
$$11 \Rightarrow 1s^2, 2s^2\ 2p^6, 3s^1$$

19. 376×10^3 Joule energy produces 6.023×10^{23} ions.

$$\therefore 1 \text{ Joule energy will produce} = \frac{6.023 \times 10^{23}}{3.76 \times 10^3}$$
$$= 1.60 \times 10^{18}\ Cs^+ \text{ ions}$$

20. In isoelectronic species, anion is larger in size than the cation.

21. Be has fully filled 2*s*-subshell $(2s^2)$ and therefore, show least tendency to accept an electron. Thus, Be^- is least stable.

22. Electronegativity on Mulliken scale and Pauling scale are given by

$$\chi_M = \chi_P \times 2.8 = 4.0 \times 2.8 = 112$$

Usually, Mulliken's value of electronegativity are 2.8 times of pauling value.

23. Generally electron gain enthalpy increases in a period from left to right but decreases in a group on moving down. Therefore, halogens have very high electron affinities. Fluorine due to its smaller size has unexpectedly low electron gain enthalpy than Cl. Similar is shown in case of O and S. Thus, the order of electron gain enthalpy is

$$Cl > F > S > O$$

24. When the electronegativity difference is more than 1.7, the bond formed will be ionic in nature.

25. $1.00 \text{ mg} = 1 \times 10^{-3} \text{ g} = \frac{1 \times 10^{-3}}{7}$ mol Li

1 mole of Li is converted by 520.3 kJ.

$\therefore \frac{1 \times 10^{-3}}{7}$ mole is converted to Li^+ by

$$= \frac{520.3 \times 1 \times 10^{-3}}{7} \text{ kJ} = 0.0743 \text{ kJ}$$

26. These are transition metals with the $(n-1)d^{1-10}\ ns^{1-2}$ configuration. The atomic and ionic radii of transition elements in a given series show a decreasing trend for first five elements and then becomes almost constant for next five elements.

27. The correct order of increasing tendency to gain electron is $A < C < B < D$. The reason is that half filled or completely filled subshells possess extra stable nature and thus, it is difficult to add or remove electron from it.

28. Element *B* is reactive alkali metal as it has lowest IE_1.

37. Given, IE_1 of $Al = 577.5 \text{ kJ mol}^{-1}$ ...(i)

$[IE_1 + IE_2 + IE_3]$ of $Al = 5140 \text{ kJ mol}^{-1}$ ...(ii)

$IE_2 = (2/3)\ IE_3$ ...(iii)

Solving (i), (ii) and (iii), we get

$$IE_2 = 1825 \text{ kJmol}^{-1}, \quad IE_3 = 2737.5 \text{ kJmol}^{-1}$$

38. Let *n* atoms of chlorine be ionised in the process $Cl \longrightarrow Cl^+ + e^-$ by the energy liberated during gain of electron by *N* atoms as following :

$$Cl + e^- \longrightarrow Cl^-$$

$\therefore$ Energy liberated during addition of electron for '*N*' Cl atoms = Energy used during removal of electron from '*n*' Cl atoms

or $\quad N \times EA = n \times IE$

or $\quad n = \frac{6.023 \times 10^{23} \times 3.61}{12.967} = 1.675 \times 10^{23}$ Cl atoms

39. $\chi_C - \chi_H = 0.208\sqrt{\Delta}$

where, $\Delta = E_{C-H} - \sqrt{E_{C-C} \times E_{H-H}}$

$$\Delta = 98.8 - \sqrt{83.1 \times 104.2}$$
$$\therefore \quad \Delta = 5.75$$
$$\chi_C - 2.1 = 0.208\sqrt{5.75}$$
$$\chi_C - 2.1 = 0.497, \quad \chi_C = 2.597$$

40. $(\chi_F)_M = \frac{IP + EA}{2}$

$$(\chi_F)_M = \frac{17.42 + 3.45}{2} = 10.435$$

$$(\chi_F)_P = \frac{10.435}{2.8} = 3.726$$

$$(\chi_F)_M : (\chi_F)_P = 2.80 : 1$$

41. $Z_{eff} = Z - \sigma$; $\sigma = [0.35 \times$ electrons in nth shell excluding last electron] + [$0.85 \times$ electrons in $(n-1)$ shell]

(i) For N atom = $1s^2, 2s^2 2p^3$

$$\therefore \quad \sigma = [4 \times 0.35] + [2 \times 0.85] = 3.10$$

$$\therefore Z_{eff} = 7 - 3.10 = 3.90$$

(ii) For N^- ion $1s^2, 2s^2, 2p^4$

$$\sigma = [5 \times 0.35] + [2 \times 0.85] = 3.45$$

$$\therefore \quad Z_{eff} = 7 - 3.45 = 3.55$$

Z_{eff} (N atom) : Z_{eff} (N^- anion)

1.09 : 1

42. Due to the presence of maximum number of unpaired electrons, element having $3d^5, 4s^2$, configuration may exhibit the largest number of oxidation states in its compounds.

43. Second ionisation potential represents the amount of energy required to remove an electron from a unipositive ion. The electronic configuration of unipositive ions of given atoms is as

$C^+ (6 - 1 = 5) = 1s^2, 2s^2, 2p^1$

$N^+ (7 - 1 = 6) = 1s^2, 2s^2, 2p^2$

$O^+ (8 - 1 = 7) = 1s^2, 2s^2, 2p^3$

$F^+ (9 - 1 = 8) = 1s^2, 2s^2, 2p^4$

From the electronic configuration, it is clear that the second IP of O is highest because here the electron which is to be removed belongs to half-filled (so more stable) p orbital. Moreover, along a period, as the number of electrons increases, size decreases, effective nuclear charge increases and hence, IP increases. Thus, the correct order of second IP is $O > F > N > C$

44. $Na \underset{\Delta H = -5.1 \text{ eV}}{\overset{\Delta H = +5.1 \text{ eV}}{\rightleftharpoons}} Na^+ + e^-$, here the backward reaction releases same amount of energy and known as electron gain enthalpy.

45. Increasing order of first ionization enthalpy is, $Ba < Ca < Se < S < Ar$.

$$r_n \propto \frac{1}{Z}$$

46. For isoelectronic species $r_n \propto \frac{1}{Z}$

Species	Z	Electrons
Cl^-	17	18
Ca^{2+}	20	18
K^+	19	18
S^{2-}	16	18

Thus, ionic size is in order $Ca^{2+} < K^+ < Cl^- < S^{2-}$

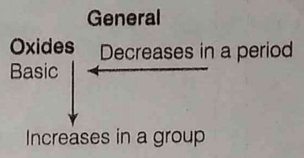
47. Oxides when dissolved in water form hydroxides.

$$Na_2O + H_2O \longrightarrow 2\,NaOH$$

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

$$Al_2O_3 + 3H_2O \longrightarrow 2Al(OH)_3$$

Smaller the size of cation and larger the charge, greater the polarising power of cation, hence greater the covalent character, hence smaller the basic nature.



Charge $Al^{3+} > Mg^{2+} > Na^+ = K^+$

Size $Al^{3+} < Mg^{2+} < Na^+ < K^+$

Polarising power $Al^{3+} > Mg^{2+} > Na^+ > K^+$

Basic nature of oxides

$$Al_2O_3 < MgO < Na_2O < K_2O$$

48. $O^{2-}, F^-, Na^+, Mg^{2+}$ and Al^{3+} are isoelectronic species and higher the nuclear charge, smaller the size of isoelectronic species.

49. Higher the charge/size ratio, more is the polarising power

$$K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$$

50. Li^+ has largest hydrated ionic size while Rb^+ has smallest. Smaller the size, greater the mobility.

51. Examine the positions in Periodic Table

B C N O F
P S

Phosphorus has stable half filled configuration. Hence, order is $B < S < P < F$.

52. (a) Metallic radii increase in a group from top to bottom.
Thus, $Li < Na < K < Rb$ is true.

(b) Electron gain enthalpy of $Cl > F$ and decreases along a group.
Thus, $I < Br < F < Cl$ is true.

(c) Ionisation enthalpy increases along a period from left to right but due to presence of half filled orbitals in N, ionisation enthalpy of $N > O$.
Thus, $B < C < N < O$ is incorrect.

53. As we go down in the group, ionic character increases, hence melting point of halides should increase but NaCl has the highest melting point (800°C) due to its high lattice energy.

54. Fluorine has the most negative $\Delta G°$ value which is dependent on hydration enthalpy.

55.

$Fe^+(26) = [Ar]\ 3d^6, 4s^1$

$Mn^+(25) = [Ar]\ 3d^5, 4s^1$

$V^+(23) = [Ar]\ 3d^2, 4s^2$

$Cr^+(24) = [Ar]\ 3d^5, 4s^0$

By first IP, the electronic configuration of Cr^+ is most stable, hence formation of Cr^{2+} by second IP requires maximum enthalpy.

56. Solubility of sulphide in aqueous medium decreases with decrease in ionic character.

Day 19

General Principles and Processes of Isolation of Metals

Day 19

Outlines ...

- Earth Crust
- Metallurgy
- Steps Involved in the Extraction of Metals
- Extraction of Crude Metal from Concentrated Ore
- Occurrence and Extraction of Some Metals

Earth Crust

Earth crust is the source of many elements. Aluminium is the most abundant metal of earth crust and iron comes second. The percentage of different elements in earth crust is

O-49%, Si-26%, Al-7.5%, Fe-4.2%, Ca-3.2%, Na-2.4%, K-2.3%, Mg-2.3%, H-1%.

Metals occur in two forms in nature (i) in native state and (ii) in combined state.

Minerals and Ores

The substance (or compound) in the form of which metal is found in nature is called a **mineral** and the mineral from which extraction of metal is beneficial and cheap is called an **ore**.

Thus, all ores are minerals but all minerals are not ores.

Types of Ores

Depending upon the nature of associated group or atom, ores are of following types

(i) **Oxide ores** e.g., Haematite (Fe_2O_3), Zincite (ZnO) etc.

(ii) **Sulphide ores** e.g., Galena (PbS), Cinnabar (HgS), Argentite (Ag_2S), Ruby silver ($Ag_2S \cdot Sb_2S_3$).

(iii) **Carbonate ores** e.g., Magnesite ($MgCO_3$), Siderite ($FeCO_3$) etc.

(iv) **Sulphate ores**, e.g., Gypsum ($CaSO_4 \cdot 2H_2O$), Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) etc.

(v) **Silicate ores** e.g., Willemite (Zn_2SiO_4), Feldspar ($NaAlSi_3O_8$).

Nitrate ores are rare because all nitrates are water soluble and at higher temperature, they decompose into oxides or metal.

Gangue or Matrix

The impurities associated with the ore are called gangue or matrix.

Metallurgy

Extraction of a metal from its ores is known as **metallurgy**. Metallurgy of a metal includes several **metallurgical operations** depending upon the nature of metal, its ore and impurities.

All metallurgical processes may be divided into three processes

Pyrometallurgical Process

[Extraction through heating]

Extraction of metals take place at very high temperature. Cu, Fe, Zn, Sn, Pb, Ni, Cr, Hg are extracted by pyrometallurgical process.

Hydrometallurgical Process

Extraction of metal by the use of their aqueous solution is called hydrometallurgical process. Ag and Au are extracted by this process.

In hydrometallurgy, metals like Fe cannot be used because it is not easy to remove excess iron from precious metal such as Ag, Au; while excess zinc can easily be removed as it is volatile.

Electrometallurgical Process

Sodium, potassium, lithium, calcium, magnesium and aluminium are extracted from their molten salt solutions through electrolytic method.

Steps Involved in the Extraction of Metals

Various steps/processes involved in the extraction of a metal are as follows.

Concentration of Ores

Removal of unwanted materials from the ores is known as **concentration of ores** or **ore dressing**.

Some of the important procedures are described below

Hydraulic Washing (levigation)

In this process, an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind. The oxides ores of iron (Fe_3O_4 and Fe_2O_3) are concentrated by this method.

Magnetic Separation

This is based on differences in magnetic properties of the ore components. If either the ore or the gangue is capable of being attracted by a magnetic field, this process is used.

In electrostatic separation, electrically charged surfaces are used to separate metallic particles from non-metallic particles of ore.

Froth Floatation Method

This method is used for the concentration of **sulphide ores**. In this process, a suspension of the **powdered ore** is made with water. To it, **collectors** and **froth stabilisers** are added.

- *Collectors (e.g. pine oil, fatty acids, xanthates etc.) enhance non-wettability of the mineral particles and froth stabilisers (e.g. cresols, aniline) stabilise the froth.*
- *Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using 'depressants', e.g. In case of an ore containing ZnS and PbS, the depressant used is NaCN.*

Leaching

Leaching is often used if the ore is soluble in some solvent (*i.e.*, acids, bases or other chemicals) but not the impurities. *e.g.*,

(i) **Leaching of alumina from bauxite** (Baeyer process)

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \xrightarrow{473-523K} \underset{\text{Sodium meta aluminate}}{2Na[Al(OH)_4](aq)}$$

$$SiO_2(s) + 2NaOH(aq) \xrightarrow{473-523K} \underset{\text{Sodium silicate}}{Na_2SiO_3(aq)} + H_2O\ Cl$$

The resulting solution is filtered, cooled and pH is adjusted by neutral with CO_2 causing precipitation of aluminium hydroxide.

$$2Na[Al(OH)_4](aq) + 2CO_2(g) \longrightarrow Al_2O_3 \cdot xH_2O(s)\downarrow + 2NaHCO_3(aq)$$

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3.

$$Al_2O_3 \cdot xH_2O(s) \xrightarrow{1470K} Al_2O_3(s) + xH_2O(g)$$

(ii) **In the metallurgy of silver and gold**

$$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \longrightarrow 4[M(CN)_2^-](aq) + \underset{(M = Ag \text{ or } Au)}{4OH^-(aq)}$$

$$2[M(CN)_2]^-(aq) + Zn(s) \longrightarrow [Zn(CN)_4]^{2-}(aq) + 2M(s)$$

Extraction of Crude Metal from Concentrated Ore

It involves two major steps conversion of concentrated ore to oxide, and reduction of the oxide to metal

Conversion of Concentrated Ore to Oxide

The following steps are considered under the conversion of concentrated ore to oxide.

(a) **Calcination**

Strong heating of ore in absence of air. *e.g.*,

$$Fe_2O_3 \cdot xH_2O(s) \xrightarrow{\Delta} Fe_2O_3(s) + xH_2O(g)$$

$$ZnCO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$

$$CaCO_3 \cdot MgCO_3(s) \xrightarrow{\Delta} MgO(s) + CaO(s) + 2CO_2(g)$$

Usually **carbonates and hydroxides are converted** into oxides by this method.

Volatile impurities of S, As and P are removed as their volatile oxides.

(b) **Roasting**

Strong heating of ore in presence of air. *e.g.*,

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

The sulphide ores of copper are heated in reverberatory furnace. If the ore contains iron, it is mixed with silica before heating. Iron oxide slags off as iron silicate and copper is produced in the form of copper matte which contains Cu_2S and FeS.

$$FeO + SiO_2 \longrightarrow FeSiO_3 \text{ (slag)}$$

SO_2 produced is utilised for manufacturing H_2SO_4.

Usually sulphide ores are converted into oxides by this method.

- *In chloridising roasting, the ore containing As, S or Sb as impurity is heated with common salt in presence of silver ores.*
- *In sulphating roasting, sulphide ores are oxidised into sulphate, e.g., ZnS is oxidised to $ZnSO_4$.*

Reduction of Oxide to Metal

Reduction of the metal oxide to metal takes place when heated with reducing agents such as C (coke,) or CO or even another metal.

The process is known as **smelting**.

$$M_xO_y + yC \longrightarrow xM + yCO$$

Some metal oxides get reduced easily while others are very difficult to be reduced.

- *Some metals like Fe dissolve the reducing agent used (carbon) in their extraction. This can be removed by heating the impure metal with more of the ore.*
- *Misch metal is used as a reducing agent for extraction of pure vanadium. Hydrogen is used as a reducing agent in extraction of pure tungsten and vanadium.*

Thermodynamics of Metallurgy

To understand the variation of temperature requirement for thermal reactions and suitable reducing agent for a given metal oxide (M_xO_y), Gibbs energy interpretations are made.

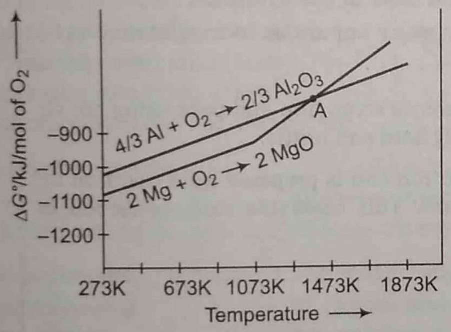
Gibbs equation,

$$\Delta G = \Delta H - T\Delta S$$

where, ΔH = enthalpy change,
ΔG = Gibbs free energy,
T = temperature,
ΔS = entropy change
$\Delta G^\circ = -2.303\, RT \log K$,
K = equilibrium constant

If $\Delta G = -$ve, process is spontaneous, $\Delta G = +$ ve, process is non-spontaneous, ΔG = zero, process is at equilibrium.

A reaction with positive ΔG can still be made to occur by coupling it with another reaction having large negative ΔG. Such coupling is easily understood through **Ellingham diagram.**



Gibbs Energy (ΔG°) *vs* T plots

(Ellingham diagram)

From Ellingham diagram, it is evident that metals which have more negative $\Delta_f G^\circ$ of their oxides can reduce those metal oxides for which $\Delta_f G^\circ$ is less negative.

- Reduction can also be done by using Al, H_2 etc. By Al oxides of Cr, Fe and Mn are reduced. A mixture of Fe_2O_3 and Al is called **thermite mixture.**
- Highly electropositive metals like Na, K, Al are reduced by the electrolysis of their fused salts. *e.g.*,

$$\underset{\text{fused}}{NaCl} \rightleftharpoons Na^+ + Cl^-$$

$$Na^+ + e^- \longrightarrow Na$$

$$Cl^- \longrightarrow Cl + e^-$$

$$\downarrow$$

$$Cl_2$$

Refining

The metal obtained from the above processes is not 100% pure, hence called **crude metal.** From the impure metal, the metal of high purity is obtained by refining. Several techniques are used in refining depending upon the differences in properties of the metal.

Distillation

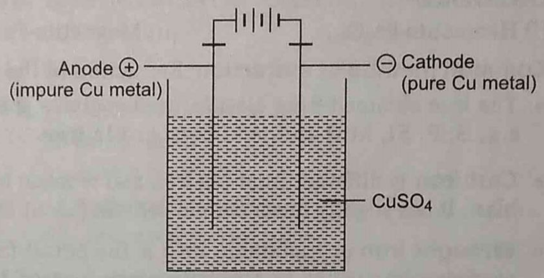
This process is very useful for low boiling metals like zinc cadmium and mercury. The impure metal is evaporated to obtain the pure metal as distillate.

Liquation

In this method, low melting metals like tin, bismuth & lead can be made to flow on a sloping surface of a reverberatory furnace & heated above their melting point. In this way it is separated from higher melting impurities.

Electrolytic Refining

Copper is refined by using an electrolytic method.



Anode $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ **Cathode** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Zone Refining

This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. This method is very useful for producing semiconductors and other metals of very high purity, *e.g.*, germanium, silicon, boron, gallium and indium.

Vapour Phase Refining

In this method, the metal is converted into its volatile compound. It is then decomposed to give pure metal, *e.g.*,

(i) Mond process for refining nickel

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

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

(ii) van Arkel method for zirconium titanium, vanadium or Thorium $Zr + 2I_2 \longrightarrow ZrI_4$ (volatile)

$$ZrI_4 \xrightarrow{1800\text{ K}} Zr + 2I_2$$

(iii) **Chromatographic method** This method is based on the principle that different components of a mixture are adsorbed differently on an adsorbent.

Occurrence and Extraction of Some Metals

Some of the important metals, their occurrence and extraction are given below.

Metal Aluminium (Al)

Occurrence

(i) Bauxite-$Al_2O_3 \cdot 2H_2O$, (ii) Cryolite-Na_3AlF_6

Common method of extraction Electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6 (Hall and Heroult process).

Metal Iron (Fe)

Occurrence

(i) Haematite-Fe_2O_3, (ii) Magnetite-Fe_3O_4

Common method of extraction Reduction of the oxide with CO and coke in blast furnace.

- The iron obtained from blast furnace contains about 4% carbon and many impurities in smaller amount (*e.g.*, S, P, Si, Mn) and is known as **pig iron.**
- **Cast iron** is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.
- **Wrought iron** or **malleable iron** is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon to carbon monoxide.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

Metal Copper (Cu)

Occurrence

(i) Copper pyrites- $CuFeS_2$ (ii) Copper glance- Cu_2S

Common method of extraction Roasting of sulphide partially and auto-reduction.

Metal Zinc (Zn)

Occurrence

(i) Zinc blende or sphalerite-ZnS
(ii) Calamine-$ZnCO_3$
(iii) Zincite-ZnO

Common method of extraction Roasting followed by reduction with coke.

The metal may be purified by fractional distillation.

Practice Zone

DAY 19

1. Which one of the following benefaction processes is used for the mineral, $Al_2O_3 \cdot 2H_2O$?
(a) Froth floatation
(b) Leaching
(c) Liquation
(d) Magnetic separation

2. In blast furnace, maximum temperature is in
(a) zone of fusion
(b) zone of combustion
(c) zone of slag combustion
(d) zone of reduction

3. Granulated zinc is obtained by
(a) suddenly cooling molten zinc
(b) adding molten zinc to water
(c) heating zinc to 100 – 150°C
(d) dropping molten zinc drop by drop

4. Use of electrolysis is
(a) electroplating
(b) electrorefining
(c) Both (a) and (b)
(d) None of these

5. In electrorefining of copper, some gold is deposited as
(a) anode mud
(b) cathode mud
(c) cathode
(d) electrolyte

6. Aluminothermic process is used for metallurgy of
(a) Pb
(b) Ag
(c) Al
(d) None of these

7. The chemical process in the production of steel from haematite ore involve
(a) reduction
(b) oxidation
(c) reduction followed by oxidation
(d) oxidation followed by reduction

8. Extraction of gold and silver involves leaching the metal with HCN^- ion. The metal is recovered by **[NCERT Exemplar]**
(a) displacement of metal by some other metal from the complex ion.
(b) roasting of metal complex
(c) calcination followed by roasting
(d) thermal decomposition of metal complex

9. Which one of the following reactions is an example of auto-reduction? **[NCERT Exemplar]**
(a) $Fe_3O_4 + 4C \rightarrow 3Fe + 4CO_2$
(b) $Cu_2O + C \rightarrow 2\,Cu + CO$
(c) $Cu^{2+}(aq) + Fe\,(s) \rightarrow Cu\,(s) + Fe^{2+}(aq)$
(d) $Cu_2O + \frac{1}{2}Cu_2\,S \rightarrow 3\,Cu + \frac{1}{2}SO_2$

10. Which metal can't be obtained from electrolysis?
(a) Ca
(b) Mg
(c) Cr
(d) Al

11. The lustre of a metal is due to
(a) its high density
(b) its high polishing
(c) its chemical inertness
(d) presence of free electrons

12. Malachite is an ore of
(a) iron (b) copper (c) mercury (d) zinc

13. When copper ore is mixed with silica, in a reverberatory furnace copper matte is produced. The copper matte contains **[NCERT Exemplar]**
(a) sulphides of copper (II) and iron (II)
(b) sulphides of copper (II) and iron (III)
(c) sulphides of copper (I) and iron (II)
(d) sulphides of copper (I) and iron (III)

14. Which of the following metals is obtained by electrolytic reduction process?
(a) Fe (b) Cu (c) Ag (d) Al

15. Cassiterite is concentrated by
(a) levigation
(b) electromagnetic separation
(c) floatation
(d) liquefaction

16. When 1.164 g of a certain metal sulphide was roasted in air, 0.972 g of the metal oxide was formed. If the oxidation number of the metal is +2, calculate the molar mass of the metal.
(a) 25.67 g
(b) 31.56 g
(c) 47.35 g
(d) 64.00 g

17. Electrolytic refining's is used to purify which of the following metals? **[NCERT Exemplar]**

(a) Cu and Zn (b) Ge and Si
(c) Zr and Ti (d) Zn and Hg

18. Among the following statements, the incorrect one is

(a) calamine and siderite are carbonates
(b) argentite and cuprite are oxides
(c) zinc blende and pyrites are sulphides
(d) malachite and azurite are ores of copper

19. Cassiterite is an ore of

(a) Mn (b) Ni (c) Sb (d) Sn

20. Which of the following fluxes is used to remove acidic impurities in metallurgical process?

(a) Silica (b) Lime stone
(c) Sodium chloride (d) Sodium carbonate

21. Which of the following elements is extracted commercially by the electrolysis of an aqueous solution of its compound?

(a) Chlorine (b) Bromine
(c) Sodium (d) Aluminium

22. Which of the following furnaces can be used to get above 3000°C temperature?

(a) Blast furnace (b) Arc furnace
(c) Muffle furnace (d) Reverberatory furnace

23. Zone refining is based on the principle that **[NCERT Exemplar]**

(a) impurities of low boiling metals can be separated by distillation
(b) impurities are more soluble in molten metal than in solid metal.
(c) different components of a mixture are differently absorbed on an adsorbent.
(d) vapours of volatile compound can be decomposed into pure metal

24. Flux is used to

(a) remove all impurities from ores
(b) reduce metal oxide
(c) remove silica
(d) remove silica and undesirable metal oxide

25. The process of converting hydrated alumina into anhydrous alumina is called

(a) roasting (b) smelting
(c) dressing (d) calcination

26. The metal always found in the free state is

(a) Au (b) Ag (c) Cu (d) Na

27. Which of the following metals is extracted by the electrometallurgical method?

(a) Cu (b) Fe
(c) Na (d) Ag

Directions (Q. Nos. 28 to 30) *The chief ore of zinc is the sulphide, ZnS. The ore is concentrated by floatation process and then heated in air which converts the ZnS to ZnO.*

$$2ZnS + 3O_2 \xrightarrow{90.6\%} 2ZnO + 2\,SO_2 \qquad \text{...(i)}$$

The ZnO is then treated with dilute H_2SO_4 to produce $ZnSO_4$ (*aq*),

$$ZnO + H_2SO_4 \xrightarrow{100\%} ZnSO_4 + H_2O \qquad \text{...(ii)}$$

which produces Zn metal on electrolysis.

$$2ZnSO_4 + 2H_2O \xrightarrow{98.\,2\%} 2Zn + 2H_2SO_4 + O_2 \qquad \text{...(iii)}$$

28. What mass of Zn will be obtained from an ore containing 225 kg of ZnS (efficiencies of the process have been indicated above the arrow mark)?

(Zn = 65, S = 32, O = 16, H = 1)

(a) 134 kg (b) 112 kg
(c) 102 kg (d) 130 kg

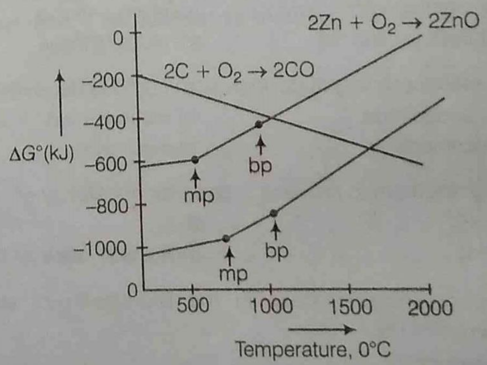
29. What amount of current is required (with 100% efficiency) in step (iii) if it takes one month?

(a) 10.2 A (b) 15.4 A
(c) 17.0 A (d) 154.0 A

30. ZnO in step (i) can also be dissolved in NaOH forming

(a) $Zn(OH)_2$ (b) Na_2ZnO_2 (c) Zn_2O_3 (d) $NaZn(OH)_4$

Directions (Q. Nos. 31 and 32) *Questions given below are based on the given diagram for extractive metallurgy.*



The points noted by arrows are the melting and boiling points of the metals zinc and magnesium. ΔG° is a function of temperature for some reactions of extractive metallurgy.

31. At what approximate temperature, zinc and carbon have equal affinity for oxygen?

(a) 1000°C (b) 1500°C (c) 500°C (d) 1200°C

32. At this temperature ΔG° of the reaction is

$$ZnO + C \longrightarrow Zn + CO$$

(a) negative (b) positive
(c) zero (d) nothing can be said

Directions (Q. Nos. 33 to 36) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

33. **Statement I** Hydrometallurgy involves dissolving the ore in a suitable reagent followed by precipitation by a more electropositve metal.

Statement II Copper is extracted by hydrometallurgy. **[NCERT Exemplar]**

34. **Statement I** Sulphide ores are concentrated by froth floatation method.

Statement II Cresoles stablise the froth in froth floatation method. **[NCERT Exemplar]**

35. **Statement I** F_2 is manufactured by electrolysis of KHF_2 but here anhydrous HF is used as solvent in place of water.

Statement II In presence of anhydrous HF, more F_2 is produced.

36. **Statement I** van Arkel method is used to prepare ultra pure sample of some metals.

Statement II It involves reaction of CO with metals to form volatile carbonyls which decompose on heating to give pure metal.

37. Which of the following statements about the advantage of roasting of sulphide ore before reduction is not true?

(a) $\Delta_f G°$ of the sulphide is greater than those of CS_2 and H_2S
(b) $\Delta_f G°$ is negative for roasting of sulphide ore to oxide
(c) Roasting of sulphide to oxide is thermodynamically feasible
(d) Carbon and hydrogen are suitable reducing agents for metal sulphides

38. The value of $\Delta_f G°$ for the formation of Cr_2O_3 is -540 kJ mol^{-1} and that of Al_2O_3 is -827 kJ mol^{-1}. Is the reduction of Cr_2O_3 with Al is feasible reaction?

(a) The data is incomplete
(b) The reaction is feasible
(c) The reaction is not feasible
(d) The reaction may or may not be feasible

39. Free energies of formation ($\Delta_f G$) of MgO (*s*) and CO (*g*) at 1273 K and 2273 K are given below :

$$\Delta_f G\ (MgO(s)) = -941\ kJ / mol\ at\ 1273\ K$$
$$\Delta_f G\ (MgO(s)) = -314\ kJ / mol\ at\ 2273\ K$$

and $\Delta_r G = \Delta_f G$ (products) $- \Delta_f G$ (reactants)

$$\Delta_f GCO(g) - \Delta_f GMgO(s)$$
$$= (-439) - (-941) = +502\ kJ\ mol^{-1}$$

$$\Delta_f G(CO(g)) = -439\ kJ\ mol\ at\ 1273\ K$$
$$\Delta_f G(CO(g)) = -628\ k\ J\ mol\ at\ 2273\ K$$

On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for MgO(*s*).

(a) 2273
(b) 1273
(c) Both (a) and (b)
(d) None of these

40. From these two statements, estimate the quantity of Mg that has been produced since the metal was discovered.

All the Mg produced in the world could have been made from as little as 4 km^3 of sea water.

The quantity of Mg^{2+} in sea water is 1272 g $Mg^{2+}/10^6$ kg sea water (the density of sea water is 1.03 g cm^{-3}, $1 km^3 = 10^{15}\ cm^3$)

(a) 3.48×10^6 kg
(b) 5.24×10^6 kg
(c) 50.8×10^3 kg
(d) 4.82×10^{12} kg

41. Use the relationship $\Delta G° = -nFE°_{cell}$ to estimate the minimum voltage required to electrolyse Al_2O_3 in the Hall-Heroult process

$$\Delta_f G°(Al_2O_3) = -1520\ kJ\ mol^{-1}$$
$$\Delta_f G°(CO_2) = -394\ kJmol^{-1}$$

(a) 0.8 V
(b) 1.60 V
(c) 2.8 V
(d) 3.0 V

42. Which method of purification is represented by the following equation?

$$Ti(s) + 2I_2(g) \xrightarrow{523\ K} TiI_4(g) \xrightarrow{1700\ K} Ti(s) + 2I_2(g)$$

(a) Zone refining
(b) Cupellation
(c) Polling
(d) van-Arkel

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43. Calcination is the process in which **[Online JEE (Main) 2013]**

(a) removal of water takes place
(b) decomposition of carbonates takes place
(c) oxidation of sulphides takes place
(d) All of the above

44. In Goldschmidt alumino thermic process which of the following reducing agent is used? **[Online JEE (Main) 2013]**

(a) Calcium
(b) Coke
(c) Al powder
(d) Sodium

45. Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly? **[AIEEE 2008]**

(a) CO_2 is more volatile than CS_2
(b) Metal sulphides are thermodynamically more stable than CS_2
(c) CO_2 is thermodynamically more stable than CS_2
(d) Metal sulphides are less stable than corresponding oxides

46. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in presence of **[IIT JEE 2008]**

(a) nitrogen
(b) oxygen
(c) carbon dioxide
(d) argon

47. Extraction of zinc from zinc blende is achieved by **[IIT JEE 2007]**

(a) electrolytic reduction
(b) roasting followed by reduction with carbon
(c) roasting followed by reduction with another metal
(d) roasting followed by self reduction

48. Which ore contains both iron and copper? **[IIT JEE 2005]**

(a) Cuprite
(b) Chalcocite
(c) Chalcopyrite
(d) Malachite

49. During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are **[AIEEE 2005]**

(a) Fe and Ni
(b) Ag and Au
(c) Pb and Zn
(d) Se and Ag

50. The methods chiefly used for the extraction of lead and tin from their ores are respectively **[IIT JEE 2004]**

(a) self reduction and carbon reduction
(b) self reduction and electrolytic reduction
(c) carbon reduction and self reduction
(d) cyanide process and carbon reduction

51. Which one of the following ores is best concentrated by froth floatation method? **[AIEEE 2004]**

(a) Magnetite
(b) Cassiterite
(c) Galena
(d) Malachite

52. In the process of extraction of gold,

$$\text{Roasted gold ore} + CN^- + H_2O \xrightarrow{O_2} [X] + OH^-$$
$$[X] + Zn \longrightarrow [Y] + Au$$

Identify the complexes [X] and [Y]. **[IIT JEE 2003]**

(a) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_4]^{2-}$
(b) $X = [Au(CN)_4]^{3-}$, $Y = [Zn(CN)_4]^{2-}$
(c) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_6]^{4-}$
(d) $X = [Au(CN)_4]^-$, $Y = [Zn(CN)_4]^{2-}$

53. Which of the following processes is used in extractive metallurgy of magnesium? **[IIT JEE 2002]**

(a) Fused salt electrolysis
(b) Self reduction
(c) Aqueous solution electrolysis
(d) Thermite reduction

54. Refining of impure copper with zinc impurity is to be done by electrolysis using electrodes as **[AIEEE 2002]**

	Cathode	Anode
(a)	Pure copper	Pure zinc
(b)	Pure zinc	Pure copper
(c)	Pure copper	Impure copper
(d)	Pure zinc	Impure zinc

Answers

1. (b) **2.** (b) **3.** (b) **4.** (c) **5.** (a) **6.** (d) **7.** (d) **8.** (a) **9.** (d) **10.** (c)
11. (d) **12.** (b) **13.** (d) **14.** (d) **15.** (b) **16.** (d) **17.** (a) **18.** (b) **19.** (d) **20.** (b)
21. (a) **22.** (c) **23.** (b) **24.** (d) **25.** (d) **26.** (a) **27.** (c) **28.** (a) **29.** (d) **30.** (b)
31. (a) **32.** (c) **33.** (c) **34.** (b) **35.** (c) **36.** (c) **37.** (d) **38.** (b) **39.** (a) **40.** (b)
41. (b) **42.** (d) **43.** (b) **44.** (c) **45.** (d) **46.** (b) **47.** (b) **48.** (c) **49.** (b) **50.** (a)
51. (c) **52.** (c) **53.** (a) **54.** (a)

Hints & Solutions

1. $Al_2O_3 \cdot 2H_2O$ (bauxite) is concentrated by leaching with NaOH, Al_2O_3 dissolves leaving other impurities undissolved.

2. In blast furnace, zone of combustion (1500 – 1600C°) has maximum temperature.

3. When molten zinc is added to water, zinc in the granular form is obtained.

4. Electrolysis is done to achieve electroplating and electrorefining of metals.

5. In electrorefining of copper, impure copper is made anode while pure Cu strip is made cathode.

   On passing current, impurities like Fe, Zn, Ni, Co dissolved in the solution and Au, Ag etc settle down below as anode mud.

6. Thermite process is not used for the metallurgy of Pb, Al and Ag.

7. Haematite (Fe_2O_3) having little FeO is removed by acidic flux SiO_2 in form of slag $FeSiO_3$.

8. $$2[Ag(CN)_2]^- + Zn \longrightarrow 2Ag + [Zn(CN)_4]^{2-}$$
   $$2\,[Au(CN)_2]^- + Zn \longrightarrow 2Au + [Zn(CN)_4]^{2-}$$

9. $$Cu_2O + \frac{1}{2}Cu_2S \longrightarrow 3Cu + \frac{1}{2}SO_2$$

10. Cr is less electropositive and can be obtained by the reduction of its oxide by aluminium.

11. Lustre of metals is due to the presence of mobile electrons.

12. Malachite is basic copper carbonate ($CuCO_3 \cdot Cu(OH)_2$).

13. Matte comprises of Cu_2S and FeS.

14. Electrolytic refining is used to purify Cu and Zn.

15. Cassiterite is tin stone (SnO_2) which is non-magnetic and contains wolframite, $FeWO_4$ (magnetic) impurities. These are separated by electromagnetic separation.

16. Formula of sulphide is *MS* because oxidation number of metal ion being +2.
    $$\underset{\substack{(M+32)\\1.164}}{MS} + \frac{3}{2}O_2 \longrightarrow \underset{\substack{(M+16)\\0.972}}{MO} + SO_2$$
    $$\frac{M+32}{1.164} = \frac{M+16}{0.972} \quad \text{or} \quad M = 64$$

17. Impurities are highly soluble in molten state than their solid state.

18. Argentite (Ag_2S) is a sulphide ore and cuprite (Cu_2O) is an oxide ore.

19. SnO_2 (tin stone) is also called cassiterite.

20. Lime stone ($CaCO_3$) is a basic flux. It is used to remove acidic impurities like SiO_2 as $CaSiO_3$ (slag).

21. Electrolysis of aqueous solution of NaCl (brine) gives Cl_2 at anode.

22. Muffle furnace is used to get above 3000°C temperature.

23. $CaSiO_3$ is called slag which is fusible and lighter than the molten metal and is removed easily.

24. Flux removes silica and undesirable metal oxide as silicate.

25. In calcination, moisture or hydrated water is removed on heating.
    $$Al_2O_3 \cdot 2H_2O \longrightarrow Al_2O_3 + 2H_2O \uparrow$$

26. Au is always found in free state.

27. Na is extracted by the electrometallurgical method.

28. $$\underset{97\text{ g}}{1\,ZnS} = \underset{65\text{g}}{1\,Zn}$$
    225×10^3 g of ZnS will produce Zn
    $$= \frac{65 \times 225 \times 10^3\text{g}}{97} \text{ (for 100\% efficiency)}$$
    $$= \frac{65 \times 225 \times 10^3 \times 90.6 \times 100 \times 98.2}{97 \times 100 \times 100 \times 100}$$
    (given efficiency)
    $$= 134.14 \text{ kg}$$

29. $w = ZIt$
    $$I = \frac{w}{Zt} = \frac{134.14 \times 10^3 \text{ g}}{\left(\frac{65}{2 \times 96500}\right)(30 \times 24 \times 60 \times 60)} = 154 \text{ A}$$

30. $$ZnO + 2NaOH \longrightarrow \underset{\text{sodium zincate}}{Na_2ZnO_2} + H_2 \uparrow$$

31. At 1000°C, zinc and carbon have equal affinity for oxygen.

32. $$ZnO \longrightarrow Zn + \frac{1}{2}O_2; \qquad \Delta G^\circ_1 = x$$
    $$C + \frac{1}{2}O_2 \longrightarrow CO; \qquad \Delta G^\circ_2 = -x$$
    $$ZnO + C \longrightarrow Zn + CO; \quad \Delta G^\circ_3 = 0$$
    System is at equilibrium, $\Delta G^\circ_1 = \Delta G^\circ_2$, since, zinc and carbon have equal affinity for oxygen.

33. Hydrometallurgy is used for the extraction of low grade copper while pyrometallurgy is used for the extraction of bulk quantities of copper.

34. Statement II is correct explanation of statement I.

35. F_2 produced, violently reacts with water.

36. van Arkel method involves use of I_2 to form volatile iodide of metals which on decomposition gives pure metal.

37. Both C and H_2 are not suitable for reducing sulphide ore because $\Delta_f G^\circ$ of metal sulphide is more than that of CS_2 and H_2S which will be formed as a result of reduction.

38. $$\frac{4}{3}Cr\,(s) + O_2(g) \longrightarrow \frac{2}{3}Cr_2O_3(s); \;\; \Delta_f G^\circ = -540\text{kJ} \qquad \text{...(i)}$$
    $$\frac{4}{3}Al\,(s) + O_2(g) \longrightarrow \frac{2}{3}Al_2O_3(s); \;\; \Delta_f G^\circ = -827\text{kJ} \qquad \text{...(ii)}$$

Eq. (ii) – (i)

$$\frac{2}{3}Cr_2O_3(s) + \frac{4}{3}Al(s) \longrightarrow \frac{2}{3}Al_2O_3(s) + \frac{4}{3}Cr(s);\ \Delta_f G° = -287\,kJ$$

Since, $\Delta G°$ comes out to be negative, the reaction is feasible.

39. At 1273 K,

(i) $Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s) \quad \Delta_f G = -941\ kJ\ mol^{-1}$

(ii) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \quad \Delta_f G = -439\,kJ\ mol^{-1}$

The redox equation for the reduction of MgO to Mg by C can be obtained by subtracting Eq (i) from Eq (ii). Thus,

$$MgO(s) + C(s) \longrightarrow Mg(s) + CO(g);\ \Delta_f G = +\ 502\,kJ\ mol^{-1}$$

Since, $\Delta_r G$ of the above reduction reaction is +ve, the reduction of MgO by C is not feasible at 1273 K.

At 2273 K,

(iii) $Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s), \Delta_f G = -314\ kJ\ mol^{-1}$

(iv) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \Delta_f G = -628\ kJ\ mol^{-1}$

Subtracting Eq. (iii) from Eq (iv), the redox equation is

$$MgO(s) + C(s) \longrightarrow Mg(s) + CO(g)$$

$$\begin{aligned}\Delta_r G &= \Delta_f G(\text{products}) - \Delta_f G(\text{reactants})\\ &= \Delta_f G(CO(g)) = \Delta_f G(MgO(s))\\ &= (-628) - (314) = -\ 314\ kJ\ mol^{-1}\end{aligned}$$

Since, $\Delta_r G$ for the above reaction is –ve, the reduction of MgO by carbon at 2273 is feasible.

40. 4 km^3 of sea water $= 4 \times 10^{15} cm^3 = 4 \times 10^{15} \times 1.03\ g$

$$= 4 \times 10^{12} \times 1.03 kg$$

$$Mg^{2+}\ \text{present} = \frac{4 \times 10^{12} \times 1.03 \times 1272}{10^6}\,g$$

$$= \frac{4 \times 10^{12} \times 1.03 \times 1272}{10^6 \times 10^3}\,kg$$

$$= 5.24 \times 10^6 kg$$

41. $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$

$$\begin{aligned}\Delta_r G° &= 3\Delta G°(CO_2) - 2\Delta G°(Al_2O_3)\\ &= 3 \times (-394) - 2 \times (-1520)\\ &= 1858 kJ = 1858 \times 10^3\,J\end{aligned}$$

$\therefore \quad nFE° = 1858 \times 10^3 \quad (n = 12\ \text{electrons})$

$\therefore \quad E° = \frac{1858 \times 10^3}{12 \times 96500} = 1.60\ V$

42. van-Arkel (and de Boer) process is based on the thermal decomposition of a volatile compound like an iodide, which is first formed by direct combination of metal to be purified and iodine. Metal formed is in purest form. Titanium and zirconium are purified by this method.

43. Calcination is a thermal treatment in the presence of air to ores and other solid materials to bring about a thermal decomposition, phase transition or removal of volatile fractions.

$$M_2CO_3 \xrightarrow{\Delta} M_2O + CO_2$$

44. In Goldschmidt aluminothermic pricess, oxides of Cr, Fe etc., are treated with Al powder which reduces these oxides into crude metal. Thus, acts as reducing agent here.

$$Fe_2O_3 + \underset{\text{reducing agent}}{2Al} \longrightarrow Al_2O_3 + 2Fe$$

45. $2MS + C \longrightarrow 2M + CS_2; \quad \Delta G_1 = +ve$

$2MO + C \longrightarrow 2M + CO_2; \quad \Delta G_2 = -ve$

The value of ΔG for the formation of CO_2 is negative, *i.e.*, it is thermodynamically more stable than CS_2. Also metal sulphides are thermodynamically more stable than the corresponding oxides, so they are roasted to convert into less stable oxides.

46. A water soluble complex of silver with a dilute aqueous solution of NaCN is sodium argentocyanide. In the cyanide process, the native form is crushed and treated with 0.1 – 0.2% solution of NaCN and aerated.

$$4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

Argentocyanide is soluble. Further metal is recovered from the complex by reduction with zinc.

47. Zinc blende is roasted and then treated with coke for reduction.

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2\uparrow$$

$$ZnO + C \xrightarrow{\Delta} Zn + CO\uparrow$$

48. Cuprite — Cu_2O

Chalcocite — Cu_2S

Chalcopyrite — $CuFeS_2$

Malachite — $Cu(OH)_2 \cdot CuCO_3$

49. During electrolysis, noble metals (inert metals) like Ag, Au and Pt are not affected and separate as anode mud from the impure anode.

50. The methods chiefly used for the extraction of lead and tin from their ores are self reduction and carbon reduction respectively. Because the process of heating the ore strongly in the presence of excess of air is called roasting. It is mainly used in case of sulphide ores and the process of extracting a metal by fusion of the oxide ore with carbon is known as carbon reduction.

51. Galena (PbS) is sulphide ore, hence concentrated by froth floatation process.

52. $\underset{\text{from gold ore}}{Au} + 4CN^- + H_2O + \frac{1}{2}O_2 \longrightarrow 2\underset{(X)}{[Au(CN)_2]^-} + 2OH^-$

$$2\underset{(X)}{[Au(CN)_2]^-} + Zn \longrightarrow \underset{(Y)}{[Zn(CN)_4]^{2-}} + 2Au$$

53. In extraction of metal, Mg is usually extracted by the electrolysis of fused oxide or fused anhydrous $MgCl_2$ because of its reactive nature.

$$MgCl_2 \longrightarrow \underset{\text{cathode}}{Mg^{2+}} + \underset{\text{anode}}{2Cl^-}$$

At anode $2Cl^- \longrightarrow Cl_2 + 2e^-$

At cathode $Mg^{2+} + 2e^- \longrightarrow Mg$

54. For purification, impure metal gets oxidised (deelectronation) falling into solution with mud, that's why impure metal is used as anode.

Day 20

Hydrogen

Day 20 Outlines ...

- Occurence of Hydrogen
- Position of Hydrogen in Periodic Table
- Isotopes and Allotropes of Hydrogen
- Commercial Production of Dihydrogen
- Compounds of Hydrogen
- Water
- Hydrogen Peroxide (H_2O_2)

Occurence of Hydrogen

Dihydrogen (H_2) is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist of mainly hydrogen.

Position of Hydrogen in Periodic Table

The position of hydrogen in Periodic Table is uncertain as it shows resemblance with alkali metals as well as with halogens. However, on the basis of electronic configuration ($1s^1$), it is placed above lithium in the Periodic Table but still, it is not considered as the member of that group. It is the lightest element known.

Isotopes and Allotropes of Hydrogen

Hydrogen has three isotopes : protium (^1_1H), deuterium or heavy hydrogen (^2_1H or D) and tritium (^3_1H or T). Out of these isotopes, only tritium is radioactive and emits low energy β^- particles. These three isotopes have different masses, hence, their rates of reaction and equilibrium constants are different. This is known as **isotopic effect.**

Because of the extreme temperature of sun fusion of hydrogen atoms occurs, which liberates large amount of energy.

$$4\,{}_1^1\text{H} \longrightarrow {}_2^4\text{He} + \underset{\text{positron}}{2\,{}_1^0e} + \text{energy}$$

Allotropes of hydrogen are *ortho* hydrogen (o-H_2) (in which proton spin in same direction) and *para* hydrogen (p-H_2) (in which proton spin in opposite direction). Similarly, deuterium and tritium also exhibit spin isomerism and exist in *ortho* and *para* forms.

Commercial Production of Dihydrogen

(i) Electrolysis of acidified water using platinum electrodes gives dihydrogen. Hydrogen is liberated at cathode while O_2 is liberated at anode.

(ii) Dihydrogen of high purity (> 99.95%) is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.

(iii) The mixture of CO and H_2 is called **water gas.** As this mixture is used for the synthesis of methanol and a number of hydrocarbons, it is also called **synthesis gas** or ***syn*** **gas.** Now a days '*syn* gas' is produced from sewage, scrap wood, news papers etc.

The process of producing syn gas from coal is called coal gasification. **(Bosch process)**

$$C(s) + H_2O(g) \xrightarrow{1270\text{ K}} CO(g) + H_2(g)$$

$$CO(g) + H_2O(g) \xrightarrow[\text{Iron chromate (catalyst)}]{673\text{ K}} CO_2(g) + H_2(g)$$

CO_2 is removed by passing the mixture through water at very high pressure. (CO_2 is dissolved completely in water).

(iv) **Lane's process** involves decomposition of super heated steam by heated Fe (550 – 800°C). This reaction is known as **gassing reaction.**

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2\uparrow$$

$$\Delta H = -160.7\text{ kJ}$$

By the action of water gas, Fe_3O_4 is again reduced to iron.

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$

$$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$$

(v) As a by product of brine electrolysis process for the manufacture of NaOH, petroleum cracking plants and many electrolytic reactions.

Properties and Uses of Hydrogen

Hydrogen is colourless, tasteless, odourless gas. It is lightest and slightly soluble in water.

- It is a neutral and highly combustible gas, so in presence of air it burns with pale blue flame to form water.
- **Reducing action** Hydrogen reduces the oxides of less elctropositive elements but cannot reduces the oxides of alkali metals and alkaline earth metals.

$$ZnO\,(s) + H_2(g) \longrightarrow Zn + H_2O$$

$$Fe_3O_4(s) + 4H_2\,(g) \longrightarrow 3Fe + 4H_2O$$

- **Hydrogenation**

$$\text{Vegetable oil} + H_2 \xrightarrow{\text{Ni/473K}} \text{vegetable ghee}$$

$$CH_2{=\!=}CH_2 + H_2 \xrightarrow{\text{Ni or Pt}/\Delta} CH_3{-}CH_3$$

- **Reaction with CO**

$$CO\,(g) + 2H_2(g) \xrightarrow[\Delta]{ZnO/Cr_2O_3} CH_3OH\,(l)$$

- With dinitrogen, it forms ammonia **(Haber's process).**

$$N_2(g) + 3H_2(g) \xrightarrow[\text{Fe, Mo}]{673\text{ K, 200 atm}} 2NH_3(g)$$

- **Uses**
  - (a) In hydrogenation of oils.
  - (b) In preparation of synthetic petrol.
  - (c) In oxy-hydrogen flame.
  - (d) In hydrogen-oxygen fuel cells to produce electricity.

In a fuel cell, electrical energy is generated by the reaction of H_2 and O_2without evolution of heat (cold combustion).

- (e) Liquid hydrogen is used as rocket fuel.
- (f) As a reducing agent in extraction of metals.

H_2 is environmentally clean fuel. It has highest calorific value and hence, is a better fuel than any other fuel. This proposal is referred as hydrogen economy. Very high efficiency is obtained when H_2 is used to produce electricity in fuel cells.

Atomic Hydrogen

Hydrogen gas dissociates into atoms when it is subjected to an electric discharge under low pressure.

$$H_2 \xrightarrow{\text{Electric discharge}} 2\,H$$

Atomic hydrogen is very reactive and can be used as a reducing agent as well as oxidising agent.

Reducing power of atomic hydrogen is more than that of nascent hydrogen.

Compounds of Hydrogen

The detailed description of the compounds of hydrogen e.g., hydrides, water, hard and soft water etc. are given below.

Hydrides

Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called **hydrides**. *The hydrides are classified into four categories.*

Ionic or Saline or Salt like Hydrides

Ionic hydrides are stoichiometric compounds of dihydrogen formed with most of the *s*-block elements, which are highly electropositive in character, *e.g.*, LiH, BeH_2 and MgH_2. In fact, BeH_2 and MgH_2 are polymeric in structure.

Due to their high reactivity with water ionic hydrides are used to remove traces of water from organic solvents.

Covalent or Molecular Hydrides

Dihydrogen forms molecular compounds with most of the *p*-block elements. Most familiar examples are CH_4, NH_3, H_2O and HF etc. Molecular hydrides are further classified, according to the relative number of electrons and bonds in their Lewis structure, into following types

- **(i) Electron deficient hydrides** have incomplete octet, so behave as Lewis acids, *i.e.*, are electron acceptors. *e.g.*, B_2H_6. These hydrides are formed by the elements of group 13.
- **(ii) Electron precise hydrides** are obtained from elements of group 14 (*e.g.*, CH_4) which are tetrahedral in geometry.
- **(iii) Electron rich hydrides** have excess electrons, which are present as lone pairs. Elements of group 15-17 form such type of hydrides. *e.g.*, $\ddot{N}H_3$ (1 lone pair), $H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}$ (2 lone pairs) and $H\overset{\bullet\bullet}{\underset{\bullet\bullet}{F}}\colon$ (3 lone pairs).

Metallic or Non-stoichiometric or Interstitial Hydrides

These are formed by many *d*-block and *f*-block elements, however, the metals of group 7, 8 and 9 do not form hydride (hydride gap). *These hydrides are mainly formed by*

- (a) transition metals of group 3, 4, 5 of d-block
- (b) Cr metal of group 6
- (c) f-block elements *e.g.*, $LaH_{2.87}$, $YbH_{2.55}$ etc.

Metallic hydrides are non-stoichiometric. They have metallic lattice and hydrogen is present at the interstitial sites. These conduct heat and electricity just like metals except hydrides of Eu and Yb. (EuH_2 and YbH_2 are ionic and stoichiometric)

Polymeric Hydrides and Complex Hydrides

Polymeric hydrides are formed by elements having electronegativity in the range 1.4 to 2.0, *e.g.*, $(BeH_2)_n$, $(AlH_3)_n$ etc. In complex hydrides, H^- acts as ligand and is attached to central metal atom. *e.g.*, $LiAlH_4$, $LiBH_4$ etc.

Water (H_2O)

The water molecule contains one oxygen and two hydrogen atoms connected by covalent bonds. *The physical and chemical properties of water as given below.*

Physical Properties

Water (H_2O) is polar in nature. It exists in liquid state at room temperature due to intermolecular hydrogen bonding. HOH bond angle is 104.5° and O—H bond length is 95.7 pm. H_2O (ice) has four hydrogen bonds per molecule and hence, has a highly ordered three dimensional cagelike structure. Ice has low density than H_2O (liquid) but H_2O has maximum density at 3.98°C.

Chemical Properties

(i) Water is amphoteric in nature.

$$\underset{\text{base}}{H_2O(l)} + \underset{\text{acid}}{HCl(aq)} \rightleftharpoons \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{Cl^-(aq)}$$

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{NH_3(aq)} \rightleftharpoons \underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{OH^-(aq)}$$

(ii) Water reacts with metals and non-metals both.

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$
$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+ + 4F^- + O_2(g)$$

(iii) In **hydrated salts**, water may remain in five types such as coordinated water, hydrogen bonded water, lattice water, clathrate water and zeolite water.

Zeolites are the open structures of SiO_4 and AlO_4 tetrahedron that contains cavities or certain channels in which H_2O molecules gets trapped.

Clathrate contains host molecules that crystallises with an open structure containing water molecules.

(iv) A number of compounds such as calcium hydride, calcium phosphide etc., undergo hydrolysis with water.

The hydrolysis of hydrides with H_2O *is highly exothermic and may be explosive as* H_2 *catches fire.* CO_2 *is reduced by hot metal hydride, so it cannot use to extinguish such fire.*

Hard and Soft Water

The water which lathers with soap is soft, if not, is hard. Hardness of water is of two types

(i) temporary hardness *(ii) permanent hardness*

Temporary Hardness of Water

It is due to the presence of magnesium and calcium hydrogen carbonates. It can be removed either by **boiling**, through which the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed into insoluble $CaCO_3$. These precipitates can be removed by filtration or by **Clark's method**, which involves the addition of calculated amount of lime to hard water.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$

Permanent Hardness of Water

It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates. It can be removed by the following methods

- Sodium hexa meta phosphate ($Na_6P_6O_{18}$), commercially called calgon, when added to hard water, the calcium and magnesium ions present in hard water react with calgon and form soluble complex salts (**Calgon's method**) which does not cause any hinderance in other information.

$$2M^{2+} + Na_2[Na_4(PO_3)_6] \rightarrow \underset{\text{Soluble}}{Na_2[M_2(PO_3)_6]} + 4\,Na^+$$

$[M^{2+} = Ca^{2+}, Mg^{2+}]$

- **Ion-exchange method or permutit process** is also used to remove permanent hardness.

$$2NaZ(s) + M^{2+}(aq) \longrightarrow MZ_2(s) + 2Na^+(aq)$$
$$(M = Mg, Ca)$$

- Where, NaZ is sodium aluminium silicate ($NaAlSiO_4$). This is also known as sodium zeolite. It is regenerated for further use by treating with an aqueous NaCl solution (brine).
- Now-a-days hard water is softened by using synthetic cation exchangers (called **synthetic resins method**). Cation exchange resins contain large organic molecules with $—SO_3H$ group and are water insoluble. Ion exchange resin (RSO_3H) is changed to RNa by treating it with NaCl.

$$2RNa + M^{2+}(aq) \longrightarrow R_2M(s) + 2Na^+(aq)$$
$$(M^{2+} = Ca^{2+}, Mg^{2+})$$

The resin can be regenerated by adding aqueous NaCl solution.

Heavy Water (D_2O)

- It has quite similar physical and chemical properties to those of H_2O. Dielectric constant of D_2O is lower than that of H_2O and rate of reactions are much slower than H_2O.
- It is used as a moderator in nuclear reactions, as trace compound for studying reaction mechanism, for the preparation of deuterium.

Hydrogen Peroxide (H_2O_2)

Hydrogen peroxide is a compound with an oxygen-oxygen single bond. It is also a strong oxidizer.

Preparation

$$BaO_2 \cdot 8H_2O(s) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$$

H_2O_2 is commercially represented in terms of volume strength.

(i) Volume strength $= 5.6 \times$ normality

$$= 5.6 \times \frac{\text{percentage strength}}{\text{eq wt.of } H_2O_2 \ (i.e.,17)} \times 10$$

(ii) Volume strength $= 11.2 \times$ molarity

$$= 11.2 \times \frac{\text{percentage strength}}{\text{mol. wt.of } H_2O_2 \ (i.e.,34)} \times 10$$

(iii) % strength $= \frac{17}{56} \times$ volume strength

Chemical Properties

(i) Oxidising action in acidic medium

$$2Fe^{2+}(aq) + 2H^+(aq) + H_2O_2(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O(l)$$

$$PbS(s) + 4H_2O_2 \longrightarrow PbSO_4(s) + 4H_2O(l)$$

(ii) Reducing action in acidic medium

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

(iii) Oxidising action in basic medium

$$Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$$

(iv) Reducing action in basic medium

$$I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$$

(v) Many reactions of H_2O_2 are radical reactions, therefore a mixture of H_2O_2 and Fe (II) is a source of hydroxyl radicals for organic reactions.

Storage

H_2O_2 decomposes slowly on exposure to light.

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

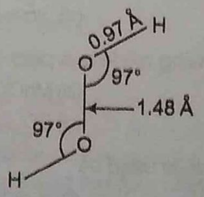
In the presence of metal surfaces or traces of alkali (present in glass containers), the above is catalysed. It is therefore, stored in wax lined glass or plastic vessels in dark. Urea can be added as a stabiliser.

Uses of H_2O_2

1. Aqueous solution of H_2O_2 is used as germicide, antiseptic, preservative for milk and wine, bleaching agent for soft materials.

   30% H_2O_2 *is called perhydrol. Its volume strength is* 100 *and molarity is* 8.8.
2. It is used as an antichlor and in refreshing old oil paintings which became black.

Structure of H_2O_2



Practice Zone

DAY 20

1. Nascent hydrogen consists of

(a) hydrogen atoms with excess of energy
(b) hydrogen molecules with excess energy
(c) hydrogen ions in excited state
(d) solvated protons

2. The oxidising property of H_2O_2 is best explained by assuming that two oxygen atoms in its molecule are bonded

(a) differently (b) similarly
(c) covalently (d) by hydrogen bonds

3. Heavy water (D_2O) freezes at

(a) 0°C (b) 3.8°C
(c) – 3.8°C (d) 38°C

4. Boiling point of heavy water is

(a) 100°C (b) 99°C
(c) 101.4°C (d) 110°C

5. A mixture of hydrazine (N_2H_4) and 58 – 60% solution of H_2O_2 is used as

(a) antiseptic (b) fertiliser
(c) rocket fuel (d) None of these

6. Which of the following oxide is a peroxide ?

(a) Na_2O_2 (b) MnO_2
(c) BaO (d) SO_2

7. Hydrogen peroxide is used as

(a) an oxidant only (b) a reductant only
(c) an acid only (d) All of these

8. Which of the following statements is not correct ?

(a) H_2O_2 oxidises Fe (II) to Fe (III)
(b) H_2O_2 can be obtained by electrolysis of dilute H_2SO_4
(c) H_2O_2 reduces Mn (VII) to Mn (II)
(d) H_2O_2 is a weak base

9. *Ortho* and *para* hydrogens differ in the

(a) number of protons
(b) molecular weight
(c) nature of spins of protons
(d) nature of spins of electrons

10. Moist hydrogen cannot be dried over conc. H_2SO_4 because

(a) it can catch fire (b) it is reduced by H_2SO_4
(c) it is oxidised by H_2SO_4 (d) it decomposes H_2O_2

11. Which of the following hydrides is electron precise hydride? **[NCERT Exemplar]**

(a) B_2H_6 (b) NH_3
(c) H_2O (d) CH_4

12. Decomposition of H_2O_2 is favoured by

(a) traces of acids (b) alcohol
(c) acetanilide (d) MnO

13. The maximum possible number of hydrogen bonds a water molecule can form in ice is

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

14. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water, the sodium ions are exchanged with

(a) H^+ ion (b) Ca^{2+} ion
(c) SO_4^{2-} ion (d) OH^- ion

15. One would expect proton to have very large

(a) charge (b) ionisation potential
(c) hydration energy (d) radius

16. The O— O—H bond angle in H_2O_2 is

(a) 106° (b) 109°28' (c) 120° (d) 97°

17. The oxide that gives H_2O_2 on treatment with dilute acid is

(a) PbO_2 (b) Na_2O_2
(c) MnO_2 (d) TiO_2

18. Acidified solution of chromic acid on treatment with H_2O_2 yields

(a) $CrO_3 + H_2O + O_2$ (b) $Cr_2O_3 + H_2O + O_2$
(c) $CrO_5 + H_2O + K_2SO_4$ (d) $H_2Cr_2O_7 + H_2O + O_2$

19. Nascent hydrogen is prepared by

(a) Na and C_2H_5OH (b) Al and NaOH
(c) Zn and dil H_2SO_4 (d) All of these

20. The molarity of a 100 mL solution containing 5.1 g of hydrogen peroxide is
(a) 0.15 M (b) 1.5 M (c) 3.0 M (d) 50.0 M

21. In aqueous solution, hydrogen peroxide oxidises H_2S to
(a) sulphur (b) sulphuric acid
(c) Caro's acid (d) Marshall's acid

22. The volume strength of 1 molar solution of H_2O_2 is
(a) 11.2 (b) 22.4 (c) 5.6 (d) 56

23. Which of the following reactions increases production of dihydrogen from synthesis gas? **[NCERT Exempler]**
(a) $CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270\,K} CO(g) + 3H_2(g)$
(b) $C(s) + H_2O(g) \xrightarrow{1270\,K} CO(g) + H_2(g)$
(c) $CO(g) + H_2O(g) \xrightarrow[catalyst]{673K} CO_2(g) + H_2(g)$
(d) $C_2H_6 + 2H_2O \xrightarrow[Ni]{1270K} 2CO + 5H_2$

24. Last molecule of H_2O is evolved from H_2O_2 by
(a) crystallisation
(b) evaporation
(c) distillation under reduced pressure
(d) electrolysis

25. NH_3 and H_2O form NH_4OH by
(a) electrovalent bond (b) covalent bond
(c) coordination bond (d) None of these

26. The metal, which gives hydrogen on treatment with acid as well as sodium hydroxide is
(a) Fe (b) Zn
(c) Cu (d) None of these

27. The ionisation of hydrogen atom gives
(a) hydride ion (b) hydronium ion
(c) proton (d) hydroxyl ion

28. 1000 g aqueous solution of $CaCO_3$ contains 10 g of calcium carbonate, hardness of the solution is
(a) 10 ppm (b) 100 ppm (c) 1000 ppm (d) 10000 ppm

Directions (Q. Nos. 29 to 31) *Hydrogen peroxide can be prepared by the action of dil H_2SO_4 or H_3PO_4 on barium peroxide or by bubbling carbon dioxide through a thin paste of barium peroxide. On an industrial scale, it can be prepared by hydrolysis of peroxodisulphuric acid obtained by electrolysis of 50% H_2SO_4 or an equimolar mixture of H_2SO_4 and ammonium sulphate. The strength of H_2O_2 solution can be expressed in a number of ways namely normality, molarity, percentage strength and volume strength. Volume strength refers to the volume of O_2 produced at NTP by decomposition of 1 mL H_2O_2 solution. H_2O_2 acts as an oxidising as well as reducing agent both in acidic and basic media.*

29. The volume of 10 volume H_2O_2 solution that decolourises 200 mL of 2N $KMnO_4$ solution in acidic medium is
(a) 112 mL (b) 336 mL
(c) 220 mL (d) 224 mL

30. Hydrolysis of 1 mole of peroxodisulphuric acid produces
(a) two moles of sulphuric acid.
(b) two moles of peroxomonosulphuric acid
(c) one mole of sulphuric acid and one mole of peroxomonosulphuric acid
(d) one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide

31. 100 volume hydrogen peroxide solution means
(a) 17.86 N (b) 30.36% H_2O_2
(c) 8.93 M (d) All are correct

Directions (Q. Nos. 32 and 33) *Depletion of resources of fossil fuels will at some future time make hydrogen, either for use directly by combustion and electrochemically in fuel cells or indirectly via hydrogenation of coal, the major alternative to nuclear energy, hence arises the current interest in the so called hydrogen economy.*

A thermochemical cycle for hydrogen production involves atleast one element that can exist in two different oxidation states.

$$2H_2O \longrightarrow 2H_2 + O_2$$

32. Production of H_2 from H_2O requires a net input of energy that would come from
(a) nuclear source (b) solar source
(c) Both (a) and (b) (d) None of these

33. In the above thermochemical cycle, $FeCl_2$ is one of the catalyst involved and thus, regenerated at the end of the reaction, after formed into
(a) $FeCl_3$, FeO, Fe_2O_3
(b) $FeCl_3 \cdot Fe_2O_3 \cdot Fe_3O_4$
(c) $FeCl_3$, FeO
(d) $FeCl_3 \cdot Fe_3O_4$

Directions (Q. Nos. 34 to 37) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

34. Statement I Density of ionic hydrides such as LiH is greater than metals from which they are formed.
Statement II Small H^- (hydride ions) occupy holes in the lattice of metal without distorting metal lattice.

35. **Statement I** Melting point of D_2O is higher than H_2O.

Statement II Heavy water is more viscous than ordinary water, H_2O.

36. **Statement I** H_2O_2 acts as an oxidising agent as well as reducing agent.

Statement II In H_2O_2, oxygen has −1 oxidation state and it can increase or decrease its oxidation state.

37. **Statement I** Oxy-hydrogen flame produces higher temperature than oxy-atomic hydrogen flame.

Statement II The heat generated during burning of these gases in oxygen is used to melt substances.

38. Market prices of Fe, Zn and Al scraps per kg are 4, 15, 20 respectively. If H_2 is prepared by the reaction of these metals with H_2SO_4, which one will be the most expensive to use?

(a) Fe (b) Zn
(c) Al (d) Fe or Zn

39. What will be the volume of oxygen at NTP liberated upon the complete decomposition of 100 mL of the 2 M hydrogen peroxide solution?

(a) 2.24 L (b) 22.4 L (c) 44.8 L (d) 11.2 L

40. 100 mL of tap water containing $Ca(HCO_3)_2$ was titrated with $\frac{N}{50}$ HCl with methyl orange as indicator. If 30 mL of HCl was required, the temporary hardness of water, as parts of $CaCO_3$ per 10^6 parts of water was

(a) 150 ppm (b) 600 ppm
(c) 275 ppm (d) 300 ppm

41. Excess of KI and dil H_2SO_4 were mixed in 50 mL H_2O_2. Thus, I_2 liberated requires 20 mL of 0.1 N $Na_2S_2O_3$. What will be the strength of H_2O_2 in g L^{-1}?

(a) 0.034 (b) 0.68 (c) 6.80 (d) 5.80

42. H_2O_2 is marked "22.4 volume". How much of it (in mL) are required to oxidise 3.4 g H_2S gas?

(a) 10 mL (b) 70 mL (c) 100 mL (d) 1000 mL

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43. Very pure hydrogen (99.9) can be made by which of the following processes? **[AIEEE 2012]**

(a) Reaction of methane with steam
(b) Mixing natural hydrocarbons of high molecular weight
(c) Electrolysis of water
(d) Reaction of salts like hydrides with water

44. In context with the industrial preparation of hydrogen from water gas ($CO + H_2$), which of the following is the correct statement? **[AIEEE 2008]**

(a) CO is oxidised to CO_2 with steam in the presence of catalyst followed by absorption of CO_2 in alkali
(b) CO and H_2 are fractionally separated using differences in their densities
(c) CO is removed by absorption in aqueous Cu_2Cl_2 solution
(d) H_2 is removed through occlusion with Pd

45. Which one of the following processes will produce hard water? **[AIEEE 2003]**

(a) Saturation of water with $CaSO_4$
(b) Saturation of water with $CaCO_3$
(c) Addition of Na_2SO_4 to water
(d) Saturation of water with $MgCO_3$

46. Which one is used as propellants for rockets? **[AIEEE 2002]**

(a) Liq. H_2 + Liq. O_2 (b) Liq. N_2 + Liq. O_2
(c) Liq. H_2 + Liq. N_2 (d) Liq. O_2 + Liq. air

47. Polyphosphates are used as water softening agent because they **[IIT JEE 2002]**

(a) form soluble complexes with anionic species
(b) precipitate anionic species
(c) form soluble complexes with cationic species
(d) precipitate cationic species

Answers

1. (b) **2.** (a) **3.** (b) **4.** (c) **5.** (c) **6.** (a) **7.** (d) **8.** (d) **9.** (c) **10.** (c)
11. (d) **12.** (d) **13.** (d) **14.** (b) **15.** (c) **16.** (d) **17.** (b) **18.** (c) **19.** (d) **20.** (b)
21. (a) **22.** (a) **23.** (c) **24.** (a) **25.** (a) **26.** (b) **27.** (c) **28.** (d) **29.** (d) **30.** (c)
31. (d) **32.** (c) **33.** (d) **34.** (a) **35.** (b) **36.** (a) **37.** (d) **38.** (b) **39.** (a) **40.** (d)
41. (b) **42.** (c) **43.** (d) **44.** (a) **45.** (a) **46.** (a) **47.** (c)

Hints & Solutions

1. Nascent hydrogen is associated with chemical energy liberated in the reaction and hence, the molecules consist of excess energy.

2. It is believed that out of two hydrogens, one is associated with each oxygen atom at a bond angle of 97°. All the four atoms H—O—O—H do not lie in the same plane.

3. Heavy water freezes at 3.8°C.

4. Boiling point of heavy water is 101.4°C.

5. A mixture of H_2O_2 and hydrazine (N_2H_4) is used as a rocket fuel.

6. Na_2O_2 is a peroxide, all others are double oxides (MnO_2, SO_2) and simple oxide (BaO).

7. H_2O_2 acts as an oxidant, reductant and an acid (weak).

8. H_2O_2 is not a weak base but a weak acid.

9. *ortho* and *para* hydrogens differ in the nature of spins of protons.

10. $$\underset{}{H_2O_2} + \underset{\text{from } H_2SO_4}{[O]} \longrightarrow H_2O + O_2$$

11. The hydride which contains exact number of electrons to form normal covalent bonds are called electron precise hydrides. *e.g.*, CH_4.

12. MnO catalyses the decomposition of H_2O_2.

13. In ice, each H_2O molecule is surrounded by four other water molecules, bonded through H-bonds.

Each H_2O molecule linked to four H_2O molecules tetrahedrally.

14. $$\underset{\text{(sodium zeolite)}}{Na_2Z} + \underset{\text{(from hard water)}}{CaCl_2} \longrightarrow \underset{\text{(calcium zeolite)}}{CaZ} + 2NaCl$$

[where, $Z = Al_2Si_2O_8 \cdot x\,H_2O$]

15. Proton (H^+) being very small in size, would have very large hydration energy.

16. O—O—H bond angle in H_2O_2 is 97°.

17. $Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$

All other oxides are dioxides.

18. $K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + H_2Cr_2O_7$

$H_2Cr_2O_7 + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$

19. $Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2[H]$

$Na + C_2H_5OH \longrightarrow C_2H_5ONa + [H]$

$Al + NaOH + H_2O \longrightarrow NaAlO_2 + 3[H]$

20. $M = \dfrac{5.1 \times 1000}{34 \times 100} = 1.5$

21. $H_2S + H_2O_2 \longrightarrow 2H_2O + S$

22. 1 molar H_2O_2 solution means 1 mole (or 34 g H_2O_2) is present in 10^3 mL solution.

$\therefore$ 68 g H_2O_2 gives 22400 mL of O_2

$\therefore$ 34 g H_2O_2 gives $\dfrac{22400 \text{ mL} \times 34}{68} = 11200$ mL of O_2

Volume strength $= \dfrac{11200}{10^3} = 112$

23. $CO\,(g) + H_2O\,(g) \xrightarrow[\text{catalyst}]{673\text{ K}} CO_2(g) + H_2(g)$

24. Last trace of water is removed from H_2O_2 by crystallisation.

25. $NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

26. Zn is amphoteric metal and reacts with acids as well as alkalies to give hydrogen gas.

27. $H(g) \xrightarrow{+\text{I.E}} H^+(g) + 1e^-$

28. Hardness of solution in ppm $= \dfrac{10 \times 10^6}{1000} = 10^4$ ppm

29. Normality of 10 volume H_2O_2

$= \dfrac{\text{volume strength}}{5.6} = \dfrac{10}{5.6}$N

Applying normality equation,

$$\underset{(H_2O_2)}{N_1V_1} = \underset{(KMnO_4)}{N_2V_2}$$

$$\frac{10}{5.6} \times V_1 = 2 \times 200$$

or $$V_1 = \frac{2 \times 200 \times 5.6}{10} = 224\text{cm}^3$$

30. $$HO—SO_2—O—O—SO_2—OH + H_2O \longrightarrow \underset{\text{sulphuric acid}}{HOSO_2OH} + \underset{\text{peroxomono sulphuric acid}}{HOOSO_2OH}$$

31. Step (1) : % strength of H_2O_2

1 litre of 100 volume H_2O_2 solution on decomposition will give 100 L of oxygen at NTP.

$$\underset{68\text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22.4\text{ L}}{O_2}$$

$\therefore$ 100 L of O_2 at NTP will obtain from

$$H_2O_2 = \frac{68 \times 100}{22.4} = 303.6 \text{ g}$$

Thus, volume strength of H_2O_2 = 303.6 g/L

$\therefore$ % volume strength $= \dfrac{303.6}{1000} \times 100 = 30.36\%$

Step (2) : Normality of $H_2O_2 = \dfrac{\text{Strength}}{\text{Equivalent Weight}} = \dfrac{303.6}{17}$

= 17.86 N

Step (3) : Molarity of $H_2O_2 = \dfrac{\text{Normality}}{2} = \dfrac{17.86}{2} = 8.93$ M

32. Direct methods of production of hydrogen are very costly. Solar energy or nuclear energy may be used for splitting of H_2O into H_2 and O_2.

33. Thermochemical method for production of H_2

$$3\,FeCl_2(s) + 4\,H_2O(g) \xrightarrow{500°C} Fe_3O_4(s) + 6\,HCl(g) + H_2(g);\ \Delta H° = 318\ kJ$$

$$Fe_3O_4(s) + \frac{3}{2}Cl_2(g) + 6\,HCl(g) \xrightarrow{100°\,C} 3\,FeCl_3(s) + 3\,H_2O(g) + \frac{1}{2}O_2(g);\ \Delta H = -249\ kJ$$

$$3\,FeCl_3(s) \xrightarrow{300°\,C} 3\,FeCl_2(s) + \frac{3}{2}Cl_2(g);\ \Delta H = 173\ kJ$$

$$H_2O(g) \longrightarrow H_2(g) + \frac{1}{2}O_2(g);\quad \Delta H° = 242\ kJ$$

34. Statement II is the correct explanation of statement I.

35. Both statements are true but statement II is not the correct explanation of statement I. D_2O shows more stronger H-bonding than H_2O and thus, shows higher melting point and boiling point.

36.

$$2e^- + \underset{\text{oxidant}}{O_2^{1-}} \longrightarrow 2\,O^{2-}$$

$$\underset{\text{reductant}}{O_2^{1-}} \longrightarrow O_2^0 + 2e^-$$

Statement II is the correct explanation of statement I.

37. Oxy-atomic hydrogen flame produces more heat.

38. (i) Cost to prepare 10 g of H_2 from Fe,

$$\underset{56g}{Fe} + H_2SO_4 \longrightarrow FeSO_4 + \underset{2g}{H_2}$$

2 g of H_2 is produced from Fe = 56 g

$\therefore$ 10 g of H_2 is produced from Fe $= \frac{56}{2} \times 10 = 280$ g

Cost of 1000 g Fe = ₹4.

$\therefore$ Cost of 280 g of Fe $= \frac{4}{1000} \times 280 =$ ₹ 1.120

(ii) Cost to prepare 10 g of H_2 from Zn,

$$\underset{65g}{Zn} + H_2SO_4 \longrightarrow ZnSO_4 + \underset{2g}{H_2}$$

$\therefore$ Cost of Zn $= \frac{65}{2} \times 10 \times \frac{15}{1000} =$ ₹ 4.875

(iii) Cost to prepare 10 g H_2 from Al

$$\underset{2\times 27=54\,g}{2Al} + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + \underset{3\times 2=6\,g}{3H_2}$$

$\therefore$ Cost of Al $= \frac{54}{6} \times 10 \times \frac{20}{1000} =$ ₹ 1.8

39. According to available data :

Molarity = 2M (or 2 mol L^{-1}),

Molecular mass of H_2O_2 = 34 g/mol

Volume of solution = 1 L

$$\text{Molarity} = \frac{\dfrac{\text{mass of } H_2O_2}{\text{molecular mass of } H_2O_2}}{\text{volume of solution in litre}}$$

$$(2\ mol\ L^{-1}) = \frac{\text{mass of } H_2O_2}{(34\ g\ mol^{-1}) \times (1L)}$$

$\therefore$ Mass of $H_2O_2 = (2\ mol\ L^{-1}) \times (34\ g\ mol^{-1}) \times (1\ L) = 68$ g

1000 mL of solution contains H_2O_2 = 68 g

100 mL of solution contains H_2O_2 = 6.8 g

Now according to decomposition equation,

68.0 g of H_2O_2 at NTP evolve oxygen = 22400mL

$\therefore$ 6.8 g of H_2O_2 at NTP will evolve oxygen

$$= \frac{22400}{68} \times 6.8 = 2240\text{mL or } 2.24\text{L}$$

40. Meq. of $CaCO_3$ = Meq. of $Ca(HCO_3)_2$ = Meq. of HCl

$$\frac{w}{100/2} \times 1000 = \frac{1}{50} \times 30$$

$$w_{CaCO_3} = \frac{3 \times 100}{5 \times 2000} = 0.03\ g$$

$\therefore$ 100 mL of H_2O contains Ca^{2+} = 0.03 g

$$10^6\text{mL } H_2O \text{ contains } Ca^{2+} = \frac{0.03 \times 10^6}{100} = 300\text{ppm}$$

41. For 20 mL of H_2O_2

Meq. of KI = Meq.of H_2O_2 in 50 mL = Meq. of $Na_2S_2O_3$

$$\frac{w \times 1000}{34/2} = 20 \times 0.1$$

$$\therefore\quad w_{H_2O_2} \text{ in 50 mL} = \frac{20 \times 0.1 \times 34}{2000} = 0.034$$

$$\therefore\quad w_{H_2O_2} \text{ in 1000 mL} = \frac{0.034 \times 1000}{50} = 0.68\ g/L$$

42. Density of "x volume" $H_2O_2 = \frac{68\ x}{22400}$ g/mL

Density of "22.4 volume" $= \frac{68 \times 22.4}{22400} = 0.068$ g/mol

$$\underset{34\,g}{H_2S} + \underset{68\,g}{H_2O_2} \longrightarrow 2\,H_2O + S$$

34 g H_2S is oxidised by = 68 g H_2O_2

3.4 g H_2S is oxidised by $= \frac{68 \times 3.4}{34} = 6.8$ g H_2O_2

0.068 g H_2O_2 is present in = 1 mL

$\therefore$ 6.8 g H_2O_2 is present in = 100 mL

43. Hydrides are instant source of hydrogen of higher purity. They react with H_2O forming H_2 gas.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2 \uparrow$$

44. $CO + H_2 + H_2O \xrightarrow{\text{Catalyst}} CO_2 + 2H_2 \xrightarrow{\text{KOH}} K_2CO_3$

45. Permanent hardness is due to the presence of chlorides and sulphates of calcium, magnesium and iron in water.

46. Liquid H_2 and liquid O_2 is used as rocket propellants.

47. Polyphosphates react with Ca^{2+} and Mg^{2+} ions present in hard water to form soluble complex.

Day 21

s-Block Elements

Day 21

Outlines ...

- Group 1 Elements Alkali Metals
- Compounds of Alkali Metals
- Biological Significance of Na and K
- Group 2 Elements Alkaline Earth Metals
- Compounds of Alkaline Earth Metals
- Biological Significance of Mg and Ca

Group 1 Elements : Alkali Metals

Lithium ($Z = 3$), sodium ($Z = 11$), potassium ($Z = 19$), rubidium ($Z = 37$), caesium ($Z = 55$) and francium ($Z = 87$) are the elements of IA (or 1) group of the Periodic Table. These elements because of the highly alkaline nature of their water soluble hydroxides are known as alkali metals.

General Characteristics of Alkali Metals

These are *s*-block elements as their last or valence electron enters in the *s*-orbitals which is also shown by their general configuration. These all are soft metals. These are so soft that these can be cut with knife.

Physical Properties

1. Alkali metals are most electropositive and on moving down the group the electropositive character increases. Therefore, they readily lose electron to give monovalent, M^+ ions.
2. The alkali metal atoms have the largest size and on moving down the group, the size of atom increases. Low densities of alkali metals are due to their large size.
3. The ionisation enthalpies of alkali metals are considerably low and decrease down the group from Li to Cs.

4. Hydration enthalpy of alkali metal ions decreases with increase in ionic size. $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

   Therefore, Li^+ has maximum degree of hydration and due to this reason lithium salts are mostly hydrated, *e.g.*, $LiCl \cdot 2H_2O$.
5. Mobility of their cations in aqueous medium is directly proportional to the size of cation due to poor hydration enthalpy.

$$\underset{\xrightarrow[\text{Mobility}]{\hspace{10em}}}{Li^+ < Na^+ < K^+ < Rb^+ < Cs^+}$$

6. Alkali metals give **flame test.** The colour of the flame depends upon the wavelength of radiation emitted. Cesium and potassium are used as electrodes in photoelectric cell due to their low ionisation enthalpy **(photoelectric effect).**
7. Alkali metals are strong reducing agent and down the group, their reducing nature increases.
8. Alkali metal compounds are most ionic in nature and down the group, ionic nature increases.
9. Alkali metal oxides are most basic in nature and down the group, basic character increases.

Chemical Properties

The alkali metals are highly reactive due to their large size and low ionisation enthalpy.

(i) Reactivity towards air

$$4Li + O_2 \longrightarrow 2Li_2O \text{ (oxide)}$$

$$2Na + O_2 \longrightarrow Na_2O_2 \text{(peroxide)}$$

$$M + O_2 \longrightarrow MO_2 \text{ (superoxide)} \quad (M = K, Rb, Cs)$$

Metal peroxides are diamagnetic and sodium peroxide is widely used as an oxidising agent in inorganic chemistry. The superoxides are paramagnetic in nature because of the presence of three electron bonds with one unpaired electron. *KO_2 is used in space capsules, sub-marines and breathing masks as it produces O_2 and removes CO_2* and CO.

(ii) With liquid ammonia The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.

$$M + (x + y)NH_3 \longrightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

The blue colour of the solution is due to the ammoniated electrons. The solutions are paramagnetic and on standing, slowly liberate hydrogen resulting in the formation of amide.

$$M^+ + e^- + NH_3(l) \longrightarrow MNH_2 + \frac{1}{2}H_2$$

(iii) Reactivity and electrode potential Reducing character or reactivity of alkali metals increases from Li to Cs, *i.e.*, $Li < Na < K < Rb < Cs$.

(v) Carbonates Alkali metals on exposure to air and moisture get converted into oxides, hydroxides and finally to carbonates, *i.e.*, get tarnished.

$$4M + O_2 \longrightarrow 2M_2O \xrightarrow{H_2O} 2MOH \xrightarrow{CO_2} M_2CO_3$$

- ⏩ *Alkali metals are stored in the inert solvents like petroleum ether.*
- ⏩ *Carbonates of alkali metals are thermally stable except Li_2Co_3 which decomposes readily to evolve CO_2 on heating. Due to the strong polarising action of small cation, Li^+ on the large carbonate ion facilitates their decomposition $Li_2CO_3 \rightarrow Li_2O + CO_2$*

Anomalous Properties of Lithium

Lithium due to its

- exceptionally small size (like Mg) and
- high polarising power (*i.e.*, charge/radius ratio) (like Mg) exhibits some properties which are different from those of the other members of first group but similar to that of magnesium (present diagonally in the following group =, *i.e.*, II group). The property of showing similarity in properties with the element present diagonally opposite in the periodic table is called **diagonal relationship.** These properties are

(a) Alkali metals do not react with nitrogen except Li.

$$6Li + N_2 \xrightarrow{\text{Heat}} \underset{\text{lithium nitride}}{2Li_3N}$$

(Li metal is used as scavenger in metallurgy to remove O_2 and N_2 gases.)

$$3Mg + N_2 \longrightarrow \underset{\text{magnesium nitride}}{Mg_3N_2}$$

(b) Alkali metal carbonates, nitrates and hydroxides do not decompose on heating into their oxides except lithium.

$$NaOH \xrightarrow{\text{Heat}} \text{No reaction}$$

$$2\,LiOH \xrightarrow{\text{Heat}} Li_2O + H_2O$$

$$Mg\,(OH)_2 \xrightarrow{\text{Heat}} MgO + H_2O$$

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

$$Li_2CO_3 \xrightarrow{\text{Heat}} Li_2O + CO_2$$

$$MgCO_3 \xrightarrow{\text{Heat}} MgO + CO_2$$

$$4\,LiNO_3 \xrightarrow{\text{Heat}} 2\,Li_2O + 4\,NO_2 + O_2$$

$$2\,Mg\,(NO_3)_2 \xrightarrow{\text{Heat}} 2\,MgO + 4\,NO_2 + O_2$$

$$2\,NaNO_3 \longrightarrow 2\,NaNO_2 + O_2$$

(c) $MgCl_2$ and LiCl are deliquescent and crystallise as their hydrates, $LiCl \cdot 2H_2O$ and $MgCl_2 \cdot 2H_2O$.

Compounds of Alkali Metals

Being highly reactive, all the elements of group 1 form compounds. Although here we will discuss only some important of them.

Sodium Carbonate
(Washing Soda, $Na_2CO_3 \cdot 10H_2O$)

Sodium carbonate is generally prepared by **Solvay process.**

$$2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + H_2O + CO_2 \longrightarrow 2NH_4HCO_3$$
$$NH_4HCO_3 + NaCl \longrightarrow NH_4Cl + NaHCO_3$$

Sodium hydrogen carbonate crystals separate out. These are heated to obtain sodium carbonate.

$$2NaHCO_3 \xrightarrow{150°C} Na_2CO_3 + CO_2 + H_2O$$

In this process NH_3 is recovered when the solution containing NH_4Cl is treated with $Ca(OH)_2$.

Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogen carbonate is too soluble to be precipitated to a saturated solution of potassium chloride.

Sodium Hydroxide (Caustic Soda, NaOH)

Sodium hydroxide is prepared commercially by the electrolysis of sodium chloride in **Castner-Kellner cell** (or mercury cathode cell).

At cathode $Na^+ + e^- \xrightarrow{Hg} Na\text{—}Hg$ (amalgam)

At anode $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$ (by-product)

The amalgam is treated with water to give sodium hydroxide and hydrogen gas.

$$2Na\text{—}Hg + 2H_2O \longrightarrow 2NaOH + 2Hg + H_2$$

Sodium hydroxide is white, translucent solid and deliquescent. It is called **caustic soda** because it breaks down proteins of skin to a pasty mass.

On exposure to atmosphere it absorbs moisture and CO_2.

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

It is a strong alkali so reacts with acids, acidic oxides and amphoteric oxides to form their corresponding salts.

Non-metals like halogens, phosphorus, sulphur, silicon, boron are attacked by NaOH.

It reacts with metals like Zn, Al, Sn and Pb and evolve H_2 gas, *e.g.*,

$$Zn + NaOH \longrightarrow Na_2ZnO_2 + H_2$$

It also reacts with metallic salts to form hydroxides.

It is used in soap manufacture, purification of bauxite, manufacture of rayon, etc.

Sodium Chloride
(Common Salt or Rock Salt, NaCl)

The three major sources of NaCl *are*

(i) Sea water (3% NaCl)
(ii) Water of inland lake,
(iii) Salt mines.

Impure NaCl is obtained by the evaporation of salty water in open air in fields. The impure sodium chloride is dissolved in minimum amount of water. Insoluble impurities (such as sulphates of sodium and magnesium along with chlorides of calcium and magnesium) are filtered off. HCl gas is passed through saturated solution to obtain NaCl crystals. (Common ion effect).

It is white crystalline solid, soluble in water.

Pure NaCl is not hygroscopic. It shows hygroscopic nature due to the presence of chlorides of Ca and Mg as an impurity.

It is used as the starting material for the preparation of NaOH, Na_2CO_3, $NaHCO_3$, etc.

It is used as a preservative for meat, fish etc. It is also used as a 'salting out' of soap and in making freezing mixtures.

Sodium Hydrogen Carbonate
(Baking Soda, $NaHCO_3$)

It is prepared as intermediate product in the Solvay ammonia soda process.

$$NH_3 + H_2O + CO_2 + NaCl \longrightarrow NaHCO_3 \downarrow + NH_4Cl$$

- It is white crystalline solid, sparingly soluble in water.
- Its aqueous solution is alkaline in nature due to hydrolysis.

$$NaHCO_3 + H_2O \rightleftharpoons NaOH + H_2CO_3$$
$$2NaHCO_3 \xrightarrow{Heat} Na_2CO_3 + H_2O + CO_2$$

- It is used as a medicine to neutralise acidity in stomach.
- It is used as a constituent of baking powder and in fire extinguisher.

Biological Significance of Na and K

1. Na^+ ions are found mainly in extracellular region (outside the cell) and play an important role in the transmission of nerve signals. They also regulate the flow of water across cell membranes and in transport of sugars and amino acid into the cells.
2. Prolonged sweating results in sodium ion loss in sweat, thus, it is important that Na^+ ions are replaced through proper diet.
3. Potassium ions are the most abundant cations within cell fluids where they activate many enzymes, participate in oxidation of glucose to produce ATP (adenosine triphosphate).
4. Potassium ions along with sodium ions are responsible for transmission of nerve signals. The functional features of nerve cells depend upon the sodium-potassium ion gradient that is established in the cell. Their ionic gradients are maintained by sodium-potassium pumps that operate across the cell membranes.

Group 2 Elements : Alkaline Earth Metals

Be, Mg, Ca, Sr, Ba and Ra also belong to s-block and are called ***alkaline earth metals.*** *These are called* ***"alkaline earth metals"*** *due to the following facts*

1. Their hydroxides form alkaline aqueous solutions.
2. Their oxides are **earthen**, *i.e.*, soil like means having very high melting points.

   Radium is the radioactive element of this group.

General Properties of Alkaline Earth Metals

These are also the elements of *s*-block. These are less metallic as compared to alkali metals. These are called alkaline earth metals because their oxides are basic in nature and these are found mostly in the earth's crust.

Physical Properties

1. The alkaline earth metals also have low ionisation enthalpies but these are higher than that of alkali metals.
2. Like alkali metal ions, the hydration enthalpies of alkaline metal ions decrease with increase in ionic size on moving down the group.

$$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

   The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions.

3. The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller size.
4. Except Be and Mg (due to their small size and high IE), all other alkaline earth metals give flame test like calcium, strontium and barium impart characteristic brick red, crimson and apple green colours, respectively to the flame.

Chemical Properties

1. **With water and acid** Except Be and Mg, all other alkaline earth metals give hydroxide with cold water while Be forms hydroxide with steam and Mg with hot water.
   - With HNO_3, Be becomes passive due to the formation of oxide layer.
   - Alkaline earth metal chlorides, nitrates and hydroxides exhibit an increase in their solubilities on moving down the group.

$$\xrightarrow{MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2}$$
$$Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$

2. **Carbonates** Carbonates of alkaline earth metals are insoluble in water. The solubility of carbonates in water decreases as the atomic number of metal ion increases. Beryllium carbonate is unstable and can be kept only in the atmosphere of CO_2. The thermal stability increases with increase in cationic size.

   Bicarbonates of alkali metals are found in solid state whereas bicarbonates of alkaline earth metals exist only in solution state. Bicarbonates of other metals are not known.

3. **Sulphates** The sulphates of alkaline earth metals are all white solids and stable to heat. $BeSO_4$ and $MgSO_4$ are readily soluble in water. Their solubility decreases from $CaSO_4$ to $BaSO_4$.
   - The insolubility of $BaSO_4$ is used for detecting obstruction in the digestive system by the technique commonly known as barium meal.

4. **Nitrides** All the alkaline earth metals form nitrides, however among the alkali metals, only Li forms nitrides.
5. **Halides** Halides of Be are essentially covalent, hygroscopic and fumes in air while halides of other alkaline earth metals are ionic and ionic character increases down the group.

   In solid state $BeCl_2$ exists in polymeric chain while in vapour state it exists as a monomer (above 1200 K). Below 1200 K it exists as dimer.
6. **Reactivity and electrode potential** Reducing character or reactivity of alkaline earth metals increases from Be to Ba, *i.e.*,

$$Be < Mg < Ca < Sr < Ba$$

$Mg(ClO_4)_2$ is used as drying agent under the name anhydrone. It is a strong oxidising agent. So, it is not used with organic material.

Anomalous Behaviour of Beryllium

Beryllium due to its exceptionally small size (like Al) and high polarising power (like Al) shows similarities with aluminium, in its properties. *These properties are*

- BeO, like Al_2O_3, is amphoteric and covalent while oxides of other alkaline earth elements are ionic and basic in nature.
- Both $BeCl_2$ and $AlCl_3$ are soluble in organic solvents because of covalent nature and both have a bridged polymeric structure.
- Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[Be(OH)_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[Al(OH)_4]^-$.
- Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-}, AlF_6^{3-}.
- Carbides of Be are covalent and react with water to produce methane gas whereas carbides of other members are ionic and produce acetylene with water.

Compounds of Alkaline Earth Metals

All the alkaline earth metals form several compounds. *Some important of which are given below.*

Lime (Quick Lime), CaO

$$\underset{\text{limestone}}{CaCO_3} \xrightarrow{800^\circ C} CaO + CO_2$$

It is used in the manufacture of $CaOCl_2$, $Ca(OH)_2$, CaC_2, glass and cement, etc.

It is used as basic lining in the furnaces.

It is used in the purification of sugar and in water softening.

Limestone, $CaCO_3$

$$\underset{\text{slaked lime}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{milky}}{CaCO_3} + H_2O$$

It is used in the manufacture of quick lime, slaked lime, cement, glass and washing soda, etc.

It is used as a flux in smelting of iron and lead ores.

Plaster of Paris, $CaSO_4 \cdot \frac{1}{2}H_2O$

$$\underset{\substack{\text{calcium sulphate}\\ \text{dihydrate or gypsum}}}{CaSO_4 \cdot 2H_2O} \xrightarrow{\Delta} \underset{\substack{\text{calcium sulphate}\\ \text{hemihydrate or}\\ \text{plaster of Paris}}}{CaSO_4 \cdot \frac{1}{2}H_2O} + 1\frac{1}{2}H_2O$$

It is used in making toys, decorative materials and casts for statues.

It is used in medical applications for setting fractured bones in the right position and in dentistry.

It is used for making smooth surfaces.

Bleaching Powder, $CaOCl_2$

$$Ca(OH)_2 + 2Cl_2 \longrightarrow CaOCl_2 + H_2O$$

It is used as a bleaching agent an well as an oxidising agent. It oxidises H_2S into S, Fe^{2+} into Fe^{3+}, NH_3 into N_2 and KNO_2 into KNO_3.

Cement

Cement is an important building material. Cement is a product obtained by combining a material such as clay which contains silica, SiO_2 alongwith the oxides of aluminium, iron and magnesium. The average composition of portland cement is CaO — 50-60%; SiO_2 — 20-25%; Al_2O_3 — 5-10% — MgO — 2-3%; Fe_2O_3 — 1-2% and SO_3 — 1-2%.

Biological Significance of Mg and Ca

- Mg^{2+} ions are present inside the animal cells while Ca^{2+} ions are in the body fluids, *i.e.,* in the extracellular region, in much the same way as K^+ are inside the cell and Na^+ ions outside the cell. All enzymes that utilize ATP in phosphate transfer require Mg^{2+} as cofactor. In green plants, magnesium is present in chlorophyll.
- Ca^{2+} and Mg^{2+} are also essential for the transmission of impulses along nerve fibres.
- In bones and teeth, Ca is present as apatite, $Ca_3(PO_4)_2$ and in enamel on teeth as fluorapatite, $2Ca_3(PO_4)_2 \cdot CaF_2$. Ca^{2+} ions play an important role in blood clotting and are required to trigger the contraction of muscles.
- Ca^{2+} ions also regulate the heart beats.Normal oxides of Li and Na are colourless and diamagnetic, but K_2O is pale yellow, Rb_2O is bright yellow and Cs_2O is orange. (Na_2O_2 is yellow due to presence of small amount of superoxide because superoxide ion, O_2^- has three electron bonds with one unpaired electron).

Comparison Between the Properties of Alkaline Earth Metals and Alkali Metals

Unlike the members of group IA, the chemistry of IIA group elements is not completely dominated by the chemistry of cations. When compared with alkali metals, it is found that

- They are less reactive than alkali metals.
- They are less electropositive, *i.e.,* less metallic than alkali metals.
- Their reducing power is much less than those of alkali metals.
- They are less basic than alkali metals.
- The gradation in properties of these elements is not as regular as in the case of alkali metals, because of different structures of their crystal lattices.

The difference in properties with alkali metals is due to

- Small size of atoms and ions.
- Stronger metallic bonds (resulting to more density and hardness).
- Higher melting and boiling points.

Practice Zone

DAY 21

1. Which of the following ions forms a hydroxide highly soluble in water?
(a) Ni^{2+} (b) K^{+} (c) Zn^{2+} (d) Al^{3+}

2. Nitrogen dioxide cannot be prepared by heating
(a) KNO_3 (b) $Pb(NO_3)_2$ (c) $Cu(NO_3)_2$ (d) $AgNO_3$

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

4. Solubility of alkaline earth metal sulphates decreases down the group 2 because
(a) they become more ionic
(b) lattice energy of sulphates does not vary significantly
(c) hydration energy decreases rapidly from Be^{2+} to Ba^{2+}
(d) lattice energy plays more predominant role than hydration energy

5. Which of the following compounds has the lowest anion to cation size ratio?
(a) LiF (b) NaF (c) CsI (d) CsF

6. The gas evolved on heating Na_2CO_3 is
(a) CO_2 (b) water vapour
(c) CO (d) No gas is evolved

7. Which is the most basic of the following?
(a) Na_2O (b) BaO (c) As_2O_3 (d) Al_2O_3

8. Microcosmic salt is
(a) $Na_2HPO_4 \cdot 2H_2O$ (b) $(NH_4)_2HPO_4 \cdot 2H_2O$
(c) $Na(NH_4)HPO_4 \cdot 4H_2O$ (d) None of these

9. 0.2 g of magnesium ribbon was placed in a crucible and heated with a lid on until the magnesium began to burn rapidly. At the end of the experiment there was 0.3 g of a white powder left. This result does not agree with the equation; $2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO\,(s)$. It can be due, to
(a) some MgO may have escaped as vapours
(b) some Mg may not have reacted
(c) some Mg_3N_2 can be formed
(d) All of the above

10. Which of the following has lowest thermal stability?
(a) Li_2CO_3 (b) Na_2CO_3
(c) K_2CO_3 (d) Rb_2CO_3

11. In the preparation of sodium carbonate (Na_2CO_3), which of the following is used?
(a) Slaked lime (b) Quick lime
(c) Limestone (d) Sodium hydroxide

12. Fires, that result from the combustion of alkali metals can be extinguished by
(a) CCl_4 (b) sand
(c) water (d) kerosene

13. A combustible gas is liberated when caustic soda solution is heated with
(a) S (b) NH_4Cl (c) I_2 (d) Zn

14. Which of the following compounds is used in gun powder?
(a) $NaNO_3$ (b) KNO_3
(c) $LiNO_3$ (d) None of these

15. Which of the following reacts with water at a high rate?
(a) Li (b) K (c) Na (d) Rb

16. The reducing power of a metal depends on various factors. Suggest the factor which makes Li, the strongest reducing agent in aqueous solution. **[NCERT Exemplar]**
(a) Sublimation enthalpy (b) Ionisation enthalpy
(c) Hydration enthalpy (d) Electron-gain enthalpy

17. When NaOH is made, the gas released at the cathode is
(a) Cl_2 (b) H_2 (c) O_2 (d) H_2O

18. Identify the correct statement.
(a) Elemental sodium can be prepared and isolated by electrolysing an aqueous solution of NaCl.
(b) Elemental Na is a strong oxidising agent.
(c) Elemental Na is insoluble in NH_3.
(d) Elemental Na is easily oxidised.

19. The electronic configuration of metal M is $1s^2, 2s^2 2p^6, 3s^1$. The formula of its oxide would be
(a) MO (b) M_2O (c) M_2O_3 (d) MO_2

20. Anhydrous magnesium chloride is prepared by

(a) dissolving Mg in dilute HCl
(b) dissolving MgO in dilute HCl
(c) passing Cl_2 over red hot mixture of MgO + C
(d) All of the above

21. The stability of the following alkali metal chlorides follows the order

(a) LiCl > KCl > NaCl > CsCl (b) CsCl > KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl > CsCl (d) KCl > CsCl > NaCl > LiCl

22. A mixture contains two moles of Na_2CO_3 and 1 mole of Li_2CO_3. What will be the volume of CO_2 formed on heating this mixture and the data is converted to STP?

(a) 22.4 L (b) 44.8 L (c) 50.2 L (d) 11.2 L

23. When CO is passed over solid NaOH heated to 200°C, it forms

(a) Na_2CO_3 (b) H_2CO_3 (c) HCOONa (d) All of these

24. A substance which gives brick red flame and breaks down on heating to give oxygen and a brown gas is **[NCERT Exemplar]**

(a) magnesium nitrate (b) calcium nitrate
(c) barium nitrate (d) strontium nitrate

25. An aqueous solution of sodium carbonate is alkaline because sodium carbonate is a salt of

(a) weak acid and weak base (b) strong acid and weak base
(c) weak acid and strong base (d) strong acid and strong base

26. A chemical *A* is used for the preparation of washing soda to recover ammonia. When CO_2 is bubbled through an aqueous solution of *A*, the solution turns milky. It is used in white washing due to disinfectant nature. What is the chemical formula of A? **[NCERT Exemplar]**

(a) $Ca(HCO_3)_2$ (b) CaO
(c) $Ca(OH)_2$ (d) $CaCO_3$

27. On dissolving moderate amount of sodium metal in liquid NH_3 at low temperature, which one of the following does not occur ?

(a) Blue coloured solution is obtained
(b) Na^+ ions are formed in the solution
(c) Liquid NH_3 solution becomes good conductor of electricity
(d) Liquid NH_3 solution remains diamagnetic

Directions (Q. Nos. 28 to 30) *One of the chief uses of sodium carbonate has been in the conversion of* $Ca(OH)_2(s)$ *to concentrated aqueous solution of NaOH which in turn was used in the manufacture of soap.*

$$Ca(OH)_2(s) + 2\,Na^+(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s) + 2\,Na^+(aq) + 2\,OH^-(aq)$$

In 1775, in order to gain independence from the importation of natural Na_2CO_3 , the French government offered a prize to anyone who could devise a process to prepare Na_2CO_3 from NaCl.

28. A more economical process but based on same princip was given by

(a) Solvay (b) Leblanc (c) Williamson (d) Haber

29. Reaction given in passage is spontaneous because

(a) NaOH formed is ionic
(b) $CaCO_3$ is removed from the reaction mixture
(c) reaction is exothermic
(d) reaction is endothermic

30. NaOH can also be prepared by electrolysis of aqueou NaCl. Amount of NaOH formed when 0.445 L of NaCl *(aq)* i electrolysed for 137s with a current of 1.08 A, is

(a) 0.09 g
(b) 0.12 g
(c) 0.06 g
(d) amount of NaCl has not been given

Directions (Q. Nos. 31 and 32) *The standard enthalpy o formation,* ΔH_f° *of hypothetical* CaCl (*s*), *theoretically found to be* -188 kJ mol^{-1} *and that of* $CaCl_2(s)$ -795 kJ mol^{-1}.

31. Which of the following compounds is more stable ?

(a) CaCl (s)
(b) $CaCl_2(s)$
(c) Both (a) and (b) are equally stable
(d) Nothing can be said

32. Select most spontaneous reaction.

(a) $2\,CaCl(s) \longrightarrow CaCl_2(s) + Ca(s)$
(b) $CaCl_2(s) + Ca(s) \longrightarrow 2\,CaCl(s)$
(c) $CaCl(s) \longrightarrow Ca(s) + Cl(g)$
(d) $CaCl_2(s) \longrightarrow Ca(s) + Cl_2(g)$

Directions (Q. Nos. 33 to 36) *Each of these questions contain two statements : Statement I (Assertion) and Statement II (Reason) Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the code (a), (b), (c) and (d) given below.*

(a) Statement I is true, Statement II is true; Statement II is a correc explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

33. **Statement I** $BaSO_4$ is likely insoluble in water but readily dissolves in solution of sodium salt of ethylene diamine tetra acetic acid (EDTA).

Statement II Ba^{2+} forms a very stable complex with the anion of sodium salt of EDTA which is water soluble.

34. **Statement I** Ether can extract LiCl from a mixture of LiCl, NaCl and KCl.

Statement II LiCl has covalent nature but NaCl and KCl are ionic compounds.

35. **Statement I** Among the alkali metals, lithium salts exhibit the least electrical conductance in aqueous solutions.

Statement II Smaller the radius of the hydrated cation, lower is the electrical conductance in aqueous solutions.

36. **Statement I** NaOH cannot be stored in a vessel made of Al or Zn.

Statement II A protective layer of oxide is formed on the surface of the metal.

37. The atomic radius for Li and Li^+ are 1.23 Å and 0.76 Å respectively. Assuming that the difference in ionic radii relates to the space occupied by 2s electrons. What will be the % of volume of Li atom occupied by single valence electron?

(a) 70.0% (b) 30.0% (c) 24.75% (d) 76.34%

38. Element '*A*' burns in nitrogen to give an ionic compound '*B*'. Compound '*B*' reacts with water to give *C* and *D*. The solution of '*C*' becomes milky on bubbling carbon dioxide. The element '*A*' is

(a) Li (b) Mg (c) Ca (d) Be

39. Sodium is heated in air at 350°C to form '*A*'. Compound '*A*' when reacts with carbon dioxide forms sodium carbonate and *Y*. Here, *Y* is

(a) hydrogen peroxide (b) hydrogen
(c) ozone (d) oxygen

40. A colourless salt (*X*) has 50% Na_2SO_3 and 50% H_2O. How much of SO_2 at NTP is obtained when 2.52 g of (*X*) reacts with excess of dil H_2SO_4?

(a) 22.4 L (b) 0.448 L (c) 44.8 L (d) 0.224 L

41. *A*, a binary salt of potassium, gives compound *B* when heated with S. Compound *B* forms white precipitate '*C*' with barium chloride which is insoluble in conc. HCl. 7.1 g of *A* gave 11.15 g of white precipitate *C*. The compound *A* is

(a) KO_2 (b) K_2SO_4 (c) KOH (d) K_2CO_3

AIEEE & JEE Main *Archive*

42. Which of the following represents the correct order of increasing first ionisation enthalpy for Ca, Ba, S, Se and Ar. **[JEE Main Online 2013]**

(a) $Ca < S < Ba < Se < Ar$ (b) $S < Se < Ca < Ba < Ar$
(c) $Ba < Ca < Se < S < Ar$ (d) $Ca < Ba < S < Se < Ar$

43. Flocculation value of $BaCl_2$ is much less than that of KCl for sol *A* and flocculation value of Na_2SO_4 is much less than that of NaBr for sol *B*. The correct statement among the following is **[JEE Main Online 2013]**

(a) Both the sols *A* and *B* are negatively charged
(b) Sol *A* is positively charged and sol *B* are negatively charged
(c) Both the sols *A* and *B* are positively charged
(d) Sol *A* is negatively charged and sol *B* is positively charged

44. Which of the following on thermal decomposition yields a basic as well as acidic oxide? **[AIEEE 2012]**

(a) $NaNO_3$ (b) $KClO_3$
(c) $CaCO_3$ (d) NH_4NO_3

45. The number and types of bonds between two carbon atoms in calcium carbide are **[AIEEE 2005]**

(a) one sigma, one pi (b) one sigma, two pi
(c) two sigma, one pi (d) two sigma, two pi

46. A sodium salt on treatment with $MgCl_2$ gives white precipitate only on heating. The anion of sodium salt is **[IITJEE 2004]**

(a) HCO_3^- (b) CO_3^{2-} (c) NO_3^- (d) SO_4^{2-}

47. One mole of magnesium nitride on reaction with an excess of water gives **[AIEEE 2004]**

(a) one mole of ammonia (b) one mole of nitric acid
(c) two moles of ammonia (d) two moles of nitric acid

48. Beryllium and aluminium exhibit many properties which are similar but the two elements differ in **[AIEEE 2004]**

(a) exhibiting maximum covalency in compounds
(b) forming polymeric hydrides
(c) forming covalent halides
(d) exhibiting amphoteric nature in their oxides

49. The solubilities of carbonates decrease down the magnesium group due to a decrease in **[AIEEE 2003]**

(a) lattice energies of solid (b) hydration energies of cations
(c) interionic attraction (d) entropy of solution formation

50. The substance used in Holmes signals of the ship is a mixture of **[AIEEE 2003]**

(a) $CaC_2 + Ca_3P_2$ (b) $Ca_3(PO_4)_2 + Pb_3O_4$
(c) $H_3PO_4 + CaCl_2$ (d) $NH_3 + HOCl$

51. Which process is used in extractive metallurgy of Mg ? **[IIT JEE 2002]**

(a) Fused salt electrolysis
(b) Self reduction
(c) Aqueous solution electrolysis
(d) Thermite reduction

52. The metallic sodium dissolves in liquid ammonia to form a deep blue coloured solution. The deep blue colour is due to the formation of **[AIEEE 2002]**

(a) solvated electron, $e^-(NH_3)_x$
(b) solvated atomic sodium, $Na(NH_3)_4$
(c) $(Na^+ + Na^-)$
(d) $NaNH_2 + H_2$

53. A metal *M* forms a water soluble MSO_4 and inert *MO*. *MO* in aqueous solution forms insoluble $M(OH)_2$, soluble in NaOH. Metal *M* is **[AIEEE 2002]**

(a) Be (b) Mg (c) Ca (d) Sr

Answers

1. (b)	**2.** (a)	**3.** (a)	**4.** (c)	**5.** (d)	**6.** (d)	**7.** (a)	**8.** (c)	**9.** (d)	**10.** (a)
11. (c)	**12.** (a)	**13.** (d)	**14.** (b)	**15.** (d)	**16.** (c)	**17.** (b)	**18.** (d)	**19.** (b)	**20.** (c)
21. (d)	**22.** (a)	**23.** (c)	**24.** (b)	**25.** (c)	**26.** (c)	**27.** (d)	**28.** (a)	**29.** (b)	**30.** (c)
31. (b)	**32.** (a)	**33.** (a)	**34.** (a)	**35.** (c)	**36.** (c)	**37.** (d)	**38.** (c)	**39.** (d)	**40.** (d)
41. (a)	**42.** (c)	**43.** (b)	**44.** (c)	**45.** (b)	**46.** (a)	**47.** (c)	**48.** (a)	**49.** (b)	**50.** (a)
51. (a)	**52.** (a)	**53.** (a)							

Hints & Solutions

1. Alkali metal hydroxides, *i.e.*, KOH is highly soluble in water.

2. Only nitrates of heavy metals and lithium decompose on heating to produce NO_2.

3. Since, $NaHCO_3$ is an acid salt of H_2CO_3, it reacts with NaOH to form Na_2CO_3 and H_2O.

$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$$

4. Due to very large size of sulphate ions, the magnitude of lattice energy of alkaline earth metal sulphates remains almost constant. Thus, their solubility is governed by only hydration energy which decreases from Be^{2+} to Ba^{2+}.

5. For anion to cation ratio to be low, the anion must be small and cation must be large, *i.e.*, Cs^+F^-.

6. On heating Na_2CO_3, no gas is evolved.

7. Alkali metal oxides (Na_2O) are most basic followed by alkaline earth metals. Al_2O_3 is, however amphoteric .

8. $Na(NH_4)HPO_4 \cdot 4H_2O$ is commonly known as microcosmic salt.

9. $$\underset{2\times 24\,g}{2\,Mg\,(s)} + O_2(g) \longrightarrow \underset{2\times 40\,g}{2\,MgO}$$

48 g of Mg gives = 80 g of MgO

0.2 g of Mg gives $= \frac{80}{48} \times 0.2 = 0.33$ g of MgO

But residue left = 0.30. It is due to all of the given options.

10. The weaker the base, the less stable is its carbonate. Since, LiOH is the weakest base, therefore Li_2CO_3 has the lowest thermal stability.

11. Limestone ($CaCO_3$) is used for producing CO_2.

12. Only CCl_4 is used to extinguish such fire because it is low boiling liquid (350K) and its vapours are non-inflammable. Its vapours surround the fire, there by cutting off air supply.

13. $2NaOH + Zn \longrightarrow Na_2ZnO_2 + H_2\uparrow$

14. Nitre (KNO_3) is used in gun powder.

15. Rb being most electropositive has the highest reactivity towards water.

16. Hydration enthalpy of Li^+ is highest among all other alkali metal due to its smaller size. Therefore, Li^+ acts as a strong reducing agent.

17. **At cathode** $H^+ + e^- \longrightarrow H$:

$H + H \longrightarrow H_2$

At anode $Cl^- \longrightarrow Cl + e^-$

$Cl + Cl \longrightarrow Cl_2$

18. Because of its low ionisation energies, elemental Na loses its valance *s*-electron easily and undergoes oxidation.

19. Electronic configuration indicates that the metal is univalent (alkali metal). Its oxide will be M_2O.

20. Anhydrous $MgCl_2$ is obtained by passing chlorine gas over red hot mixture of MgO and C.

$$MgO + C + Cl_2 \longrightarrow MgCl_2 + CO$$

21. Stability of a compound depends upon its enthalpy of formation ΔH_f. The more negative value of ΔH_f shows more stability of a compound.

Thus, KCl is more stable and LiCl is least stable.

ΔH_f for LiCl $= -408.8\ kJ\ mol^{-1}$

ΔH_f for NaCl $= -412.5\ kJ\ mol^{-1}$

ΔH_f for CsCl $= -433\ kJ\ mol^{-1}$

ΔH_f for KCl $= -436\ kJ\ mol^{-1}$

22. Decomposition of Li_2CO_3

$$\underset{1\ mol}{Li_2CO_3} \xrightarrow{\Delta} Li_2O + \underset{22.4\ L}{CO_2}$$

Na_2CO_3 is thermally stable, *i.e.*, it doesn't give CO_2 gas on heating.

Hence, volume of CO_2 formed on heating the mixture at STP = 22.4 L

23. $$\underset{solid}{NaOH} + CO \xrightarrow{200°C} \underset{sod.\ formate}{HCOONa}$$

24. Brick red colour is given by Ca while O_2 and brown colour are given by nitrate.

$$2Ca(NO_3)_2 \xrightarrow{\Delta} 2CaO + O_2 + 4NO_2$$

26. For the recovery of ammonia, $Ca(OH)_2$ is used during the preparation of washing soda.

28. A more economical process but based on same principle was given by Solvay.

29. $CaCO_3$ is removed from the reaction mixture to produce more NaOH.

30. $W = Zit = \frac{40}{96500} \times 1.08 \times 137 = 0.06\,g$

31. $CaCl_2$ is more stable than CaCl because

$$\Delta H^\circ_{f(CaCl_2)} > \Delta H^\circ_{f(CaCl)}$$

32. $2\,CaCl(s) \longrightarrow CaCl_2(s) + Ca(s)$; most spontaneous reaction.

34. Due to its smaller size lithium forms covalent halide while other alkali metal halides are ionic. Covalent compounds are soluble in non-polar solvents like ether.

35. Statement II is wrong. Li^+ ion being smallest in size becomes heavily hydrated, hence moves slowly under the influence of electric field (poorest conductor).

36. NaOH forms soluble salt of sodium aluminate or sodium zincate when stored in a vessel made of aluminium or zinc respectively. Hence, statement II is wrong.

37. Volume occupied by $Li^+ = \frac{4}{3}\pi \times (0.76 \times 10^{-8})^3$

Volume occupied by $Li^+ = \frac{4}{3}\pi \times (1.23 \times 10^{-8})^3$

$\therefore$ Volume occupied by 2s electron

$$= \frac{4}{3}\pi \times [(1.23)^3 - (0.76)^3] \times (10^{-8})^3$$

$\therefore$ % volume occupied by 2s electron of Li atom

$$= \frac{\frac{4}{3}\pi \times [\{(1.23)^3\} - (0.76)^3\} \times (10^{-8})]^3}{\frac{4}{3}\pi \times [1.23 \times 10^{-8}]^3} \times 100$$

$$= \frac{1.42}{(1.23)^3} \times 100 = 76.34\%$$

38. Carbon dioxide turns only lime water milky. Thus, the compound 'C' must be $Ca(OH)_2$ and the element 'A' must be Ca. The reactions are as follows

$$\underset{'A'}{3Ca} + N_2 \longrightarrow \underset{'B'}{Ca_3N_2}$$

$$\underset{'B'}{Ca_3N_2} + 6H_2O \longrightarrow \underset{'C'}{3Ca(OH)_2} + \underset{'D'}{2NH_3}$$

$$\underset{'C'}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{milky}}{CaCO_3} + H_2O$$

39. $$Na + O_2 \xrightarrow{350°C} \underset{'A'}{Na_2O_2}$$

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + \underset{'Y'}{O_2}$$

40. In salt $(X) = \underset{50\%}{Na_2SO_3} : \underset{50\%}{H_2O}$

Molar mass of the $Na_2SO_3 = 126$

Molar mass of the $H_2O = 18$

Hence, 7 molecules of water are attached with Na_2SO_3.

$\therefore$ Formula $= Na_2SO_3 \cdot 7H_2O$

126 : 18 × 7
126 : 126
1 : 1

$$Na_2SO_3 \cdot 7H_2O + H_2SO_4(aq) \longrightarrow SO_2(g) + Na_2SO_4(aq) + OH_2O(l)$$

$\because$ 252g $Na_2SO_3 \cdot 7H_2O$ gives $= 22.4$ L SO_2

$\therefore$ 2.52g $Na_2SO_3 \cdot 7H_2O$ will give $= \frac{22.4}{252} \times 2.52 = 0.224$ L

41. $$\underset{142\,g}{2\,KO_2} + S \xrightarrow{\Delta} K_2SO_4$$

(A) (B)

$$K_2SO_4 + BaCl_2 \longrightarrow \underset{223\,g}{BaSO_4}\downarrow + 2KCl$$

(B) (C)

$\because$ 142 g KO_2 gives = 223 g $BaSO_4$

$\therefore$ 7.1 g KO_2 will give $= \frac{223}{142} \times 7.1 = 11.15$ g $BaSO_4$

42. Order of increasing

ΔH_{1E_1} : Ba < Ca < Se < S < Ar. Ba < Ca < Se < S

On moving top to bottom ina group, size increases. So ionisation energy decreases. Ar : Maximum value of ionisation energy, since it in an inert gas.

43. Flocculation value of $BaCl_2$ is less than that of KCL so sol *A* must not be negatively charged. It should be positively charged. Similarly, flocculation value of Na_2SO_4 is much less than that of NaBr, it means sol *A* must not be positively charged. It should be negatively charged.

44. (a) $2\,NaNO_3 \xrightarrow{\Delta} 2\,NaNO_2 + O_2$

(b) $2\,KClO_3 \xrightarrow{\Delta} 2\,KCl + 3\,O_2$

(c) $CaCO_3 \xrightarrow{\Delta} \underset{\text{basic}}{CaO} + \underset{\text{acidic}}{CO_2}$

(d) $NH_4NO_3 \xrightarrow{\Delta} \underset{\text{neutral}}{N_2O} + \underset{\text{neutral}}{H_2O}$

45. In CaC_2, one sigma and two pi bonds are present in between two carbon atoms.

46. $NaHCO_3 + MgCl_2 \xrightarrow{\Delta}$ White ppt.

47. $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

48. Be (*Z* = 4) has maximum covalency of four while Al (*Z* = 13) has maximum covalency of 6.

49. Solubilities of carbonates decrease down the group because lattice energy decrease is almost constant while decrease in hydration energy happens sharply.

Finally difference of hydration energy and lattice energy decreases, thus solubility decreases.

50. In Holmes signals of the ship, mixture of CaC_2 and Ca_3P_2 is used.

51. Mg is extracted by electrolysis of fused anhydrous $MgCl_2$.

52. $$Na \rightleftharpoons Na^+(\text{in liq. } NH_3) + e^-$$

$$e^- + xNH_3 \longrightarrow \underset{\text{ammonia solvated electron}}{e(NH_3)_x^-}$$

53. On moving down, water solubility of alkaline earth metals decreases. Oxides and hydroxides of alkaline earth metals are basic, except Be, which gives amphoteric. Hence, metal is Be.

Day 22

p-Block Elements

Day 22

Outlines ...

- Concept for p-Block Elements
- Periodicity in Properties of *p*-Block Elements
- Group-13 Elements : Boron Family
- Group-14 Elements : Carbon Family
- Group-15 Elements : Nitrogen Family
- Group-16 Elements : Oxygen Family
- Group-17 Elements : Halogens

Condition for p-Block Elements

In p-block elements, the last electron enters in the outermost p-orbital. There are six groups of p-block elements in the Periodic Table, numbering from 13 to 18. Their valence shell electronic configuration is $ns^2 np^{1-6}$ *(except for He). Effective nuclear charge from first to third period decreases and from fourth period and onwards increases, due to poor shielding effect. Therefore,* ns^2 *electrons bound closely to the nucleus. Therefore, the oxidation state two unit less than the group oxidation state becomes progressively more stable in each group. This is also known as* ***inert pair effect****.*

Periodicity in Properties of *p*-Block Elements

Metallic and Non-Metallic Character

Non-metals and metalloids exist only in the *p*-block of the Periodic Table. On moving down a group metallic character increases and non-metallic character decreases. Between, metals and non-metals a few metalloids are also present.

$p\pi - p\pi$ Multiple Bonding

Second period elements have a tendency to form $p\pi - p\pi$ multiple bond (double or triple bond) due to their smaller atomic size and high bond energy. *e.g.*, $C{\equiv}C, C{=}C, N{\equiv}N, O{=}O, O{=}C{=}O$ etc.

Covalency

Elements of second period do not expand their covalency due to non availability of *d*-orbitals. Therefore, halides of such elements do not hydrolysed easily. *e.g.*, BCl_3, CCl_4 (halides) etc.

While elements of third period and onwards only form single bond and can expand their covalency due to presence of vacant *d*-orbitals. *e.g.*, P_4, S_8, $[AlF_6]^{3-}$ ion etc.

Nature of Oxides

Non-metal oxides are acidic or neutral and metal oxides are basic in nature. Generally metalloid oxides are amphoteric. In a period, from left to right acidic character increases and down a group, basic character increases. Generally oxides with higher oxidation state are more acidic in nature.

Properties of Hydrides

- **Basic character** of *p*-block hydrides decreases on moving down a group and acidic character increases. Generally left to right in a period, acidic character increases. *e.g.*,

$$NH_3 > PH_3 > AsH_3$$

(down the group basic character decreases)

$$NH_3 > H_2O > HF$$

(left to right basic character decreases)

- **Thermal stability** of hydrides on moving down a group decreases due to increase in bond length.

  Thermal stability of the hydrides decreases down the group due to which their tendency to act as reducing agent increases down the group.

- **Bond angle** of hydrides on moving down a group, decreases due to increase in the size of central atom. Charge density and repulsion interaction also decreases on moving down a group, *e.g.*,

$$\underset{\text{bond angle}}{H_2O > H_2S > H_2Se}$$

If central atoms belong to the same period and have the same hybridisation, then as the number of lone pair increases, bond angle decreases.

$$\underset{\text{bond angle}}{CH_4 > \ddot{N}H_3 > H_2\overset{..}{\underset{..}{O}}}$$

- **Boiling point** of hydrides increases on moving down a group because van der Waals' forces increases with increase in molecular mass except HF, H_2O, NH_3 etc. HF, NH_3 and H_2O have intermolecular hydrogen bonding as a result of this, they have high boiling point.

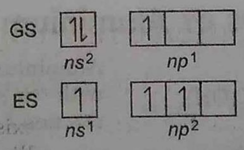
- **Unique behaviour of the first element in each group** It is due to the (i) small size (ii) high electronegativity and (iii) non-availability of *d*-orbitals in the valence shell of first element in each group.

Group-13 Elements : Boron Family

Boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Ti) are the members of group-13. Boron is non-metal while rest of the members are metals.

Important Properties

General Configuration ns^2, np^1



Oxidation State $+3, +1$

Stability of $+3$ oxidation state decreases down the group and that of $+1$ oxidation state increases down the group due to inert pair effect. Fourth period and onwards effective nuclear charge increases due to poor shielding effect, therefore the radius of gallium (135 pm) is less than that of aluminium (143 pm) and down the group, inert pair effect increases.

Hydrides

Boron hydrides exist in dimeric or polymeric form. The simplest boron hydride is diborane, B_2H_6. Aluminium forms only one colourless, solid polymeric hydride $(AlH_3)_n$, known as alane. Hydrides of Ga and In are not very much stable. B, Al and Ga form complex anionic hydrides, *e.g.*, $NaBH_4$, $LiAlH_4$ and $LiGaH_4$.

All are strong reducing agents.

$$LiAlH_4 > NaBH_4 \text{ (reducing power)}$$

Halides

Halides have incomplete octet, therefore, have a high tendency to accept electrons and behave as Lewis acid.

$$BI_3 > BBr_3 > BCl_3 > BF_3 \text{ (acidic character)}$$

BF_3 is a colourless gas, BCl_3 is a colourless fuming liquid while BI_3 is a white fusible solid. Due to back bonding and resonance, the B–F bond of BF_3 gets a bond order of 1.33.

- *$AlCl_3$ (anhydrous) is covalent and behaves as Lewis acid because Al^{3+} has small size and high polarising power but $AlCl_3$ (hydrated) is ionic in nature.*
- *Al^{3+} has small size and presence of vacant d-orbitals, therefore $AlCl_3$ easily gets hydrolysed in water and form octahedral $[Al(OH)_6]^{3+}$ ion in which the hybridisation state of Al is sp^3d^2.*

Oxides

Down the group, their basic character increases. *e.g.*, B_2O_3 is weakly acidic, Al_2O_3 is amphoteric and other oxides are basic in nature.

Preparation, Properties and Uses of Boron

Occurrence

The important minerals of boron are borax $(Na_2B_4O_7 \cdot 10H_2O)$, orthoboric acid (H_3BO_3) and kernite $(Na_2B_4O_7 \cdot 4H_2O)$

Preparation

Now a days boron is obtained by electrolysis of a fused mixture containing boric anhydride, magnesium oxide and magnesium fluoride at 1100°C.

$$2MgO \longrightarrow 2Mg + O_2$$
$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

Crystalline boron is obtained by the reduction of B_2O_3 with aluminium powder.

$$B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3$$

Amorphous boron of low purity is called **Moissan boron**. It is black in colour.

Physical Properties

Boron exists in two allotropic forms *i.e.*, amorphous and crystalline. Crystalline boron is chemically inert while amorphous boron is chemically active. It is a bad conductor of heat and electricity.

Chemical Properties

Amorphous boron on heating with air at 700°C forms a mixture of oxide and nitride.

$$4B + 3O_2 \longrightarrow 2B_2O_3$$
$$2B + N_2 \longrightarrow 2BN$$

Boron is attacked by oxidising acids like conc. H_2SO_4 and HNO_3.

$$B + 3HNO_3 \xrightarrow{H_2SO_4} H_3BO_3 + 3NO_2$$

It dissolves in fused alkalies and liberates hydrogen.

It reacts with strong electropositive metals at high temperature and forms borides such as Mg_3B_2.

It is a powerful reducing agent.

$$3CO_2 + 4B \longrightarrow 2B_2O_3 + 3C$$
$$3SiO_2 + 4B \longrightarrow 2B_2O_3 + 3Si$$

Uses

It is used as control rods in atomic reactors and as a deoxidiser.

Preparation, Properties and Uses of Aluminium

Occurrence

The important ores of aluminium are bauxite $AlO_x(OH)_{3-2x}$ (where $0 < x < 1$) and kaolinite $[Al_2(OH)_4Si_2O_5]$

Preparation

Bauxite contains SiO_2, iron oxides and titanium oxide (TiO_2) as impurities. Leaching of bauxite ore is carried out with conc. NaOH solution.

Aluminium is obtained by the electrolysis of Al_2O_3 mixed with Na_3AlF_6 or CaF_2 (Hall-Heroult process). Overall reaction is as follows $2Al_2O_3 \longrightarrow 2Al + 3O_2$

Physical Properties

It is bluish white lustrous metal and loses its lustre due to the formation of protective oxide film Al_2O_3. It is light, malleable, ductile, good conductor of heat and electricity.

Chemical Properties

It burns in oxygen producing brilliant light.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3; \qquad \Delta H = -\text{ve}$$

This reaction is used in thermite process for the reduction of oxides of Cr, Mn, Fe etc.

It decomposes boiling water evolving hydrogen.

$$2Al + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2\uparrow$$

It is rendered passive by nitric acid due to the formation of thin oxide film. It reacts with non metals and displaces less reactive metals such as copper, zinc and lead from their salt solutions.

Uses

It is used for making house hold utensils, frames, bodies of aircraft automobiles etc. It is used in making paints, as a mordant in dyeing and calico printing. **Ammonal** (mixture of Al powder and ammonium nitrate) is used as explosive. Magnalium, duralumin and alnico are important alloys of aluminium.

Some Important Compounds

Some of important compounds of group 13 elements or boron family are given below

Diborane, B_2H_6

Diborane is a colourless, highly toxic gas with a boiling point of 180 K.

Diborane catches fire spontaneously upon exposure to air.

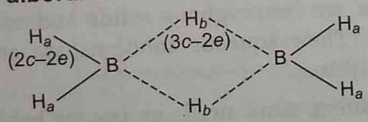
$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

With ammonia, diborane gives borazine.

$$3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\text{Heat}} \underset{\text{borazine}}{2B_3N_3H_6} + 12H_2$$

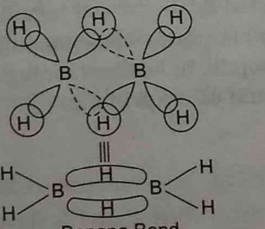
Borazine ($B_3N_3H_6$) is known as **"inorganic benzene"** in view of its ring structure with alternative BH and NH groups. However, at high temperature, inorganic graphite $(BN)_x$ is obtained instead of borazine.

Structure of diborane



(B_2H_6)

- Terminal hydrogens (H_a) are bonded by $2c-2e$ (two centred two electrons) bonding and bridge hydrogens (H_b) are bonded by $3c-2e$ (three centred held by two electrons) bonding. This type of bonding is also known as **banana bonding.** Orbital Sturcture of B_2H_6



Banana Bond

- Due to banana bonding, B_2H_6 complete its electron deficiency and obtain ethane like structure and hybridisation of B_2H_6 becomes sp^3.

$$2MH + B_2H_6 \longrightarrow 2M^+[BH_4]^- \qquad (M = \text{Li or Na})$$

It is used as a catalyst in polymerisation process, for welding torch, as reducing agent in organic reactions etc.

Borax ($Na_2B_4O_7 \cdot 10H_2O$)
[Sodium tetra borate decahydrate]

(i) It is the most important compound of boron. It is white crystalline solid.

(ii) Borax dissolves in water to give an alkaline solution.

$$Na_2B_4O_7 + 7H_2O \longrightarrow \underbrace{2NaOH + \underset{\substack{\text{orthoboric acid}\\\text{(weak acid)}}}{4H_3BO_3}}_{\text{glassy mass}}$$

(iii) On heating, it loses their water of crystalization and swells up to form a mass of a bead.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[-10H_2O]{\Delta} \underset{\substack{\text{swell up}\\\text{(sodium metaborate)}}}{Na_2B_4O_7}$$

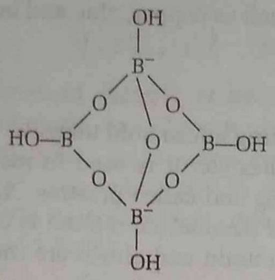
$$\xrightarrow{\Delta} \underbrace{2NaBO_2 + \underset{\text{boric anhydride}}{B_2O_3}}_{\text{glassy mass}}$$

(iv) With acids, it gives orthoboric acid, a weak acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4B(OH)_3 \text{ or } \underset{\text{orthoboric acid}}{H_3BO_3}$$

(v) **Structure**

Borax contains the tetrahedral units *i.e.*, $[B_4O_5(OH)_4]^{2-}$



Structure of $[B_4O_5(OH)_4]^{2-}$, ion

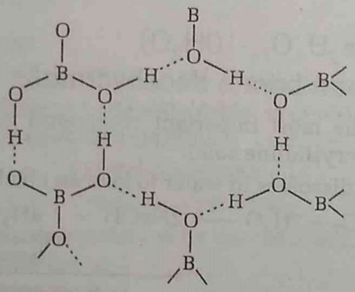
Boric Acid (H_3BO_3)

(i) Boric acid is soft white crystalline solid, soapy to touch and less soluble in cold water.

(ii) Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a **Lewis acid.**

(iii) $H_3BO_3 \xrightarrow{\text{Heat}} \underset{\text{metaboric acid}}{HBO_2} \xrightarrow{\text{Heat}} \underset{\text{boric anhydride}}{B_2O_3}$

(iv) **Structure of boric acid** shows that it has a layer structure in which planar BO_3 units are joined by H-bonds.



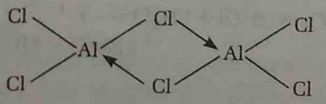
(v) It is used as an antiseptic, eye wash, as food preservative, in glass industry and in pottery.

Aluminium Chloride

(i) Anhydrous aluminium chloride is a white deliquescent solid which fumes in air. Its vapour density corresponds to the formula Al_2Cl_6.

(ii) It is covalent and soluble in organic solvents.

(iii) **Structure of $AlCl_3$**



(iv) Due to the formation of HCl, anhydrous aluminium chloride fumes in moist air.

$$\underset{\text{anhy.}}{Al_2Cl_6} + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl$$

$$Al_2Cl_6 + 12H_2O \longrightarrow \underset{\text{hydrated aluminium chloride (ionic)}}{2AlCl_3 \cdot 6H_2O}$$

(v) With ammonia, it gives addition product.

$$\underset{\text{anhy.}}{Al_2Cl_6} + 12NH_3 \longrightarrow \underset{\text{addition product}}{2[AlCl_3 \cdot 6NH_3]}$$

(vi) With NaOH, sodium meta aluminate is obtained.

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 \downarrow + 3NaCl$$

$$Al(OH)_3 + NaOH \longrightarrow \underset{\text{sodium meta aluminate}}{NaAlO_2} + 2H_2O$$

(vii) *Anhydrous* $AlCl_3$ *is used*

(a) As a reagent in Friedel-Crafts reaction.

(b) In manufacture of drugs, dyes, perfumes.

(c) In cracking of high boiling fractions of petroleum to form gasoline.

Alums

(i) These are double sulphates having composition $M_2SO_4 \cdot M'_2(SO_4)_3 \cdot 24H_2O$ (M = monovalent basic radicals such as Na^+, K^+ etc., and M' = trivalent basic radicals such as Al^{3+}, Cr^{3+} etc.)

Potash alums; $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Sodium alums; $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Ferric alums; $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$

(ii) Alums are isomorphous solids and soluble in hot water. Their aqueous solutions are acidic due to hydrolysis.

(iii) On heating, alum swells up leaving behind a porous mass, called burnt alum.

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \xrightarrow{200°C} K_2SO_4 \cdot Al_2(SO_4)_3 + 24H_2O$$

$$K_2SO_4 \cdot Al_2(SO_4)_3 \xrightarrow{\text{Red hot}} K_2SO_4 + Al_2O_3 + 3SO_3$$

(iv) It is used to purify water, stop bleeding from cuts, as an antiseptic, in leather tanning and as a mordant in dyeing and calico printing.

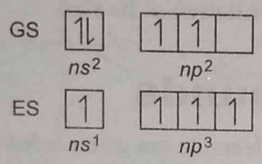
Group-14 Elements : Carbon Family

Carbon(C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb) are the members of group 14. Carbon is the seventeenth most abundant element by mass in the earth's crust. C is non-metal, Si, Ge are metalloids and Sn, Pb are metals.

Important Properties

Some of the important properties of group 14 elements or carbon family elements are given below

General configuration ns^2np^2



Catenation

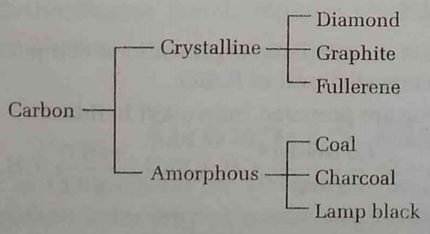
The tendency for catenation is maximum in carbon and it decreases down the group due to steady decrease in $M—M$ bond strength.

$$C >> Si > Ge \approx Sn >> Pb$$

Allotropy

All the members except Pb show allotropy.

Allotropes of carbon



Diamond

It is the purest, hardest form of carbon with high refractive index and density. In it each carbon atom (sp^3 hybridised) is tetrahedrally surrounded by four other carbon atoms. It is three dimensional polymer, has very high density and very high refractive index. It does not conduct electricity as it has no free electrons. It is used in cutting, grinding and drilling instruments and in making jewellery.

Graphite

It has two dimensional structure. sp^2 hybridised carbon atom forms three covalent bonds with three other carbon atoms in the same plane and the 4th electron of each carbon remains free and is responsible for electrical conductivity of graphite. The planar hexagonal rings get fused together to form sheets of one atom thickness. These sheets are held together by weak van der Waals' forces. These layers can slide over each other and gives softness, greasiness and lubricating property to graphite. It is used in making electrodes, lead pencils and as dry lubricant.

Fullerenes

These are the only pure form of carbon. C_{60} molecule contains 12 five membered rings and 20 six-membered rings. The five membered rings are connected to six membered rings while six membered rings are connected to both five and six membered rings. These are used in microscopic ball bearings, light weight batteries, in synthesis of new plastics and new drugs.

Oxidation States

The common oxidation states are +4 and +2. Carbon also exhibits negative oxidation states, *i.e.*, –4. Down the group, stability of +4 oxidation state decreases and of +2 oxidation state increases due to inert pair effect.

Oxides

CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature.

(i) Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

(ii) Monomeric form of CO_2 is stable due to non availability of d-orbitals. Carbon has tendency to form a multiple bond ($O{=}C{=}O$) but SiO_2 exists in three dimensional polymeric form and has high melting point and is solid at room temperature.

Reactivity Towards Water

Carbon, silicon and germanium are not affected by water. Tin decomposes with steam to form dioxide and dihydrogen gas.

$$Sn + 2H_2O \xrightarrow{Heat} SnO_2 + 2H_2$$

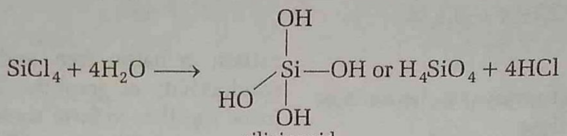
Lead remains unaffected by water, probably because of a protective oxide film formation.

Halides

GeX_4 is more stable than GeX_2, whereas PbX_2 is more stable than PbX_4 and $SnCl_2$ is more stable than $SnCl_4$. $SnCl_4$ is liquid at room temperature due to covalent character and $SnCl_2$ is solid at room temperature.

(i) Except CCl_4, other halides are easily hydrolysed due to availability of vacant *d*-orbitals.

e.g.,



$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 \text{ or } H_4SiO_4 + 4HCl$$

silicic acid

(ii) Si has vacant *d*-orbitals, so can expand its covalency and form higher halides $[SiF_6]^{2-}$ but not $[SiCl_6]^{2-}$ because larger size of chloride ions cannot be accommodated around Si^{4+} due to limitation of its size.

Some Important Compounds

Some of the important compounds of group 14 elements or carbon family elements are given below.

Water Gas or Synthesis Gas and Producer Gas

$$C(s) + H_2O(g) \xrightarrow{473\text{ K} - 1273\text{ K}} \underbrace{CO(g) + H_2(g)}_{\text{water gas}}$$

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273\text{ K}} \underbrace{2CO(g) + 4N_2(g)}_{\text{producer gas}}$$

Water gas and producer gas are very important industrial fuels.

Carbon Dioxide

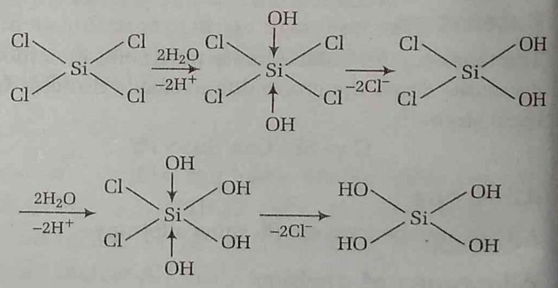
1. The combustion of fossil fuels and decomposition of limestone for cement manufacture, in recent years, seem to increase the CO_2 content of the atmosphere. This may lead to increase in green house effect and thus, raise the temperature of the atmosphere which might have serious consequences.
2. Carbon dioxide can be obtained as a solid in the form of dry ice by allowing the liquified CO_2 to expand rapidly. Dry ice is used as a refrigerant for ice-cream and frozen food.

Silicon Tetrachloride ($SiCl_4$)

(i) It is tetrahedral and essentially covalent. It is readily hydrolysed by water. It fumes in moist air liberating hydrogen chloride.

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

(ii) The hydrolysis of $SiCl_4$ occurs due to coordination of OH with empty 3*d*-orbitals in Si atom of $SiCl_4$ molecule.

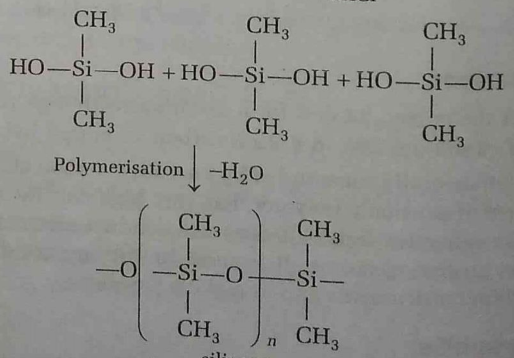


Silicones

(i) These are synthetic organosilicon compounds which has repeated unit of R_2SiO.

(ii) These are prepared from alkyl halides.

$$2CH_3Cl + Si \xrightarrow[570\text{ K}]{\text{Cu powder}} (CH_3)_2SiCl_2 \xrightarrow[-2HCl]{+2H_2O} (CH_3)_2Si(OH)_2$$



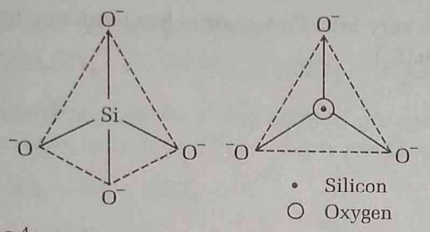
silicone

Highly cross linked silicone polymer is obtained by the hydrolysis of $RSiCl_3$.

(iii) They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

Silicates

(i) A large number of silicate minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. The basic structural unit of silicates is SiO_4^{4-}.



(ii) The SiO_4^{4-} unit is neutralised by positively charged metal ions, if all the four corners are shared with other tetrahedral units.

(iii) Generally the silicates have complex structures but they mainly differ in
  - (a) Number of oxygen atoms shared between SiO_4^{4-} tetrahedra.
  - (b) Geometric arrangement of tetrahedra.
  - (c) The number, type and arrangement of metallic cations.

Silicates are of following types

(i) Orthosilicates Simple silicates containing SiO_4^{4-} tetrahedra.

(ii) Pyrosilicate Two tetrahedral units share one O-atom to obtain $Si_2O_7^{6-}$ anion.

(iii) Cyclic silicates Two tetrahedral units share two oxygen atoms and form $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ anion.

(iv) Chain silicates Share two oxygen atoms, $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ are obtained.

(v) Sheet silicates Involve sharing of three O-atoms per tetrahedron to form $(Si_2O_5^{2-})_n$.

(vi) Three dimensional silicates All the four corners (O-atoms) of SiO_4^{4-} tetrahedra are shared with other.

(vii) Two important man made silicates are glass and cement.

Zeolites

If aluminium atoms replace few silicon atoms in three dimensional network of silicon dioxide, the obtained overall structure is known as alumino silicate and acquires a negative charge.

Cations such as Na^+, K^+ or Ca^{2+} balance the negative charge. Their examples include feldspar and zeolites.

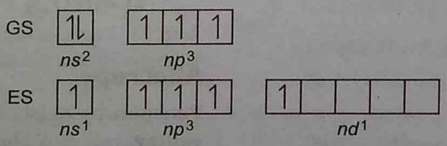
Zeolites are used as a catalyst in petrochemical industries for cracking of hydrocarbons. ZSM-5 (a type of zeolite) is used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of hard water.

Group-15 Elements : Nitrogen Family

Group 15th elements are nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids and bismuth is a typical metal.

Important Properties

General Configuration ns^2np^3



In case of nitrogen, ground state and excited state will be same due to absence of d-orbitals.

Oxidation States

The common oxidation states of these elements are −3, +3 and +5. The tendency to exhibit −3 oxidation state decreases down the group due to increase in size and metallic character. The stability of +5 oxidation state decreases down the group and that of +3 oxidation state increases down the group due to inert pair effect. Nitrogen with oxygen exhibits +1, +2, +4 oxidation states.

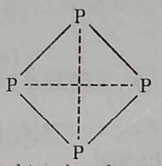
Oxidation states from +1 to +4 tend to disproportionates in acid solution. *e.g.*, $3\overset{+3}{\text{HNO}_2} \longrightarrow \overset{+5}{\text{HNO}_3} + \text{H}_2\text{O} + 2\overset{+2}{\text{NO}}$

$p\pi - p\pi$ Multiple Bonding

Only nitrogen has a tendency to form $p\pi - p\pi$ multiple bond ($N \equiv N$) due to absence of *d*-orbitals.

Chemical Reactivity

N_2 has high bond dissociation energy, therefore reactivity of free N_2 is very less. Phosphorus has tendency to form a single bond due to presence of *d*-orbitals and thus, exists in polyatomic form (P_4).



(white phosphorus)

P_4 has cyclic structure, therefore it is highly reactive and can expand its covalency as in PF_6^-.

Major Elements of Group-15

Dinitrogen

Preparation

$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

$$Ba(N_3)_2 \longrightarrow Ba + 3N_2$$

Properties

(i) Nitrogen does not react with alkali metals except Li but reacts with alkaline earth metals to give metal nitride.

$$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$$

(ii) $N_2(g) + O_2(g) \xrightarrow{2000\text{ K}} 2NO(g)$

(iii) $2B + N_2 \xrightarrow{\text{Heat}} 2BN$

(iv) $CaC_2 + N_2 \xrightarrow{1273\text{ K}} CaCN_2 + C$

Uses

(i) Liquid N_2 is used as refrigerant.

(ii) It is used in the manufacture of $HNO_3, NH_3, CaCN_2$ (calcium cyanamide) and other nitrogenous compounds.

(iii) It is used for filling electric bulbs.

Phosphorus

Preparation

(i) **Retort process**

$$\underset{\text{phosphorite}}{Ca_3(PO_4)_2} + 3H_2SO_4 \longrightarrow \underset{\substack{\text{orthophosphoric}\\ \text{acid}}}{2H_3PO_4} + 3CaSO_4$$

$$H_3PO_4 \longrightarrow \underset{\text{metaphosphoric acid}}{HPO_3} + H_2O$$

$$4HPO_3 + 10C \longrightarrow P_4 + 10CO + 2H_2O$$

(ii) **Electrothermal process** Phosphorus is obtained from direct reduction of mineral phosphorite by carbon in presence of silica.

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \xrightarrow{1400\text{-}1500°\text{C}} 6CaSiO_3 + P_4 + 10CO$$

Allotropy

Phosphorus exists in three allotropic forms, *i.e.*, white or yellow, red and black (α- and β-) phosphorus. These forms are inter convertible.

$$\text{Black phosphorus} \xleftarrow[\text{Under pressure}]{470\text{ K}} \underset{\text{white phosphorus}}{P_4} \xrightarrow{560\text{ K, inert atm.}} \text{Red phosphorus}$$

(i) **White phosphorus** is transparent, soft, poisonous, waxy solid, shows chemiluminescence and chemically more reactive.

- $P_4 + 5O_2 \longrightarrow P_4O_{10}$ or $2P_2O_5$
- $P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{sod. hypo phosphite}}{3NaH_2PO_2} + \underset{\text{phosphine}}{PH_3}$
- $6Mg + P_4 \longrightarrow \underset{\text{magnesium phosphide}}{2Mg_3P_2}$

It acts as strong reducing agent.

- $P_4 + 10H_2SO_4 \longrightarrow 4H_3PO_4 + 10SO_2 + 4H_2O$

(ii) **Red phosphorus** is the stable form of phosphorus. It is odourless, non-poisonous and less reactive.

- $2P + 5Cl_2 \xrightarrow{\text{Heat}} 2PCl_5$
- $2P + 3S \xrightarrow{\text{Heat}} P_2S_3$
- $P + 3Na \longrightarrow Na_3P$
- It is a polymer consists of chains of P_4 tetrahedra linked together.

(iii) **Black phosphorus** is obtained from white phosphorus.

$$\text{White P} \xrightarrow[\text{high pressure}]{200°C} \text{black phosphorus}$$

- It may occur in orthorhombic, rhombohedral and cubic form.

Uses

(i) Red phosphorus is used in match industry.

(ii) Radioactive phosphorus is used in treatment of leukaemia and other blood disorders.

(iii) Yellow phosphorus and zinc phosphide are used as a rat poison.

Some Important Compounds

Some of the important compounds of group 15 or nitrogen family elements are given below

Ammonia

(i) Ammonia is covalent. N-atom in NH_3 is sp^3 hybridised. Due to the presence of lone pair of electrons, it acquires pyramidal shape.

(ii) It is prepared by following methods.

$$\underset{\text{urea}}{NH_2CONH_2} + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

On large scale, ammonia is manufactured by **Haber's process**.

$$N_2(g) + 3H_2(g) \underset{723\text{ K; Catalyst}}{\overset{200\text{ atm}}{\rightleftharpoons}} 2NH_3\ ; \quad \Delta H_f^\circ = -46.1\text{ kJ/mol}$$

Catalyst–iron oxide with small amounts of K_2O and Al_2O_3 is used to increase the rate of attainment of equilibrium.

(iii) NH_3 is basic in nature, has tendency to form hydrogen bond, therefore soluble in water and form NH_4OH or $NH_3(aq)$.

(iv) Due to basic nature, NH_3 is a good complexing agent and reducing agent. *e.g.,*

$$2FeCl_3(aq) + 3NH_4OH(aq) \longrightarrow \underset{\text{brown ppt.}}{Fe_2O_3 \cdot xH_2O(s)} + 3NH_4Cl$$

$$ZnSO_4(aq) + 2NH_4OH(aq) \longrightarrow \underset{\text{white ppt.}}{Zn(OH)_2(s)} + (NH_4)_2SO_4$$

$$\underset{\text{blue}}{Cu^{2+}(aq)} + 4NH_3(aq) \rightleftharpoons \underset{\text{deep blue}}{[Cu(NH_3)_4]^{2+}(aq)}$$

$$\underset{\text{colourless}}{Ag^+(aq)} + Cl^-(aq) \longrightarrow \underset{\text{white ppt.}}{AgCl(s)}$$

$$\underset{\text{white ppt.}}{AgCl(s)} + 2NH_3(aq) \longrightarrow \underset{\text{colourless}}{[Ag(NH_3)_2]Cl(aq)}$$

(v) NH_3 is used in refrigeration due to its large heat of evaporation and in manufacture of HNO_3, $NaHCO_3$, ammonium compounds and nitrogenous fertilisers.

Nitric acid, HNO_3

(i) It was earlier known as aqua fortis. It is prepared by the following processes.

Laboratory preparation,

$$NaNO_3(s) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + HNO_3(aq)$$

Ostwald process

$$4NH_3(g) + 5O_2(g) \xrightarrow[\text{1100 K}]{\text{Pt gauge}} 4NO(g) + 6H_2O(l)\ ; \quad \Delta H = -\text{ve}$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

$$4NO_2(g) + O_2(g) + 2H_2O(l) \longrightarrow 4HNO_3(aq)$$

(ii) Anhydrous HNO_3 is a colourless fuming punget smelling liquid. It acquires yellow colour due to its decomposition.

$$4HNO_3 \xrightarrow{\text{Sunlight}} 4NO_2 + 2H_2O + O_2$$

(iii) It has corrosive action on skin and causes painful sores.

(iv) It is very strong acid and form salts on reaction with basic oxides, carbonates, hydroxides etc.

$$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$$

(v) It acts as a strong oxidising agent.

Oxidising Properties

(i) Non-metals such as C, S, P and I_2 are oxidised to carbonic acid, sulphuric acid, orthophosphoric acid and iodic acid respectively. *e.g.*,

$$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + H_2O$$
$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

(ii) Metalloids such as Sb is oxidised to antimonic acid, As to arsenic acid and Sn to stannic acid.

$$Sb + 5HNO_3 \longrightarrow H_3SbO_4 + 5NO_2 + H_2O$$
$$As + 5HNO_3 \longrightarrow H_3AsO_4 + 5NO_2 + H_2O$$
$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

(iii) Oxidation of compounds

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

NO is absorbed by $FeSO_4$ and a dark brown ring of nitroso-ferrous sulphate is formed **(ring test for nitrates)**.

(iv) $C_{12}H_{22}O_{11} + 36HNO_3 \longrightarrow \underset{\text{oxalic acid}}{6(COOH)_2} + 36NO_2 + 23H_2O$

(v) Metals like iron, cobalt, nickel, chromium, aluminium become passive in conc HNO_3 due to the formation of a thin protective film of oxide on the surface of the metal.

(vi) HNO_3 is used in the manufacture of explosives such as TNT, picric acid, nitroglycerine, dynamite etc, fertilisers, such as NH_4NO_3, basic $Ca(NO_3)_2$ etc, artificial silk, dyes, drugs.

Oxides of Nitrogen

(i) $NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + H_2O$

$N_2O(g)$ is neutral, colourless gas, with *sp* hybridisation and linear geometry **(It is also called laughing gas)**.

(ii) $2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$

NO(*g*) is colourless, neutral gas. NO(*g*) also contains odd number of electrons (paramagnetic) but in solid or liquid state NO exists in dimeric form and have paired electrons (diamagnetic). It is very reactive and harmful to health.

(iii) $2NO + N_2O_4 \xrightarrow{250\text{ K}} 2N_2O_3$

N_2O_3 is blue solid. It is acidic and planar with sp^2 hybridisation.

(iv) $2Pb(NO_3)_2 \xrightarrow{673\text{ K}} 4NO_2 + 2PbO$

$NO_2(g)$ is brown, acidic gas with angular shape and sp^2 hybridisation. NO_2 contains odd number of valence electrons (paramagnetic). On dimerisation, it gets converted to stable N_2O_4 molecule with even number of electrons (diamagnetic).

(v) $2NO_2 \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4$

N_2O_4 is colourless solid/liquid. It is acidic with planar geometry and sp^2 hybridisation. Its covalency is four (total number of bonds with central atom).

(vi) $4HNO_3 + P_4O_{10} \longrightarrow 4HNO_3 + 2N_2O_5$

N_2O_5 is colourless, acidic solid with planar shape and sp^2 hybridisation and four covalency.

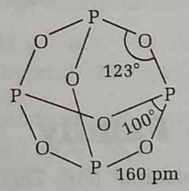
Oxides of Phosphorus

Phosphorus trioxide and phosphorus pentoxide are the two oxides of phosphorus. Oxides of phosphorus exist in dimeric forms.

(i) **Phosphorus trioxide,** P_4O_6 is prepared from white phosphorus.

$$P_4 + 3O_2 \xrightarrow[\text{(limited supply of air)}]{\text{Burning}} P_4O_6$$

- It is a poisonous waxy solid with garlic odour.
- $4P_4O_6 \xrightarrow{\text{Heat}} \underset{\text{phosphorus tetroxide}}{3P_4O_8} + 4P$
- $P_4O_6 + 4Cl_2 \longrightarrow \underset{\text{phosphorus oxychloride}}{2POCl_3} + \underset{\text{meta phosphorus oxychloride}}{2PO_2Cl}$
- $P_4O_6 + 6H_2O(\text{hot}) \longrightarrow 3H_3PO_4 + PH_3$
- Structure



(ii) **Phosphorus pentoxide,** P_4O_{10} is obtained by burning of white phosphorus in free supply of air.

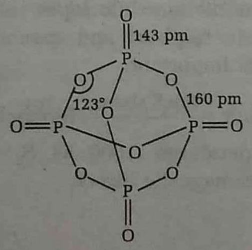
$$P_4 + 5O_2 \xrightarrow[\text{(free supply of air)}]{\text{Burning}} P_4O_{10}$$

- It is white crystalline, odourless solid which sublimes on heating.

$$P_4O_{10} \xrightarrow{2H_2O} \underset{\substack{\text{metaphosphoric}\\\text{acid}}}{4HPO_3} \xrightarrow{2H_2O} 2H_4P_2O_7$$

$$\underset{\substack{\text{pyrophosphoric}\\\text{acid}}}{2H_4P_2O_7} \xrightarrow{2H_2O} \underset{\substack{\text{orthophosphoric}\\\text{acid}}}{4H_3PO_4}$$

- It is used as most effective dehydrating agent below 100°C.
- Structure



Phosphine (PH_3)

(i) It is prepared by following methods.

- $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$
- $Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$
- $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$
- $PH_4I + KOH \longrightarrow KI + H_2O + PH_3$

(ii) It is a colourless gas with rotten fish like smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.

(iii) It forms phosphides when passed through the solutions of $CuSO_4$, $AgNO_3$ or $HgCl_2$.

- $3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$
- $3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$

(iv) Phosphine is weakly basic $PH_3 + HBr \rightarrow PH_4^+Br^-$.

Phosphorus Halides (PCl_3 and PCl_5)

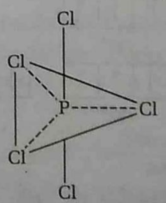
(i) Following methods are used to prepare phosphorus halides.

- $P_4 + 6Cl_2 \longrightarrow 4PCl_3$
- $P_4 + 10Cl_2 \longrightarrow 4PCl_5$
- $P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$
- $P_4 + 10\,SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$

(ii) PCl_5 is a yellowish white powder and in moist air it gets hydrolysed to $POCl_3$ and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$
$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$

(iii) PCl_5 in gaseous and liquid phases has sp^3d hybridisation and its shape is trigonal bipyramidal.



The three equatorial P—Cl bonds are equivalent while the two axial bonds are longer than equatorial bonds.

(iv) In solid state, PCl_5 exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which, the cation, $[PCl_4]^+$ is tetrahedral and the anion $[PCl_6]^-$ is octahedral.

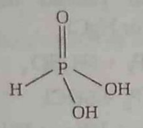
Oxoacids of Phosphorus and Nitrogen

$H_2N_2C_2$ (hyponitrous acid); HNO_2 (nitrous acid) and HNO_3 (nitric acid) are the oxoacids of nitrogen. Out of these HNO_3 is the most important. HNO_2 (conc) is strong oxidising agent e.g.,

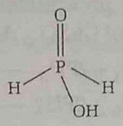
$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$P_4 + 20HNO_3\ (\text{conc.}) \longrightarrow 4H_3PO_3 + 20NO_2 + 4H_2O$$

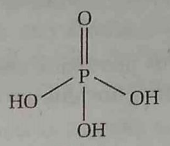
The structure of oxoacids of phosphorus are given below :



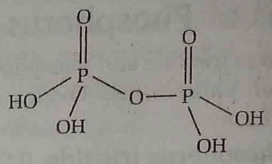
H_3PO_3
(orthophosphorous acid)
sp^3, diprotic



H_3PO_2
(hypophosphorous acid)
monoprotic, sp^3



H_3PO_4
(orthophosphoric acid)
triprotic, sp^3



$H_4P_2O_7$
(pyrophosphoric acid)
sp^3

Pyrophosphorous acid $= H_4P_2O_5$

Hypophosphoric acid $= H_4P_2O_6$

- H_3PO_3 on heating, disproportionates to give orthophosphoric acid and phosphine.

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

- The acids which contain P—H bond, have strong reducing properties, thus hypophosphorous acid is a good reducing agent as it contains two P—H bonds. *e.g.,*

$$4\,AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4\,Ag + 4HNO_3 + H_3PO_4$$

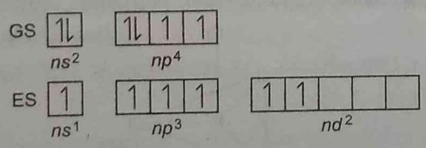
Group-16 Elements : Oxygen Family

16th group elements are sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). This is sometimes known as group of ***chalcogens*** *(due to ore forming nature). Oxygen is the most abundant of all the elements on earth. Oxygen and sulphur are non-metals, selenium and tellurium are metalloids and polonium is radioactive metal.*

Important Properties

The group 16 elements exihibit the properties may be given as

General Configuration ns^2np^4



Oxidation States

Oxidation states exhibited by 16th group elements are −2, +2, +4, +6 but +4 and +6 are more common. On moving down the group stability of +6 oxidation state decreases and that of +4 oxidation state increases due to inert pair effect. The oxidation state of O is −1 and $-\frac{1}{2}$ in peroxides and superoxides respectively.

In case of OF_2, O_2F_2, oxidation states of oxygen are +2, +1 respectively.

$p\pi$-$p\pi$ Multiple Bonding

Oxygen has a tendency to form $p\pi$-$p\pi$ multiple bond (O═O) due to absence of *d*-orbitals and high bond dissociation enthalpy.

Sulphur has tendency to form single bond due to presence of *d*-orbitals and exist in polyatomic (S_8) form.

Allotropy

Oxygen exists in two molecular allotropic forms; the diatomic molecule, O_2 (most stable) and the triatomic molecule, O_3 (ozone comparatively less stable).

Sulphur forms numerous allotropes, out of which the yellow rhombic (α-sulphur) and monoclinic (β-sulphur) forms are the most important.

$$\text{Rhombic sulphur} \xrightarrow{\text{369 K above}} \text{Monoclinic sulphur}$$

At elevated temperatures (1000 K), S_2 is the dominant species and is paramagnetic like O_2.

Hydrides

Down the group acidic character increases from H_2O to H_2Se. All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te.

Oxides

All these elements (except O_2) form MO_2 type oxides. SO_2 is gas while SeO_2 is solid. Reducing property of dioxide decreases from SO_2 to TeO_2. SO_2 is reducing while TeO_2 is an oxidising agent.

Halides

The stability of the halides decreases in the order $F^- > Cl^- > Br^- > I^-$

Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. SF_6 is exceptionally stable for steric reasons.

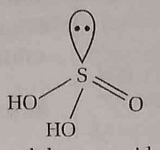
SF_4 is a gas, SeF_4 is a liquid and TeF_4 is a solid. These fluorides have sp^3d hybridisation and see-saw geometry.

The well known mono halides are dimeric in nature. Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below

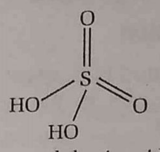
$$2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$$

Oxoacids

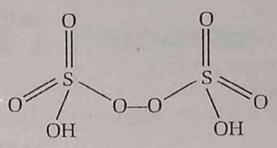
The structures of oxoacids of sulphur are as follows



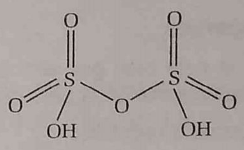
sulphurous acid
(H_2SO_3)



sulphuric acid
(H_2SO_4)



peroxodisulphuric acid
($H_2S_2O_8$)



pyrosulphuric acid (oleum)
($H_2S_2O_7$)

Group-16 : Some Important Compounds

Some of the important compounds considered under group 16 are given below

Dioxygen

Preparation

(i) **Laboratory method**

$$2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$$

(ii) It is manufactured from liquid air. Air is liquefied by making use of Joule Thomson effect. Liquid air is a mixture of liquid nitrogen and liquid oxygen.
The difference in their boiling points is about 12.8°C, hence they are easily separated by fractional evaporation.

(iii) **By electrolysis of water** (acidified water)

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

At cathode

$$2H^+ + 2e^- \longrightarrow H_2$$

At anode $$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$$

Properties

(i) colourless, odourless, tasteless gas which is slightly soluble in water. Liquid oxygen exhibits paramagnetism.

(ii) It is non-inflammable but a supporter of combustion.

(iii) O=O bond dissociation energy is high, therefore it reacts with metals or non-metals after external heating to start the reaction.

$$N_2 + O_2 \xrightarrow{3300\text{ K}} 2NO$$

$$4Na(s) + O_2(g) \xrightarrow{\text{Room temperature}} 2Na_2O(s)$$

$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$$

Uses

(i) In oxyacetylene and oxyhydrogen flames.

(ii) Liquid O_2 is used as a rocket fuel.

(iii) For life support systems, *e.g.*, in hospitals and in water diving for divers, for miners and mountaineers.

(iv) As an oxidising and bleaching agent.

Ozone

It is formed in the upper layer of atmosphere by the action of UV rays from sun on oxygen. It prevents the UV rays from entering the earth's atmosphere. CFCs, common refrigerants deplete the ozone layer.

Preparation

It is prepared in ozoniser by subjecting dry and cold dioxygen to the action of silent electric discharge.

$$3O_2(g) \xrightleftharpoons{\text{Silent electric discharge}} 2\,O_3(g)$$

Properties

- It is pale blue gas with pungent odour. It is diamagnetic and poisonous.
- Ozone is unstable;

$$2O_3 \xrightarrow{\text{Heat}} 3O_2$$

- It acts as a powerful oxidising agent. It liberates iodine from neutral KI solution and the liberated I_2 turns starch paper blue.

$$2\,KI + H_2O + O_3 \longrightarrow 2KOH + I_2 + O_2$$

$$I_2 + \text{starch} \longrightarrow \text{Blue colour}$$

- Alkaline KI is oxidised to potassium iodate and periodate.

$$KI + 3O_3 \longrightarrow \underset{\text{pot. iodate}}{KIO_3} + 3O_2$$

$$KI + 4\,O_3 \longrightarrow \underset{\text{pot. periodate}}{KIO_4} + 4\,O_2$$

- $H_2S + O_3 \longrightarrow H_2O + S + O_2$
- Mercury loses its meniscus in contact with ozone (tailing of mercury).

$$2\,Hg + O_3 \longrightarrow Hg_2O + O_2$$

Uses

- As a germicide and disinfectant for sterilizing water.
- As a bleaching agent for oils, ivory wax and delicate fibre.
- For detecting the position of double bond in unsaturated compounds.
- In destroying odours coming from cold storage room, slaughter houses and kitchen of hotels.

Allotropic forms of Sulphur

It exists in several allotropic forms.

Rhombic Sulphur (α-sulphur)

It is common crystalline form of sulphur, yellow in colour. melting point 114.5°C and specific gravity 2.06. Its crystals are prepared by evaporating sulphur solution in CS_2. It is insoluble in water but readily soluble in CS_2.

Monoclinic Sulphur (β-sulphur)

It is stable above 95.6°C. Its crystals are amber yellow in colour, m.pt 119°C, specific gravity 1.98. It is insoluble in CS_2. It is prepared by melting rhombic sulphur in a dish followed by cooling till crust is formed.

$$\text{Rhombic sulphur} \xrightleftharpoons{95.6^\circ\text{C}} \text{Monoclinic sulphur.}$$

At 95.6°C both the form are stable. This temperature is called **transition temperature.** S_8 rings in both the forms is puckered and has a crown shape.

Plastic Sulphur

It is obtained by pouring boiling sulphur into cold water. It is amber brown in colour, specific gravity 1.95 and insoluble in CS_2.

Milk of Sulphur

It is obtained by boiling milk of lime with sulphur and decomposing the products formed with HCl. It is used in medicines.

Colloidal Sulphur

It is prepared by passing H_2S through a solution of an oxidising agent such as nitric acid etc.

$$2HNO_3 + H_2S \longrightarrow 2NO_2 + 2H_2O + S$$

colloidal sulphur changes into ordinary form on heating.

Sulphuric Acid (H_2SO_4)

Preparation

Sulphuric acid is one of the most important industrial chemicals world wide. It is manufactured by **contact process** which involves three steps

- Burning of sulphur ores in air to generate SO_2.
- Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5).

$$2\,SO_2(g) + O_2(g) \xrightarrow[\text{2 bar, 720 K}]{V_2O_5} 2\,SO_3\,(g)$$

- Absorption of SO_3 in H_2SO_4 to give oleum ($H_2S_2O_7$)
  $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$ oleum

Properties

- Concentrated sulphuric acid is a strong dehydrating agent.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

- Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids.

$$S + 2H_2SO_4\,(\text{conc.}) \longrightarrow 3SO_2(g) + 2H_2O$$

$$C + 2H_2SO_4(\text{conc.}) \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

Uses

(i) In the manufacture of fertilisers
(ii) Petroleum refining
(iii) In manufacture of pigments, paints and dyestuff.
(iv) Detergent industry
(v) Metallurgical application
(vi) Storage batteries
(vii) As a laboratory reagent

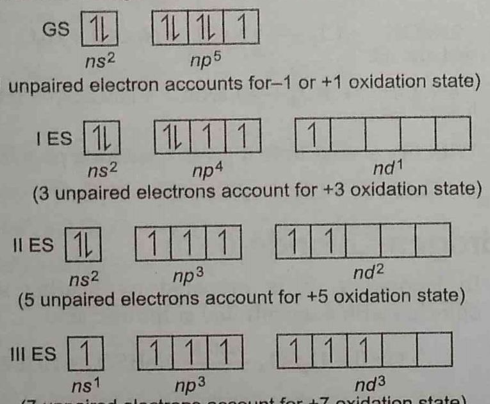
H_2SO_3 acts as bleaching agent but it is temporary and the bleached material regains its colour due to oxidation.

Group-17 Elements : Halogens

Group 17 members are fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Astatine is a radioactive element. The halogens are highly reactive non-metallic elements. Fluorine is most electronegative atom and strong oxidising agent.

Important Properties

Electronic configuration and oxidation state



(1 unpaired electron accounts for –1 or +1 oxidation state)

(3 unpaired electrons account for +3 oxidation state)

(5 unpaired electrons account for +5 oxidation state)

(7 unpaired electrons account for +7 oxidation state)

Ground state and excited state in fluorine will be same due to absence of *d*-orbitals and oxidation state of fluorine is always –1.

All the halogens are highly reactive. Halogens are strong oxidising agent and their oxidising power decreases down the group.

$$F_2 > O_2 > Cl_2 > Br_2 > I_2$$

Oxidising power decreases

e.g., $F_2 + 2X^- \longrightarrow 2F^- + X_2 \quad (X = \text{Cl, Br and I})$

$$2F_2(g) + 2H_2O(l) \longrightarrow 4HF(aq) + O_2(g)$$

$$X_2(g) + H_2O(l) \longrightarrow HX(aq) + HOX(aq)$$

(where, X = Cl or Br)

The reaction of I_2 with water is non-spontaneous. However, I^- can be oxidised by oxygen in acidic medium.

$$4I^-(aq) + 4H^+(aq) + O_2(g) \longrightarrow 2I_2(s) + 2H_2O(l)$$

Bond Dissociation Enthalpy

- The order of bond dissociation enthalpy is
  $Cl{-}F > Cl_2 > Br_2 > F_2 > I_2$
- Fluorine shows anomalous behaviour because of its very small size and high electronegativity. F_2 has less bond enthalpy than Cl_2 and Br_2 and absence of *d*-orbitals in valence shell.

Hydrides

Down the group, their acidic character increases and bond dissociation enthalpy decreases.

HI > HBr > HCl > HF

Acidic character decreases

HF is a liquid while rest of hydrogen halides are gases. It reacts with glass, so it is stored in waxed glass bottles. This property of HF to act on glass is utilised in etching of glass.

Oxides

Fluorine forms two oxides, OF_2 and O_2F_2, but only OF_2 is thermally stable at 298 K. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used for removing plutonium as PuF_6 from spent nuclear fuel.

(i) Chlorine forms a number of oxides such as, Cl_2O, Cl_2O_3, Cl_2O_5, Cl_2O_7, ClO_2. ClO_2 is used as a bleaching agent for paper pulp, textiles and in water treatment.

(ii) Br_2O, BrO_2, BrO_3 are the least stable bromine oxides and exist only at low temperatures. They are very powerful oxidising agents.

(iii) The iodine oxides, *i.e.*, I_2O_4, I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

Oxoacids of Halogens

Higher oxoacids of fluorine such as HFO_2, HFO_3 do not exist because fluorine is most electronegative and has absence of *d*-orbitals. +3 oxidation state of bromine and iodine are unstable due to inert pair effect, therefore $HBrO_2$ and HIO_2 do not exist.

Decreasing order of acidic nature

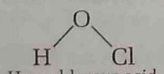
$$\underset{\text{(hypofluorous acid)}}{HOF} > \underset{\text{(hypochlorous acid)}}{HOCl} > \underset{\text{(hypobromous acid)}}{HOBr} > \underset{\text{(hypoiodous acid)}}{HOI}$$

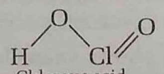
$$\longrightarrow \underset{\text{(chloric acid)}}{HOClO_2} > \underset{\text{(bromic acid)}}{HOBrO_2} > \underset{\text{(iodic acid)}}{HOIO_2}$$

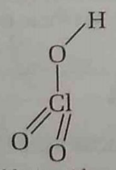
$$\longrightarrow HOClO_3 > HOClO_2 > HOClO > HOCl$$

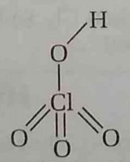
$$\longrightarrow HClO_4 > HBrO_4 > HIO_4$$

Structures of Oxoacids of Chlorine


Hypochlorous acid


Chlorous acid


Chloric acid


Perchloric acid

Pseudo halide ions are stronger ligands than halide ions and these can function as ambidentate ligands as they are made up of two hetero atoms.

Interhalogen Compounds

- When two different halogens react with each other, interhalogen compounds are formed. These compounds are covalent and diamagnetic in nature. They are volatile solids or liquids except ClF which is a gas at 298 K. Interhalogen compounds are more reactive than halogens (except fluorine).
- The XY_3 type compounds have bent 'T' shape, XY_5 type compounds have square pyramidal shape and IF_7 has pentagonal bipyramidal structure.

Chlorine (Cl_2)

Preparation

(i) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$ (Lab. Method)

(ii) $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$ (Deacon's process)

(iii) Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode (electrolytic process). It is also obtained as a by-product in many chemical industries.

Properties

(i) It is a greenish yellow gas with pungent and suffocating odour. It is soluble in water.

(ii) $8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$

(iii) $NH_3 + \underset{\text{excess}}{3Cl_2} \longrightarrow \underset{\text{explosive}}{NCl_3} + 3HCl$

(iv) $\underset{\text{cold and dil.}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$

(v) $\underset{\text{hot and conc.}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

(vi) With dry slaked lime it gives bleaching powder.

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

Hydrogen Chloride (HCl)

(i) In laboratory, it is prepared by heating sodium chloride with concentrated sulphuric acid.

$$NaCl + H_2SO_4 \xrightarrow{420\ K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823\ K} Na_2SO_4 + HCl$$

HCl gas can be dried by passing through concentrated sulphuric acid.

(ii) It is a colourless and pungent smelling gas. Its aqueous solution is caled hydrochloric acid.

(iii) When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua-regia is formed which is used for dissolving noble metals. *e.g.*, gold, platinum.

Group-18 Elements : Noble Gases

Elements of 18 group are helium (He), *neon* (Ne), *argon* (Ar), *krypton* (Kr), *xenon* (Xe) *and radon* (Rn) *(radioactive). All of these are gases and chemically unreactive. Down the group their ionisation enthalpy decreases, therefore* Xe *reacts with oxygen and fluorine and forms different compounds. Xenon and radon are the rarest elements of the group.*

First prepared noble gas compound by Neil Bartlett in 1962 is $XePtF_6$.

Occurrence

On account of their inert nature, the noble gases always occur in the free state. Argon is the most abundant noble gas in the atmosphre while radon is not present in atmosphere. He, Ar and Ne are also found as constituents of dissolved gas of certain spring waters.

Important Properties

General configuration ns^2np^6 (except helium)

Preparation and Properties of Some Compounds

- $\underset{\text{(Xe in excess)}}{Xe(g)} + F_2(g) \xrightarrow{673\text{ K, 1 bar}} XeF_2(s)$
- $\underset{\text{(1 : 5 ratio)}}{Xe(g) + 2F_2(g)} \xrightarrow{873\text{K, 7 bar}} XeF_4(s)$
- $Xe(g) + 3F_2(g) \xrightarrow{573\text{ K, 60-70 bar}} XeF_6(s)$
- $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$
- $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24\,HF + 3O_2$
- $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$
- Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.
- XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K. They are powerful fluorinating agents.
- XeF_6 is extremely reactive. It cannot be stored in glass or quartz vessels as it readily reacts with SiO_2 present in glass.
- XeO_3 is a colourless, explosive solid and has a pyramidal shape. $XeOF_4$ is a colourless, volatile liquid and has a square pyramidal shape. XeF_2 is linear and XeF_4 is square planar. XeF_6 has a distorted octahedral shape.

Uses

(i) He is used in filling balloons for meteorological observations. It is used in gas cooled reactor, to produce powerful superconducting magnets and as a diluent for oxygen in diving apparatus.

(ii) Ne is used in discharge tubes and fluorescent bulbs.

(iii) Ar is used in filling bulbs and to produce inert atmosphere in various metallurgical operations.

Practice Zone

DAY 22

1. When concentrated HNO_3 is heated with P_2O_5, it forms

(a) N_2O (b) NO (c) NO_2 (d) N_2O_5

2. A hydride of nitrogen which is acidic, is

(a) NH_3 (b) N_2H_4
(c) N_2H_2 (d) N_3H

3. Carborundum is obtained when silica is heated at high temperature with

(a) carbon (b) carbon monoxide
(c) carbon dioxide (d) calcium carbonate

4. Boric acid is called acid because its molecule

(a) contains replaceable H^+ion
(b) gives up a proton
(c) accepts OH^- from water releasing proton
(d) combines with proton from water molecule

5. Extra pure N_2 can be obtained by heating

(a) NH_3 with CuO (b) NH_4NO_3
(c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$

6. Which of the following is a component of ruby?

(a) $CaCO_3$ (b) $MgCO_3$
(c) Al_2O_3 (d) $Al(OH)_3$

7. Red lead is

(a) PbO (b) Pb_3O_4
(c) PbO_2 (d) Pb_4O_3

8. When orthoboric acid (H_3BO_3) is heated, the residue is

(a) boron (b) metaboric acid
(c) boric anhydride (d) borax

9. Which of the following halides is least stable and has doubtful existence?

(a) CI_4 (b) GeI_4 (c) SnI_4 (d) PbI_4

10. The shape of gaseous $SnCl_2$ is

(a) tetrahedral (b) linear
(c) angular (d) T-shaped

11. Mark the oxide which is amphoteric in character.

(a) CO_2 (b) SiO_2 (c) SnO_2 (d) CaO

12. Which of the following is most stable?

(a) Sn^{2+} (b) Ge^{2+} (c) Si^{2+} (d) Pb^{2+}

13. The number of σ bonds in P_4O_{10} is

(a) 6 (b) 16 (c) 20 (d) 7

14. PH_3, the hydride of phosphorus is

(a) metallic
(b) ionic
(c) non-metallic
(d) covalent

15. Of the following compounds, the most acidic is

(a) As_2O_3 (b) P_2O_5
(c) Sb_2O_3 (d) Bi_2O_3

16. Graphite is a soft, solid lubricant, extremely difficult to melt. The reason for this anomalous behaviour is that graphite

(a) is an allotropic form of diamond
(b) has molecules of variable molecular masses like polymers
(c) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds
(d) is a non-crystalline substance

17. Among the following, the number of compounds that can react with PCl_5 to give $POCl_3$ is

O_2, CO_2, SO_2, H_2O H_2SO_4, P_4O_{10}.

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

18. Which one of the following compounds has the smallest bond angle in its molecule?

(a) OH_2 (b) SH_2
(c) NH_3 (d) SO_2

19. H_3BO_3 is

(a) monobasic and weak Lewis acid
(b) monobasic and weak Bronsted acid
(c) monobasic and strong Lewis acid
(d) tribasic and weak Bronsted acid

20. The mixture of conc HCl and HNO_3 made 3 : 1 ratio contains

(a) ClO_2 (b) NOCl
(c) NCl_3 (d) N_2O_4

21. Which is not a mineral of aluminium?

(a) Anhydrite (b) Bauxite
(c) Corundum (d) Diaspore

22. When conc. H_2SO_4 is heated with P_2O_5, the acid is converted to

(a) sulphur trioxide
(b) sulphur dioxide
(c) sulphur
(d) a mixture of sulphur dioxide and sulphur trioxide

23. For making good quality mirrors, plates of flint glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be

(a) tin (b) sodium
(c) magnesium (d) mercury

24. Nitrogen shows different oxidation states in the range

(a) 0 to +5 (b) –3 to +5 (c) –5 to +3 (d) –3 to+3

25. Which of the following acids possesses oxidising, reducing and complex forming properties?

(a) HCl (b) HNO_2 (c) H_2SO_4 (d) HNO_3

26. Strong reducing behaviour of H_3PO_2 is due to : **[NCERT Exemplar]**

(a) Low oxidation state of phosphorus
(b) presence of two-OH groups & one P-H band
(c) Presence of one-OH group & two P-H bands
(d) high electron gain enthalpy of phosphoreus

27. Carbogen is

(a) mixture of $O_2 + 5-10\ \%\ CO_2$
(b) used by pneumonia patient for respiration
(c) used by victims of CO poisoning for respiration
(d) All of the above

Directions (Q. Nos. 28 to 30) *The noble gases have closed shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.*

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6. XeF_4 reacts violently with water to give XeO_3. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell.

28. Argon is used in arc welding because of its

(a) low reactivity with metal
(b) ability to lower the melting point of metal
(c) flammability
(d) high calorific value

29. The structure of XeO_3 is

(a) linear (b) planar
(c) pyramidal (d) T-shaped

30. XeF_4 and XeF_6 are expected to be

(a) oxidising (b) reducing
(c) unreactive (d) strongly basic

Directions (Q. Nos. 31 to 33) *There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridisation easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorus.*

31. Among the following, the correct statement is

(a) phosphates have no biological significance in humans
(b) between nitrates and phosphates, nitrates are less abundant in earth's crust
(c) between nitrates and phosphates, phosphates are less abundant in earth's crust
(d) oxidation of nitrates is possible in soil

32. Among the following, the correct statement is

(a) between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies spherical '*s*' orbital and is less directional
(b) between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(c) between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(d) between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies spherical '*s*' orbital and is less directional

33. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a

(a) dimerisation reaction
(b) disproportionation reaction
(c) condensation reaction
(d) precipitation reaction

Directions (Q. Nos. 34 to 38) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I
(c) Statement I is true; Statement II is false
(d) Statement I is false; Statement II is true

34. Statement I Between $SiCl_4$ and CCl_4, only $SiCl_4$ reacts with water.

Statement II $SiCl_4$ is ionic and CCl_4 is covalent.

35. Statement I Boron always forms covalent bond.

Statement II The small size of B^{3+} favours formation of covalent bond.

36. Statement I In water, orthoboric acid behaves as a weak monobasic acid.

Statement II In water, orthoboric acid acts as a proton donor.

37. Statement I Pb^{4+} compounds are stronger oxidising agents than Sn^{4+} compounds.

Statement II The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to inert pair effect.

38. Statement I Although PF_5, PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed.

Statement II Phosphorus has lower electronegativity than nitrogen.

39. When sulphuric acid reacts with hot solution of copper, how does the oxidation number of sulphur change?

(a) From + 4 to + 6
(b) From + 6 to + 4
(c) From + 6 to + 8
(d) From + 8 to + 6

40. An inorganic compound '*X*', made of two most occurring elements in the earth's crust and used in building construction, when reacts with carbon, forms a diatomic molecule, which is poisonous in nature. Compound '*X*' may be

(a) SiO_2
(b) Al_2O_3
(c) CaO
(d) CO_2

41. Which one of the following reactions does not occur ?

(a) $F_2 + Cl^- \longrightarrow 2F^- + Cl_2$
(b) $Cl_2 + 2F^- \longrightarrow 2Cl^- + F_2$
(c) $Br_2 + 2I^- \longrightarrow 2Br^- + I_2$
(d) $Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$

42. An inorganic compound containing (3*c*-2*e*) and (2*c*-2*e*) bonds when reacts with NH_3, at a certain temperature, gives a compound '*X*' which is isostructural with benzene and when reacts at high temperature, forms a substance '*Y*'. The substance '*Y*' is

(a) B_2H_6
(b) $B_3N_3H_6$
(c) inorganic graphite
(d) $B_2H_6 \cdot 2NH_3$

AIEEE & JEE Main *Archive*

43. The catenation tendency of C, Si and Ge is in the order Ge < Si < C. The bond energies (in kJ mol^{-1}) of C—C, Si—Si and Ge—Ge bonds are respectively **[JEE Main Online 2013]**

(a) 348, 297, 260
(b) 297, 348, 260
(c) 348, 260, 297
(d) 260, 297, 348

44. The solubility order of alkali metal fluoride in water is **[JEE Main Online 2013]**

(a) LiF < RbF < KF < NaF
(b) RbF < KF < NaF < LiF
(c) LiF > NaF > KF > RbF
(d) LiF < NaF < KF < RbF

45. Which of the following exists as covalent crystals in the solid state? **[JEE Main Online 2013]**

(a) Silicon
(b) Sulphur
(c) Phosphorus
(d) Iodine

46. Which of the following is the wrong statement? **[JEE Main Online 2013]**

(a) O_3 molecule is bent
(b) Ozone is violet black in solid state
(c) Ozone is diamagnetic gas
(d) ONCl and ONO^- are not isoelectronic

47. The molecule having smallest bond angle is **[AIEEE 2012]**

(a) NCl_3
(b) $AsCl_3$
(c) $SbCl_3$
(d) PCl_3

48. Which of the following statements is wrong? **[AIEEE 2011]**

(a) The stability of hydrides increases from NH_3 to BiH_3 in group 15 of the Periodic Table
(b) Nitrogen can't form $d\pi$-$p\pi$ bond
(c) Single N—N bond is weaker than the single P—P bond
(d) N_2O_4 has two resonance structures

49. Which of the following statements regarding sulphur is incorrect? **[AIEEE 2011]**

(a) S_2 molecule is paramagnetic
(b) The vapour at 200°C consists mostly of S_8 rings
(c) At 600°C the gas mainly consists of S_2 molecules
(d) The oxidation state of sulphur is never less than + 4 in its compounds

50. Boron cannot form which one of the following anions? **[AIEEE 2011]**

(a) BF_6^{8-}
(b) BH_4^-
(c) $B(OH)_4^-$
(d) BO_2^-

51. In which of the following arrangements, the sequence is not strictly according to the property written against it? **[AIEEE 2009]**

(a) $CO_2 < SiO_2 < SnO_2 < PbO_2$: increasing oxidising power
(b) HF < HCl < HBr < HI : increasing acid strength
(c) $NH_3 > PH_3 < AsH_3 < SbH_3$: increasing basic strength
(d) B < C < O < N : increasing first ionisation enthalpy

52. Which one of the following reaction of xenon compounds is not feasible? **[AIEEE 2009]**

(a) $XeO_3 + 6HF \longrightarrow XeF_6 + 3H_2O$

(b) $3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + 1.5\,O_2$

(c) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$

(d) $XeF_6 + RbF \longrightarrow Rb[XeF_7]$

53. Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis, is **[AIEEE 2008]**

(a) R_3SiCl (b) R_4Si (c) $RSiCl_3$ (d) R_2SiCl_2

54. Aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 gives **[IIT JEE 2008]**

(a) $Na_2S_4O_6$ (b) $NaHSO_4$ (c) NaCl (d) NaOH

55. Identify the incorrect statement among the following. **[AIEEE 2007]**

(a) Ozone reacts with SO_2 to give SO_3.

(b) Silicon reacts with NaOH (*aq*) in the presence of air to give Na_2SiO_3 and H_2O.

(c) Cl_2 reacts with excess of NH_3 to give N_2 and NH_4Cl.

(d) Br_2 reacts with hot and strong NaOH solution to give NaBr, $NaBrO_4$ and H_2O.

56. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4)] + H_2O$

How can this reaction is made to proceed in forward direction? **[IIT JEE 2006]**

(a) Addition of *cis* 1, 2-diol (b) Addition of borax

(c) Addition of *trans* 1, 2-diol (d) Addition of Na_2HPO_4

57. Which of the following statements is true? **[AIEEE 2006]**

(a) H_3PO_3 is a stronger acid than H_2SO_3

(b) In aqueous medium, HF is a stronger acid than HCl

(c) $HClO_4$ is weaker acid than $HClO_3$

(d) HNO_3 is a stronger acid than HNO_2

58. Name of the structure of silicates in which three oxygen atoms of $[SiO_4]^{4-}$ are shared, is **[IIT JEE 2005]**

(a) pyrosilicate (b) sheet silicate

(c) linear chain silicate (d) three dimensional silicate

59. Heating of an aqueous solution of aluminium chloride to dryness will give **[AIEEE 2005]**

(a) $Al(OH)Cl_2$ (b) Al_2O_3 (c) Al_2Cl_6 (d) $AlCl_3$

60. When I^- is oxidised by MnO_4^- in alkaline medium, I^- converts into **[IIT JEE 2004]**

(a) IO_3^- (b) I_2 (c) IO_4^- (d) IO^-

61. In curing cement plasters water is sprinkled from time to time. This helps in **[AIEEE 2003]**

(a) keeping it cool

(b) developing interlocking needle like crystals of hydrated silicates

(c) hydrating sand and gravel mixed with cement

(d) converting sand into silicic acid

62. The number of S–S bonds in sulphur trioxide trimer (S_3O_9) is **[IIT JEE 2001]**

(a) three (b) two (c) one (d) zero

Answers

1. (d)	**2.** (d)	**3.** (a)	**4.** (c)	**5.** (d)	**6.** (c)	**7.** (b)	**8.** (c)	**9.** (d)	**10.** (c)
11. (c)	**12.** (d)	**13.** (b)	**14.** (d)	**15.** (b)	**16.** (c)	**17.** (d)	**18.** (b)	**19.** (a)	**20.** (b)
21. (a)	**22.** (a)	**23.** (a)	**24.** (b)	**25.** (b)	**26.** (c)	**27.** (d)	**28.** (a)	**29.** (c)	**30.** (a)
31. (b)	**32.** (c)	**33.** (b)	**34.** (c)	**35.** (a)	**36.** (c)	**37.** (c)	**38.** (b)	**39.** (b)	**40.** (a)
41. (b)	**42.** (c)	**43.** (a)	**44.** (d)	**45.** (c)	**46.** (a)	**47.** (c)	**48.** (a)	**49.** (d)	**50.** (a)
51. (c)	**52.** (a)	**53.** (c)	**54.** (b)	**55.** (d)	**56.** (a)	**57.** (d)	**58.** (b)	**59.** (b)	**60.** (a)
61. (b)	**62.** (d)								

Hints & Solutions

1. $4HNO_3 + 2P_2O_5 \xrightarrow{\Delta} 2N_2O_5 + 4HPO_3$

2. $[N \equiv N^+ - N^-]^- \longrightarrow [N^- - N^+ \equiv N]^-$

3. $SiO_2 + 3\,C \xrightarrow[\text{2300 K}]{\text{High temp.}} \underset{\text{carborundum}}{SiC} + 2CO$

4. Due to the small size of boron atom and presence of six electrons. Boric acid accepts a pair of electron from OH^- ion of H_2O thereby releasing a proton.

5. $Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba(s) + 3N_2(g)$

Azide salt of barium can be obtained in purest form as well as the decomposition product contain solid Ba as by-product along with gaseous nitrogen.

6. Al_2O_3 is a component of ruby $(Al_2O_3 + Cr_2O_3)$, red precious stone.

7. Pb_3O_4 or $PbO_2 \cdot 2PbO$ is called red lead.

8. $\underset{\text{orthoboric acid}}{H_3BO_3} \xrightarrow[\text{above 370 K}]{\Delta} \underset{\text{metaboric acid}}{HBO} \xrightarrow{\Delta} \underset{\text{boric anhydride}}{B_2O_3}$

9. Pb^{4+} will readily oxidise iodide and itself will get reduced to Pb^{2+}. Thus, PbI_2 will be formed, $PbI_4 \longrightarrow PbI_2 + I_2$

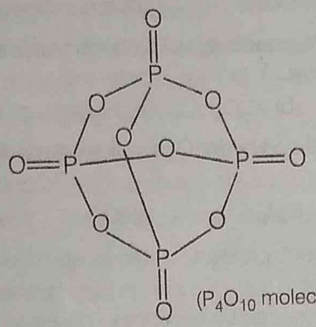
10. Gaseous $SnCl_2$ is angular with sp^2 hybridisation, bond angle being 119° due to presence of one lone pair of electrons on Sn.

11. SnO_2 is amphoteric. It dissolves in acids as well as in alkalies. *e.g.*,

$$SnO_2 + 2H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2H_2O$$
$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$$

12. Due to inert pair effect, Pb^{2+} is most stable.

13. The number of σ bonds in P_4O_{10} is 16. There are also four π-bonds present in P_4O_{10} molecule.



(P_4O_{10} molecule)

14. PH_3 is a covalent hydride.

15. Pentoxides are more acidic than trioxides and their acidic character decreases down the group from N to Bi.

16. Graphite has carbon atoms arranged in large hexagonal layers with weak van der Waals' interactions between the layers.

17. PCl_5 produces $POCl_3$ with the following reagents.

$$2\,PCl_5 + SO_2 \longrightarrow POCl_3 + SOCl_2$$
$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$
$$2PCl_5 + H_2SO_4 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$
$$6PCl_5 + P_4O_{10} \longrightarrow 10POCl_3$$

18. Bond angles are OH_2 (104°), H_2S (92°), NH_3 (107°) and SO_2 (119.5°).

19. H_3BO_3 is a monobasic weak Lewis acid.

20. $3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2[Cl]$

21. Anhydrite, anhydrous $CaSO_4$ is not a mineral of Al.

22. When conc H_2SO_4 is heated with P_2O_5, the acid is converted into sulphur trioxide.

$$2H_2SO_4 + 2P_2O_5 \longrightarrow 2SO_3 + 4HPO_3$$

23. Melting point of tin is lower than glass.

24. Nitrogen shows all the oxidation states ranging from –3 to +5 in its compounds.

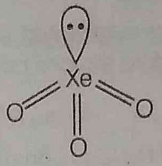
25. HNO_2 posseses oxidising, reducing and complex forming properties as in it oxidation number of nitrogen is +3 (*i.e.*, in between –3 to +5).

26. Due to the presence of one-OH group, H_3PO_2 act as reducing agent.

27. Options (a), (b) and (c) are correct.

28. Argon is used in arc welding to cause the inert atmosphere around without interaction with metal.

29. In XeO_3, total electron pairs = 4 (3*bp* + 1*lp*), *i.e.*, sp^3 hybridisation ⇒ pyramidal shape.



30. XeF_4 oxidises potassium iodide.

$$XeF_4 + 4I^- \longrightarrow 2I_2 + 4F^- + Xe$$

XeF_6 oxidises hydrogen like other xenon fluorides.

31. Due to greater solubility and nature to be prone to microbial action, nitrates are less abundant in earth's crust.

32. NH_3 is better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional.

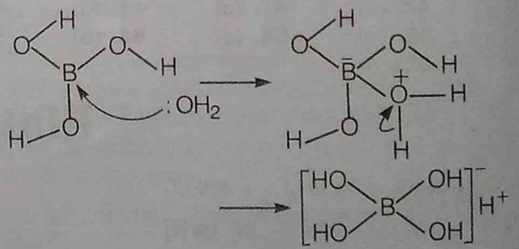
33. White phosphorus on reaction with NaOH gives PH_3 as one of the product in disproportionation reaction.

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$$

34. Statement I is correct but statement II is incorrect ($SiCl_4$ is also covalent bonded).

35. Boron always forms covalent bond because boron requires very high energy to form B^{3+} and again B^{3+} due to its very small size, have high polarising power, thus cause greater polarisation and eventually significant covalent characteristics, Fajan's rule.

36. In water, orthoboric acid behave as a weak mono basic Lewis acid.



37. In early *p*-block, on moving top to bottom, the stability of lower oxidation state increases due to inert pair effect. Pb^{4+} is less stable than Sn^{4+}, making it, a better oxidising agent. The lower oxidation state for the group 14 elements are more stable for the heavier members.

38. Due to absence of *d*-orbitals in nitrogen, it does not form pentahalides. Electronegativity of nitrogen is greater than phosphorus. Hence, statement I and statement II both are correct but statement II is not a correct explanation of statement I.

39. $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

Sulphuric acid reacts with Cu(s) to produce Cu^{2+} and SO_2.

O.S. of S in H_2SO_4

$2 \times (+1) + x + 4 \times (-2) = 0 = 6$

O.S. of S in SO_2 $x + 2 \times (-2) = 0 = 4$

40. The two most abundant elements in the earth's crust are Si and oxygen and the compound made by them is SiO_2. This compound is used in building construction.

$$SiO_2 + 2C \longrightarrow Si + \underset{\text{poisonous}}{2CO}$$

41. With progressive increase in atomic number, the reduction potential of halogens decreases, thus oxidising power also decreases. Hence, a halogen with lower atomic number will oxidise the halide ion of higher atomic number and therefore, will liberate them from their salt solution. Hence, the reaction, $Cl_2 + 2F^- \longrightarrow 2Cl^- + F_2$ is not possible.

42. B_2H_6 contains (3c-2e) and (2c-2e) bonds.

$$B_2H_6 + 2NH_3 \xrightarrow{\text{Low temp.}} B_2H_6 \cdot 2NH_3 \xrightarrow{200°C} \underset{\text{inorganic benzene}}{\underset{'X'}{B_3N_3H_6}}$$

$$B_2H_6 + NH_3 \xrightarrow{\text{High temp.}} \underset{\text{inorganic graphite}}{\underset{'Y'}{(BN)_x}}$$

43. Higher the catenation tendency, higher is the bond energy.

∴ The bond energies of C—C, Si—Si and Ge—Ge bonds are respectively 348, 297 and 260 kJ mol^{-1}.

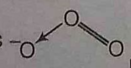
44. For a substance to dissolve, the hydration energy must be greater than lattice energy. Due to small size of Li^+ ion, the hydration energy of LiF is considerably high, but it has low solubility in water because of its higher lattice energy.

On moving down the group lattice energy decreases which results in increased solubility. Thus, the order of solubility for alkali metal fluorides in water is

$$LiF < NaF < KF < RbF$$

45. S_i exists as covalent solid

46. O_3 molecule, is



bent in shape.

47. N, P, As, Sb] Group = 15

Valence electrons] = 5

MCl_3 has sp^3 hybridised M-element with one lone-pair.

Lone-pair and bond-pair repulsion decreases bond angle. However, the bond-pairs of electrons are much farther away from the central atom in $SbCl_3$ than they are in NCl_3. Thus, lone-pair causes even greater distortion in PCl_3, $AsCl_3$ and $SbCl_3$. Hence, bond angle decreases from NCl_3 (maximum) to $SbCl_3$ (minimum).

48. (a) Thermal stability of the hydrides decrease as we go down the group in Periodic Table for group 15 (N-family)

$$BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$$

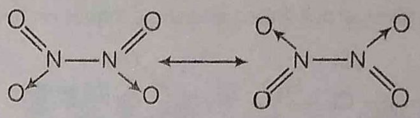
Least stable Most stable

	BiH_3	SbH_3	AsH_3	PH_3	NH_3
M–H bond energy (kJ mol^{-1})	–	255	247	322	391

(b) Due to absence of d-orbital, nitrogen can't from $d\pi$-$p\pi$ bond, thus it is correct.

(c) The N—N bond (BE 160 kJ mol^{-1}) is weaker than P—P bond (BE 209 kJ mol^{-1}). thus it is correct.

(d) N_2O_4 can form two resonance structures :



Thus, it is correct.

49. (a) S_2 molecule is paramagnetic due to unpaired electrons in MO and is blue-coloured compound-thus true.

(b) The vapour at 200°C consists mostly of S_8 rings, thus correct.

(c) At 600°C, the gas mainly consists of S_2 molecuels-thus correct.

(d) Oxidation states of sulphur are

-2 in H_2S

0 in S_8

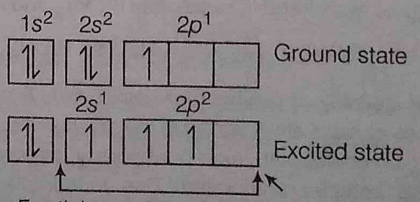
$+2$ in $S_2O_3^{2-}$

$+4$ in SO_2

$+6$ in SO_3

Thus, incorrect (Valency can be less than 4.)

50. B_5



Fourth lone pair is accomodated in this empty orbital

Maximum covalency = 4

Due to absence of 2d-orbital, maximum covalency is four. Thus BF_6^{3-} is not formed.

BH_4^- $(BH_3 + H^-)$; $B(OH)_4^-$ $(B(OH)_3 + OH^-)$ and BO_2^- are formed.

51. The correct increasing basic strength

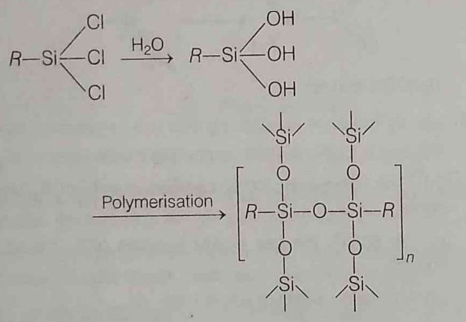
$$SbH_3 < AsH_3 < PH_3 < NH_3$$

NH_3 is the most basic because of its small size, the electron density of electron pair is concentrated over small region. As the size increases, the electron density gets diffused over a large surface area and hence the ability to donate the electron pair (basicity) decrease.

52. XeF_6 has much tendency to hydrolyse. The reverse reaction is more spontaneous.

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

53. $RSiCl_3$, gives cross linked silicone polymer on hydrolysis.



54. Sodium thiosulphate, $Na_2S_2O_3$ gets oxidised by chlorine water.

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$$

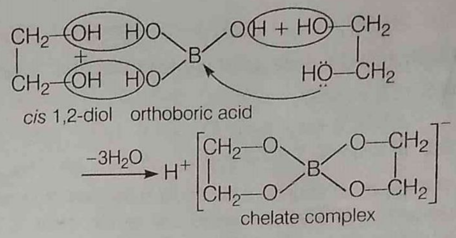
55. Br_2 reacts with hot and strong NaOH to give NaBr, $NaBrO_3$ and H_2O.

56. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na^+[B(OH)_4]^- + H_2O$

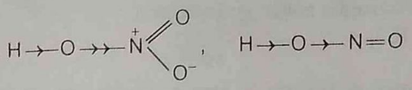
This reaction is reversible reaction because sodium metaborate, $Na^+[B(OH)_4]^-$ formed by the reaction between $B(OH)_3$ and NaOH gets hydrolysed to regenerate $B(OH)_3$ and NaOH.

$$Na^+[B(OH)_4]^- \xrightarrow{\text{Hydrolysis}} NaOH + B(OH)_3$$

If some quantity of polyhydroxy compounds like *cis* 1,2-diol, catechol, glycerol etc is added to the reaction mixture, then the $B(OH)_3$ combines with such polyhydroxy compounds to give chelated complex compound. Due to complex compound formation, stability increases and due to higher stability of complex, reaction moves in forward direction.



57.



Polarity along O—H in HNO_3 is more in comparison to —O—H in HNO_2.

58. The structure of silicates has been found with the help of X-ray diffraction techniques. Sheet silicates are formed when three oxygen atoms (bridging O-atoms) of each $(SiO_4)^{4-}$ unit are shared. Hence, the general formula of sheet silicates is $(Si_2O_5)^{2n-}$.

59. Aqueous solution of $AlCl_3$ is acidic due to hydrolysis.

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$$

On strong heating, $Al(OH)_3$ is converted into Al_2O_3.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

60. When I^- is oxidised by MnO_4^- in alkaline medium, I^- converts into IO_3^-.

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

$$2K_2MnO_4 + 2H_2O \longrightarrow 2MnO_2 + 4KOH + 2[O]$$

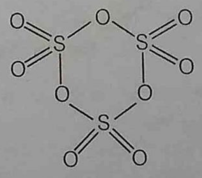
$$2KMnO_4 + H_2O \xrightarrow{\text{Alkaline}} 2MnO_2 + 2KOH + 3[O]$$

$$KI + 3[O] \longrightarrow KIO_3$$

$$2KMnO_4 + KI + H_2O \longrightarrow 2KOH + 2MnO_2 + KIO_3$$

61. The hydration of calcium aluminates and silicates involved in the setting of cement is an endothermic process, hence cement structures have to be cooled during setting by sprinkling water.

62. S_3O_9 is as



Hence, number of S—S bond = 0.

Day 23

The *d*- and *f*- Block Elements

Day 23

Outlines ...

- d-Block Elements
- Electronic Configuration
- General Properties of the Transition Elements
- Some Important Compounds of Transition Elements
- Inner Transition Elements (*f*-Block Elements)

d- and *f*- Block Elements

These are the elements having completely filled outermost shell and incomplete inner shall. If last electron enters in penultimate $(n-1)$ d-orbital the elements are called d-block elements and if enters in $(n-2)f$-orbital, the elements are called f-block elements.

d-Block Elements

d-block elements are present from fourth period onwards. There are mainly three series of the transition metals, (a) 3*d* series (Sc to Zn), (b) 4*d* series (Y to Cd) and (c) 5*d* series (La to Hg, omitting Ce to Lu).

d-block elements are known as transition elements because their position in the Periodic Table is between the s-block and p-block elements.

Electronic Configuration

Electronic configuration of the *d*-block elements is $(n-1)d^{1-10}ns^{1-2}$ but Cu^{+}, Zn, Cd, Hg etc., $[(n-1)d^{10}]$ are *d*-block elements, but not transition metals because these have completely filled *d*-orbitals.

Transition Metals or *d*-Block Elements

3rd group	4th group	5th group	6th group	7th group	8th group	9th group	10th group	11th group	12th group
$ns^2(n-1)d^1$	$ns^2(n-1)d^2$	$ns^2(n-1)d^3$	$ns^1(n-1)d^5$	$ns^2(n-1)d^5$	$ns^2(n-1)d^6$	$ns^2(n-1)d^7$	$ns^2(n-1)d^8$	$ns^2(n-1)d^9$	$ns^2(n-1)d^{10}$
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

General Properties of the Transition Elements

The general properties of d-block elements and their trends are discussed below.

1. Atomic and Ionic Radii

In transition metals, left to right net nuclear charge increases due to poor shielding effect. Due to this, the atomic and ionic radii for transition elements for a given series show a decreasing trend for first five elements and then becomes almost constant for next five elements of the series. At the end of the period, there is a slight increase in the atomic radii.

The atomic and ionic radii of the elements of 4 *d*-series are higher than corresponding element of 3*d* series due to increase in number shells. However, the elements of 4*d* and 5*d* series have almost constant values *e.g.*, Zr radii – 160 pm, Hf radii 159 pm. It is due to lanthanoid contraction.

Zr and Hf have very similar physical and chemical properties due to almost same size. Nb and Ta, Mo and W also have nearly same size due to lanthanoid contraction.

2. Enthalpies of Atomisation

Transition elements exhibit higher enthalpies of atomisation because of large number of unpaired electrons in their atoms.

They have stronger interatomic interaction and hence, stronger bond. Hence, transition elements have very high melting and boiling points.

3. Ionisation Enthalpies

The first ionisation enthalpy lies in between *s*-block and *p*-block elements. In a series from left to right, ionisation enthalpy increases due to increase in nuclear charge.

The irregular trend in the first ionisation enthalpy of the 3*d* metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4*s* and 3*d* orbitals.

Ionisation enthalpy values for 5*d*-series are higher than that of 3*d* and 4*d*-series due to weak shielding effect of 4*f* electrons present in 5*d*-series transition elements.

Ionisation enthalpy values of Zn, Cd and Hg are abnormally higher on account of greater stability of s-subshell.

4. Oxidation States

Transition metals show variable oxidation states due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are

$$\text{Sc}(+3), \text{Ti}\ (+4), \text{V}(+5), \text{Cr}(+3,+6), \text{Mn}(+2,+7),$$
$$\text{Fe}(+2,+3)\ \text{Co}(+2,+3), \text{Ni}(+2), \text{Cu}(+2), \text{Zn}(+2)$$

In each period, the highest oxidation state increases with increase in atomic number, attains a maximum value in the middle and then decreases, for example, Mn (3d series), Ru (4 d series) and Os (5d series) has maximum value for oxidation state as + 7, + 8, + 8 respectively.

The transition elements in their lower oxidation states (+2 and + 3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent. Ni and Fe in $Ni(CO)_4$ and $Fe(CO)_5$ show zero oxidation state.

5. Trends in the Standard Electrode Potentials

Transformation of the solid metal atoms to M^{2+} ions in solution is their standard electrode potentials.

If sum of the first and second ionisation enthalpies is greater than hydration enthalpy, standard potential $(E^\circ_{M^{2+}/M})$ will be positive and reactivity will be lower and *vice-versa*.

- *$HgCl_2$ is corrosive sublimate. It is poisonous and best antidote for it is white of an egg.*
- *Hg_2Cl_2 is calomel. It is used for making calomel electrode, used as a reference electrode.*

6. Trends in Stability of Higher Oxidation States

The highest oxidation numbers are achieved in TiX_4, VF_5 and CrF_6. The +7 state for Mn is not represented in simple halides but MnO_3F is known and beyond Mn no metal has a trihalide except FeX_3 and CoF_3 and increasing order of oxidising power in the series is

$$VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$$

The highest oxidation states of transition metals are found in their compounds with fluorine and oxygen only because of their higher electronegativity and small atomic size.

7. Magnetic Properties

The magnetic properties of a d-block elements are due to only spin of unpaired electrons. The magnetic moment is determined by the number of unpaired electrons (n) which is given by $\nu = \sqrt{n(n+2)}$

When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed : diamagnetism and paramagnetism. Paramagnetism is due to the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum.

If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

8. Formation of Coloured Ions

The *d*-orbitals are non degenerated in presence of ligands. When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of required wavelength is absorbed and rest light is transmitted out. Therefore, the colour observed corresponds to the complementary colour of the light absorbed.

In V_2O_5, V is in +5 oxidation state. In spite of d^0 it is coloured compound. This colour arises due to defects in the crystal lattice.

9. Formation of Complex Compounds

Transition metals have small size and high nuclear charge which facilitate the acceptance of lone pair of electrons from ligands.

They have vacant *d*-orbitals of appropriate energy in order to accommodate the lone pair of electrons.

10. Catalytic Properties

Transition metals have two incomplete outermost shells and ability to adopt multiple oxidation states and to form complexes, therefore used as a catalyst.

Transition metals also provide larger surface area for the reactant to be adsorbed.

11. Formation of Interstitial Compounds

Small atoms of non-metals (H, C, N) fit into the voids of crystalline solid of transition metals and form interstitial compounds. *The principal physical and chemical characteristics of these compounds are as follows*

(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard. Some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

12. Alloy Formation

Alloy is the homogeneous solid solution of two or more metals. Transition metals have approximate same size, therefore in molten form they can fit to each other's crystalline structure and form homogeneous mixture and form the alloy. *e.g.*, brass (copper-zinc) and bronze (copper-tin) etc.

Additional Information

- ScC_2 contains Sc^{3+} and C_2^{2-}. The extra electron lies in conduction band and make it conductor.
- Silvering of mirror is based on reduction of ammonical silver nitrate solution by neutral solution of tartarate or glucose in cold.
- The transition metals except iron are resistant to corrosion. Chromium is highly corrosion resisting metal.

Some Important Compounds of Transition Elements

The transition elements are those elements having a partially filled d or f subshell in any common oxidation state. the term transition elements most commonly refers to the d-block transition elements.

1. Potassium Dichromate ($K_2Cr_2O_7$)

Ore

Ferrochrome or chromite ($FeO \cdot Cr_2O_3$) or ($FeCr_2O_4$)

Preparation

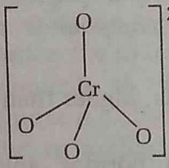
$$4FeO \cdot Cr_2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow \underset{\text{(yellow)}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + 2H^+ \longrightarrow \underset{\text{(orange)}}{Na_2Cr_2O_7} + 2Na^+ + H_2O$$

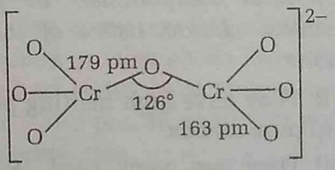
$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Sodium dichromate is more soluble than potassium dichromate.

Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.



chromate ion
*sp*³



dichromate ion
*sp*³

Properties

Sodium and potassium dichromates are strong oxidising agents, thus, acidified $K_2Cr_2O_7$ will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

$$Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$$

Uses

(a) $K_2Cr_2O_7$ is used as oxidising agent in volumetric analysis.

(b) It is used in mordant dyes, leather industry, photography (for hardening of film).

(c) It is used in chromyl chloride test.

(d) It is used in cleaning glassware.

(e) It is used in the preparation of chrome alum $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$.

2. Potassium Permanganate ($KMnO_4$)

Ore

Pyrolusite (MnO_2)

Preparation

$$2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{green}}{2K_2MnO_4} + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Commercial Preparation

$$MnO_2 \xrightarrow[\text{oxidised with air or } KNO_3]{\text{Fused with KOH,}} \underset{\text{manganate ion}}{MnO_4^{2-}}$$

$$MnO_4^{2-} \xrightarrow[\text{(alkaline medium)}]{\text{Electrolytic oxidation}} \underset{\substack{\text{permanganate ion}\\ \text{(purple)}}}{MnO_4^-}$$

Properties

It acts as strong oxidising agent.

(a) In presence of dilute H_2SO_4, $KMnO_4$ is reduced to manganous salt.

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

Acidic $KMnO_4$ solution oxidises oxalate to CO_2, iron (II) to iron (III), nitrites to nitrates and iodides to iodine. The half-reactions of reductants are

$$C_2O_4^{2-} \longrightarrow CO_2 + 2e^-$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$NO_2^- \longrightarrow NO_3^- + 2e^-$$

$$2I^- \longrightarrow I_2 + 2e^-$$

To acidify $KMnO_4$, only H_2SO_4 is used and not HCl or HNO_3 because HCl reacts with $KMnO_4$ and produce Cl_2 while HNO_3, itself acts as oxidising agent.

(b) In alkaline medium, $KMnO_4$ is reduced to insoluble MnO_2. $MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$

Alkaline or neutral $KMnO_4$ solution oxidises I^- to IO_3^-, $S_2O_3^{2-}$ to SO_4^{2-}, Mn^{2+} to MnO_2 etc.

Uses

(a) In laboratory preparation of Cl_2.

(b) As an oxidising agent, disinfectant.

(c) In making Baeyer's reagent.

Structure of Permanganate Ion

Mn in MnO_4^- undergoes sp^3 hybridisation and hence, four O atoms are arranged tetrahedrally around Mn.

Inner Transition Elements (*f*-Block Elements)

The f-block consists of the two series, lanthanoids and actinoids. Lanthanoids are known as rare earth metals and actinoids are known as radioactive elements (Th to Lr).

Lanthanoids

General configuration [Xe] $4f^{1-14}, 5d^{0-1}, 6s^2$.

Atomic and ionic size, from left to right, decreases due to increase in nuclear charge. This is known as **lanthanoid contraction.** All the lanthanoids are silvery white soft metals and tarnish rapidly in air.

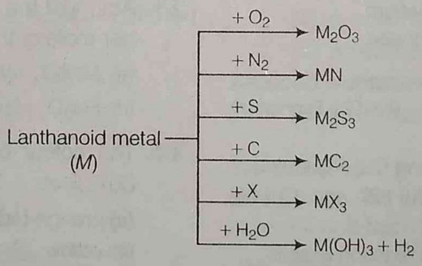
Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so. Lanthanoid ions with *xf* electrons have similar colour to those with $(14 - x)\, f$ electrons.

The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism arises to maximum in neodymium.

Oxidation states Ce^{4+} (in some elements) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The E°_{value} for Ce^{4+}/Ce^{3+} is +1.74 V, the reaction rate is very slow and hence, Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides. Eu^{2+} is formed by losing the two *s*-electrons and its f^7 configuration accounts for the formation of this ion. However, Eu^{2+} is a strong reducing agent changing to the common +3 state.

Similarly Yb^{2+} which has f^{14} configuration is a reductant, Tb^{4+} has half-filled *f*-orbitals and is an oxidant.

Reactivity Lanthanoid are very reactive metals like alkaline earth metals.



The hydroxides are ionic and basic. The base strength decreases from $Ce(OH)_3$ to $Lu(OH)_3$.

Alloy Misch metals, contain lanthanoids about 90–95% (Ce 40.5%. Lanthanum and neodymium 44%) iron 4.5%, calcium, carbon and silicon about 10.5%, are used in cigarete and gas lighters, toys, tank and tracer bullets. It is a pyrophoric alloy, *i.e.*, takes up fire easily.

Actinoids

General configuration [Rn] $5f^{1-14}, 6d^{0-2}, 7s^2$.

Actinoids exhibit a range of **oxidation states** due to comparable energies of $5f, 6d$ and $7s$ orbitals. The general oxidation state of actinoids is +3.

All the actinoids are strong reducing agents and very reactive.

Actinoids also react with oxygen, halogen, hydrogen and sulphur, etc., like lanthanoids.

Actinoids are radioactive in nature and therefore, it is difficult to study their chemical nature.

The atomic and ionic radii of actinoids decreases regularly across the series due to poor shielding effect of 5*f*-electrons. This is known as **actinoid contraction.**

The allocation of electrons to the 5*f* or 6*d*-orbitals in the actinoid atoms is more uncertain than the allocation to the 4*f* or 5*d* orbitals in the lanthanoid atoms, because the external shielding of the 5*f* electrons is less than that of the 4*f*-electrons.

The magnetic properties of *f*-block elements are due to both the orbital motion as well as spin magnetic moment for *d*-block elements.

Magnetic moment for *f*-block elements,

$$\mu = \sqrt{4s\,(s + 1) + l\,(l + 1)}$$

where, *s* is the sum of spin quantum numbers and *l* is the angular momentum quantum numbers.

Practice Zone

DAY 23

1. Railway wagon axles are made by heating rods of iron rod embedded in charcoal powder. The process is known as
(a) case hardening
(b) sherardising
(c) annealing
(d) tempering

2. An explosion takes place when conc H_2SO_4 is added to $KMnO_4$. Which of the following is formed?
(a) Mn_2O_7
(b) MnO_2
(c) $MnSO_4$
(d) Mn_2O_3

3. Atomic number of an element is 26. The element shows
(a) ferromagnetism
(b) diamagnetism
(c) paramagnetism
(d) None of these

4. In an aqueous solution, Cu (+1) salts are unstable because **[NCERT Exemplar]**
(a) Cu(+1) has a $3d^{10}$ configuration
(b) they disproportionate easily to the Cu and Cu(+2) states
(c) they disproportionate easily to the Cu(+2) and Cu(+3) states
(d) the change in free energy of the overall reaction is zero

5. Which of the following compounds is not coloured?
(a) Na_2CuCl_4
(b) Na_2CdCl_4
(c) $FeSO_4$
(d) VI_3

6. Ferric sulphate on heating gives
(a) SO_2 and SO_3
(b) SO_2 only
(c) SO_3 only
(d) S

7. The colour of the solution obtained by adding excess of KI in the solution of $HgCl_2$ is
(a) orange
(b) brown
(c) red
(d) colourless

8. The formula of green vitriol is
(a) $FeSO_4 \cdot 7H_2O$
(b) $MgSO_4 \cdot 7H_2O$
(c) $ZnSO_4 \cdot 7H_2O$
(d) $CuSO_4 \cdot 5H_2O$

9. Iron is rendered passive by treatment with conc
(a) HCl
(b) H_2SO_4
(c) H_3PO_4
(d) HNO_3

10. The correct order of $E^\circ_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is
(a) Mn > Cr > Fe > Co
(b) Cr > Fe > Mn > Co
(c) Fe > Mn > Cr > Co
(d) Cr > Mn > Fe > Co

Anhydrous iron (III) chloride can be prepared by
(a) dissolving $Fe(OH)_3$ in conc HCl
(b) dissolving $Fe(OH)_3$ in dil HCl in presence of chlorine
(c) passing chlorine over heated iron
(d) passing dry HCl over heated iron

12. Nitriding is the process of surface hardening steel by treating it in an atmosphere of
(a) NH_3
(b) O_3
(c) N_2
(d) H_2S

13. Amongst the following the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by
(a) $MnSO_4 \cdot 4H_2O$
(b) $CuSO_4 \cdot 5H_2O$
(c) $FeSO_4 \cdot 6H_2O$
(d) $NiSO_4 \cdot 6H_2O$

14. The colour of light absorbed by an aqueous solution of $CuSO_4$ is
(a) orange-red
(b) blue-green
(c) yellow
(d) violet

15. In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agent used are
(a) O_2 and CO respectively
(b) O_2 and Zn dust respectively
(c) HNO_3 and Zn dust respectively
(d) HNO_3 and CO respectively

16. Which of the following ions will finally give a black precipitate with Ag^+ ion?
(a) SO_3^{2-}
(b) Br^-
(c) CrO_4^{2-}
(d) $S_2O_3^{2-}$

17. One of the products formed due to the reaction between $KMnO_4$ and HCl is
(a) red liquid
(b) MnO_2
(c) greenish yellow gas
(d) $HClO_4$

18. Which one of the following compounds does not decolourise an acidified aqueous solution of $KMnO_4$?
(a) Sulphur dioxide
(b) Ferric chloride
(c) Hydrogen peroxide
(d) Ferrous sulphate

19. Hair dye contains
(a) copper nitrate (b) gold chloride
(c) silver nitrate (d) lead nitrate

20. Turnbull's blue is a compound called
(a) ferricyanide (b) ferrous ferrocyanide
(c) ferrous cyanide (d) ferri ferrocyanide

21. MnO_4^- on reduction in acidic medium forms
(a) MnO_2 (b) Mn^{2+} (c) MnO_4^{2-} (d) Mn

22. Which oxide of manganese is amphoteric?
(a) MnO (b) MnO_2
(c) Mn_2O_3 (d) Mn_2O_7

23. Arrange Ce^{3+}, La^{3+}, Pm^{3+} and Yb^{3+} in increasing order of their ionic radii.
(a) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
(b) $Ce^{3+} < Yb^{3+} < Pm^{3+} < La^{3+}$
(c) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$
(d) $Pm^{3+} < La^{3+} < Ce^{3+} < Yb^{3+}$

24. The atomic numbers of V, Cr, Mn and Fe are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionisation enthalpy?
(a) Cr (b) Mn (c) Fe (d) V

25. Among $FeSO_4 \cdot 7H_2O$ (*A*), $CuSO_4 \cdot 5H_2O$ (*B*), $ZnSO_4 \cdot 7H_2O$ (C), $MnSO_4 \cdot 4H_2O$ (*D*) isomorphous salts are
(a) *A* and *C* (b) *A* and *D*
(c) *C* and *B* (d) *A* and *B*

26. In an aqueous solution, it is easier to oxidize **[NCERT Exemplar]**
(a) $[Fe^{II}(CN)_6]^{4-}$ ions than $[Fe^{II}(H_2O)_6]^{3+}$ ions
(b) $[Fe^{II}(H_2O)_6]^{2+}$ ions than $[Fe^{II}(H_2O)_6]^{3+}$ ions
(c) $[Fe^{II}(CN)_6]^{4-}$ ions than $[Fe^{III}(CN)_6]^{3-}$ ions
(d) $[Fe^{II}(CN)_6]^{4-}$ ions than $Fe^{IV}O_4^{4-}$ ions

27. MnO_4^- is of intense pink colour, though Mn is in (+7) oxidation state. It is due to
(a) oxygen gives colour to it
(b) charge transfer when oxygen gives its electron to Mn making it Mn (VI) hence coloured
(c) charge transfer when Mn gives its electron to oxygen
(d) None of the above is correct

Directions (Q.Nos. 28 to 30) *Many ionic and covalent compounds of transition elements (and also inner transition elements) are coloured. In contrast compounds of the s-and p-block elements are almost always white. Colour may arise from an entirely different cause in ions with incomplete d or f shells. In a free isolated gaseous ions, the five d-orbitals are degenerate, that is, they are identical in energy. The surrounding groups, which can be solvent molecules in solution or ligands in a complex or other ions in a crystal lattice, affect the energy of some d-orbitals more than others. Thus, the d-orbitals are no longer degenerate and at their simplest they form two groups of orbitals of different energy.*

28. The sets of *d*-orbitals with different energies in an octahedral complex are
(a) $d_{z^2}, d_{x^2-y^2}$ and d_{xy}, d_{yz}, d_{zx}
(b) d_{z^2}, d_{yz}, d_{xz} and $d_{x^2-y^2}, d_{xy}$
(c) $d_{x^2-y^2}, d_{xy}, d_{yz}, d_{zx}$ and d_{z^2}
(d) d_{z^2}, d_{xy} and $d_{x^2-y^2}, d_{yz}, d_{xz}$

29. Consider the following statements.
A. Colour of a transition metal complex is dependent on energy difference between two *d*-levels.
B. Colour of the complex is dependent on the nature of the ligand and the type of complex formed.
C. $ZnSO_4$ and TiO_2 are white in both $d-d$ spectra are impossible.
Select the correct statements.
(a) *A, B, C* (b) *A, B* (c) *B, C* (d) *A, C*

30. The colour of $[Ti(H_2O)_6]^{3+}$ is due to
(a) transfer of an electron from one Ti to another
(b) presence of water molecule
(c) excitation of electrons from $d \to d$
(d) intermolecular vibration

Directions (Q.Nos. 31 and 32) *Green solution of potassium manganate (VI), turns purple and a brown solid is precipitated when CO_2 is bubbled into the solution.*

31. Purple colour is due to the formation of
(a) manganese dioxide (IV)
(b) potassium permanganate (VII)
(c) manganese (II) ion
(d) None of the above

32. Brown solid that is precipitated is of
(a) manganese dioxide (IV)
(b) potassium permanganate (VII)
(c) manganese oxide (II)
(d) manganese trioxide (III)

Directions (Q. Nos. 33 to 36) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

33. **Statement I** To a solution of potassium chromate, if a strong acid is added, it changes its colour from yellow to orange.

Statement II The colour change is due to the change in oxidation state of potassium chromate.

34. **Statement I** Zn^{2+} is diamagnetic .

Statement II The electrons are lost from 4s-orbital to form Zn^{2+}.

35. **Statement I** Out of Mn^{2+}, Fe^{2+} and Cr^{2+}, Mn^{2+} is readily oxidised.

Statement II Mn^{2+} is more stable than Fe^{2+} and Cr^{2+} due to completely filled *d*-orbitals.

36. **Statement I** Oxidation number of Cr in K_3CrO_8 is +6.

Statement II It contains tetraperoxo species *i.e.*, $[Cr(O_2)_4]^{3-}$.

37. 12 g of silver was extracted from a sample of an ore from which the only source of silver was Ag_2S. How many gram of Ag_2S were in the original sample?

(a) 27.6 g (b) 13.8 g
(c) 8.6 g (d) 5.2 g

38. A 0.081 g sample of pyrolusite ore (impure MnO_2) is treated with 1.651 g of oxalic acid ($H_2C_2O_4 \cdot H_2O$) in an acidic medium. Following this reaction the excess oxalic acid is titrated with 30.6 mL of 0.1 M $KMnO_4$, the percentage of MnO_2 in the ore will be (Mn = 55)

$$H_2C_2O_4 + MnO_2 + 2H^+ \longrightarrow Mn^{2+} + 2H_2O + 2CO_2$$

$$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

(a) 25% (b) 50%
(c) 70% (d) 82%

39. The magnetic moment of a transition metal of 3*d* series is 6.92 BM. Its electronic configuration would be

(a) $3d^4 4s^2$ (b) $3d^5 4s^1$
(c) $3d^8 4s^1$ (d) $3d^5 4s^0$

40. Compound '*A*' on strong heating gives two oxides of sulphur. If aqueous NaOH solution is added to the aqueous solution of '*A*', a dirty green precipitate is formed which starts turning brown on exposure to air. Compound '*A*' is

(a) ferrous hydroxide (b) ferric sulphate
(c) ferrous sulphate (d) ferric oxide

41. When a certain compound (*X*) (used in laboratory for analysis) is added to copper sulphate solution a yellow-brown precipitate is obtained which turns white on addition of excess of $Na_2S_2O_3$ solution. On addition to Ag^+ ion solution, a yellow curdy precipitate is obtained which is insoluble in NH_4OH. The (*X*) is

(a) H_2S (b) HCl
(c) KI (d) NaCN

AIEEE & JEE Main Archive

42. Which of the following arrangements does not represent the correct order of the property stated against it? **[JEE Main Online 2013]**

(a) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour
(b) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
(c) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
(d) Sc < Ti < Cr < Mn : number of oxidation states

43. When a small amount of $KMnO_4$ is added to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Compound may be **[JEE Main Online 2013]**

(a) $MnSO_4$ (b) Mn_2O_7 (c) MnO_2 (d) Mn_2O_3

44. Identify the incorrect statement. **[JEE Main Online 2013]**

(a) Cu_2O is colourless
(b) Copper (I) compounds are colourless except where colour results from charge transfer.
(c) Copper (I) compounds are diamagnetic
(d) Cu_2S is black

45. Consider the following reaction,

$$xMnO_4^- + yC_2O_4^{2-} + zH^+ \longrightarrow xMn^{2+} + 2\,yCO_2 + \frac{z}{2}H_2O$$

The values of *x*, *y* and *z* in the reaction are, respectively **[JEE Main Online 2013]**

(a) 5, 2 and 16 (b) 2, 5 and 8
(c) 2, 5 and 16 (d) 5, 2 and 8

46. The structure of which of the following chloro species can be explained on the basis of dsp^2 hybridization? **[JEE Main Online 2013]**

(a) $PdCl_4^{2-}$ (b) $FeCl_4^{2-}$
(c) $CoCl_4^{2-}$ (d) $NiCl_4^{2-}$

47. Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown-red vapours of **[JEE Main Online 2013]**

(a) CrO_3 (b) $CrCl_3$ (c) CrO_2Cl_2 (d) Cr_2O_3

48. The element with which of the following outer electron configuration may exhibit the largest number of oxidation states in its compounds **[JEE Main Online 2013]**

(a) $3d^5 4s^2$ (b) $3d^8 4s^2$ (c) $3d^7 4s^2$ (d) $3d^6 4s^2$

49. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^\circ_{M^{3+}/M^{2+}}$ value? **[JEE Main Online 2013]**

(a) Mn (Z = 25) (b) Fe (Z = 26)
(c) Co (Z = 27) (d) Cr (Z = 24)

50. Which of the following arrangements does not represent the correct order of the property stated against it? **[JEE Main Online 2013]**

(a) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
(b) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: Stability in aqueous solution
(c) $Sc < Ti < Cr < Mn$: number of oxidation states
(d) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: Paramagnetic behaviour

51. Consider the following reaction

$$xMnO^{-4} + y\,C_2O^{2-4} + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O$$

The values of x, y and z in the reaction are **[JEE Mains 2013]**

(a) 2, 5 and 8
(b) 2, 5 and 16
(c) 5, 2 and 8
(d) 5, 2 and 16

52. For the given aqueous reaction which of the statement is not true?

$$KI + K_3\,[Fe(CN)_6] \xrightarrow{\text{Dilute } H_2SO_4} \text{Brownish yellow solution}$$
$$\downarrow ZnSO_4$$
$$\text{White precipitate + Brownish yellow filtrate}$$
$$\downarrow Na_2S_2O_3$$
$$\text{Colourless solution.}$$

[IIT JEE 2012]

(a) The first reaction is a redox reaction.
(b) White ppt. is $Zn_3[Fe(CN)_6]_2$
(c) Addition of filtrate to starch solution gives blue colour.
(d) White ppt. is soluble in NaOH solution.

53. Iron exhibits +2 and+3 oxidation states. Which of the following statements about iron is incorrect? **[AIEEE 2012]**

(a) Ferrous oxide is more basic in nature than the ferric oxide.
(b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
(c) Ferrous compounds are less volatile than the corresponding ferric compounds.
(d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.

54. In context of the lanthanoids, which of the following statements is not correct? **[AIEEE 2011]**

(a) There is a gradual decrease in the radii of the members with increasing atomic number in the series.
(b) All the members exhibit + 3 oxidation state.
(c) Because of similar properties the separation of Lanthanoids is not easy.
(d) Availability of 4*f* electrons results in the formation of compounds in + 4 state for all the members of the series.

55. The outer electron configuration of Gd (at. no. 64) is 5 **[AIEEE 2011]**

(a) $4f^3\ 5d^5\ 6s^2$
(b) $4f^8\ 5d^0\ 6s^2$
(c) $4f^4\ 5d^4\ 6s^2$
(d) $4f^7\ 5d^1\ 6s^2$

56. Knowing that the Chemistry of lanthanoids (Ln) is dominated by its + 3 oxidation state, which of the following statements is incorrect? **[AIEEE 2009]**

(a) Because of the large size of the Ln (III) ions the bonding in its its compounds is predominantly ionic in character.
(b) The ionic sizes of Ln (III) decrease in general with increasing atomic number.
(c) Ln (III) compounds are generally clourless.
(d) Ln (III) hydroxide are mainly base in character.

57. In context with the transition elements, which of the following statements is incorrect? **[AIEEE 2009]**

(a) In addition to the normal oxidation state, the zero oxidation state is also shown by these elements in complexes.
(b) In the highest oxidation states, the transition metal shows basic character and form cationic complexes.
(c) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4*s* and 3*d* electrons are used for bonding.
(d) Once the d^5 configuration is exceeded, the tendency to involve all the 3*d* electrons in bonding decreases.

58. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being **[AIEEE 2008]**

(a) 4*f* orbitals are more diffused than the 5*f* orbitals
(b) lesser energy difference between 5*f* and 6*d* than between 4*f* and 5*d* orbitals
(c) more energy difference between 5*f* and 6*d* than between 4*f* and 5*d* orbitals
(d) more reactive nature of the actinoids than the lanthanoids

59. Among the following, the coloured compound is **[IIT JEE 2008]**

(a) CuCl
(b) $K_3[Cu(CN)_4]$
(c) CuF_2
(d) $[Cu(CH_3CN)_4]BF_4$

60. Identify the incorrect statement among the following. **[AIEEE 2007]**

(a) *d*-block elements show irregular and erratic chemical properties among themselves
(b) La and Lu have partially filled *d*-orbitals and no other partially filled orbitals
(c) The chemistry of various lanthanoids is similar
(d) 4*f* and 5*f* orbitals are equally shielded

61. Lanthanoid contraction is caused due to **[AIEEE 2006]**

(a) the appreciable shielding on outer electrons by 4*f* electrons from the nuclear charge
(b) the appreciable shielding on outer electrons by 5*d* electrons from the nuclear charge
(c) the same effective nuclear charge from Ce to Lu
(d) the imperfect shielding on outer electrons by 4*f* electrons from the nuclear charge

62. Which pair of compounds is expected to show similar colour in aqueous medium? **[IIT JEE 2005]**

(a) $FeCl_3$ and $CuCl_2$
(b) $VOCl_2$ and $CuCl_2$
(c) $VOCl_2$ and $FeCl_2$
(d) $FeCl_2$ and $MnCl_2$

63. Calomel (Hg_2Cl_2) on reaction with ammonium hydroxide gives **[AIEEE 2005]**

(a) HgO (b) Hg_2O

(c) $NH_2—Hg—Hg—Cl$ (d) $HgNH_2Cl$

64. $(NH_4)_2Cr_2O_7$ on heating gives a gas which is also given by **[IIT JEE 2004]**

(a) heating NH_4NO_2 (b) heating NH_4NO_3

(c) $Mg_3N_2 + H_2O$ (d) Na (compound) + H_2O_2

65. Cerium ($Z = 58$) is an important member of the lanthanides. Which of the following statements about cerium is incorrect? **[AIEEE 2004]**

(a) The common oxidation states of cerium are + 3 and +4.

(b) The +3 oxidation state of cerium is more stable than +4 oxidation state.

(c) The +4 oxidation state of cerium is not known in solutions.

(d) Cerium (IV) acts as an oxidising agent.

66. When MnO_2 is fused with KOH, a coloured compound is formed, the product and its colour is **[IIT JEE 2003]**

(a) K_2MnO_4, purple colour (b) $KMnO_4$, purple

(c) Mn_2O_3, brown (d) Mn_3O_4, black

67. A red solid is insoluble in water however, it becomes soluble, if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is **[AIEEE 2003]**

(a) $(NH_4)_2Cr_2O_7$ (b) HgI_2

(c) Hg (d) Pb_3O_4

Answers

1. (a)	**2.** (a)	**3.** (a)	**4.** (b)	**5.** (b)	**6.** (c)	**7.** (d)	**8.** (a)	**9.** (d)	**10.** (a)
11. (c)	**12.** (a)	**13.** (b)	**14.** (a)	**15.** (b)	**16.** (d)	**17.** (c)	**18.** (b)	**19.** (c)	**20.** (b)
21. (b)	**22.** (b)	**23.** (a)	**24.** (a)	**25.** (a)	**26.** (c)	**27.** (b)	**28.** (a)	**29.** (a)	**30.** (c)
31. (b)	**32.** (a)	**33.** (c)	**34.** (a)	**35.** (d)	**36.** (d)	**37.** (b)	**38.** (d)	**39.** (b)	**40.** (c)
41. (c)	**42.** (a)	**43.** (b)	**44.** (a)	**45.** (c)	**46.** (a)	**47.** (c)	**48.** (a)	**49.** (c)	**50.** (d)
51. (b)	**52.** (b)	**53.** (d)	**54.** (d)	**55.** (d)	**56.** (c)	**57.** (b)	**58.** (b)	**59.** (c)	**60.** (d)
61. (d)	**62.** (b)	**63.** (d)	**64.** (a)	**65.** (c)	**66.** (a)	**67.** (b)			

Hints & Solutions

1. Heating rods of iron or steel embedded in charcoal powder is known as case hardening.

2. $2KMnO_4 + \underset{\text{conc.}}{H_2SO_4} \longrightarrow Mn_2O_7 + K_2SO_4 + H_2O$

3. Iron, atomic number = 26 shows ferromagnetism.

4. Cu^{1+} salts are unstable because Cu^{1+} salts disproportionate into Cu & Cu^{2+} salts.

5. Na_2CdCl_4 does not have unpaired electrons.

6. $Fe(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$

7.
$$HgCl_2 + 2KI \longrightarrow \underset{\text{(red ppt)}}{HgI_2} \downarrow + 2KCl$$
$$\underset{\text{(red ppt)}}{HgI_2} + 2KI \longrightarrow \underset{\text{soluble, colourless}}{K_2[HgI_4]}$$

8. $FeSO_4 \cdot 7H_2O$ is green vitriol.

9. Conc HNO_3 renders iron passive, by forming a thin protective film of Fe_3O_4 on its surface.

10. Usually across the first transition series, the negative values for $E°$ decrease except for Mn due to stable d^5 configuration. So, the correct order is Mn > Cr > Fe > Co.

11. $2Fe + 3Cl_2 \xrightarrow{\Delta} Fe_2Cl_6$

12. When steel is treated in the presence of NH_3, iron nitride on the surface of steel is formed which imparts a hard coating. This process is called nitriding.

13. Mn^{2+} in $MnSO_4 \cdot 4H_2O$ has d^5 configuration (five unpaired electrons); Cu^{2+} in $CuSO_4 \cdot 5H_2O$ has d^9 configuration (one unpaired electron); Fe^{2+} in $FeSO_4 \cdot 6H_2O$ has d^6 configuration (four unpaired electrons); Ni^{2+} in $NiSO_4 \cdot 6H_2O$ has d^8 configuration (two unpaired electrons). Thus, $CuSO_4 \cdot 5H_2O$ has lowest degree of paramagnetism.

14. The aqueous solution of $CuSO_4$ consists of the complex $[Cu(H_2O)_4]^{2+}$ ion which absorbs in orange red region and impart deep blue colouration to the solution.

15. The reactions involved in the extraction of silver by cyanide process are

$$Ag_2S + 2CN^- + O_2 \longrightarrow 2[Ag(CN)_2]^- + SO_2 \quad \ldots(i)$$
$$[Ag(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + Ag \quad \ldots(ii)$$

In the first reaction sulphide is oxidised by oxygen to SO_2 and in the second reaction, silver ion is reduced by Zn to Ag. Therefore, O_2 is oxidising agent and Zn is reducing agent.

16. $2Ag + S_2O_3^{2-} \longrightarrow Ag_2S_2O_3$,white ppt which readily changes to yellow, orange, brown and finally black due to formation of silver sulphide.

$$Ag_2S_2O_3 + H_2O \longrightarrow H_2SO_4 + Ag_2S \text{ (black)}$$

17. $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

$$2HCl + O \longrightarrow H_2O + \underset{\text{(greenish yellow gas)}}{Cl_2 \uparrow}$$

18. $FeCl_3$ is not a reducing agent, it will not react with oxidising agent $KMnO_4$ and no colour is discharged.

19. Hair dye contains silver nitrate.

20. Ferrous ferrocyanide $Fe_2[Fe(CN)_6]$ is Turnbull's blue and ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$ is Prussian blue.

21. MnO_4^- on reduction in acidic medium forms Mn^{2+} ion .

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

22. MnO_2 is amphoteric, MnO and Mn_2O_3 are basic, whereas, Mn_2O_7 is acidic.

23. Ionic size decreases from La^{3+} to Lu^{3+} due to lanthanide contraction.

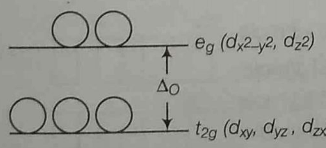
24. $Cr = 3d^5 4s^1$; After removing $4s^1$ electron, the next electron is to be removed from relatively more stable half filled $3d^5$ subshell, which will require more energy for its ionisation.

25. $FeSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 7H_2O$ have similar crystalline form and chemical composition *i.e.*, these are isomorphous.

26. It is easier to oxidize $[Fe^{II}(CN)_6]^{4-}$ ion than $[Fe^{III}(CN)_6]^{3-}$

27. Pink colour of MnO_4^- is due to the charge transfer when oxygen gives its electron to Mn making it Mn (+VI) hence, coloured.

28. The sets of *d*-orbitals with different energies in an octahedral complex are



29. Colour of transition metal complex is dependent on energy difference between t_{2g} and e_g. Sets of *d*-orbitals, nature of ligand and type of complex formed. *d*-*d* transition is possible in d^1 to d^9 ions. That is why such ion complexes are coloured. On the other hand d^0 and d^{10} ions cannot show *d*-*d* transition, hence colourless.

30. Ti^{3+} ion is coloured due to excitation of electrons from $d \rightarrow d$.

31. CO_2 in aqueous solution is acidic.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

In the presence of H^+ ions, MnO_4^{2-} disproportionates to MnO_4^- purple by oxidation and MnO_2, a brown solid by reduction.

$$\underset{+\text{(VI)}}{3MnO_4^{2-}} + 4H^+ \longrightarrow \underset{\substack{+\text{(VII)}\\ \text{(purple)}}}{2MnO_4^-} + \underset{\substack{+\text{(IV)}\\ \text{(brown)}}}{MnO_2} + 2H_2O$$

32. Brown solid is manganese dioxide (IV), MnO_2

33. $2K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$

$$\underset{\text{(yellow)}}{2\overset{+6}{Cr}O_4^{2-}} + SO_4^{2-} + 2H^+ \longrightarrow \underset{\text{orange}}{\overset{+6}{Cr_2}O_7^{2-}} + SO_4^{2-} + H_2O$$

No change in oxidation state

Thus, statement II is wrong.

34. $Zn^{2+} = [Ar]\,3d^{10}$; No unpaired electrons, hence diamagnetic.

35. Mn^{2+} cannot be oxidised easily whereas Cr^{2+} and Fe^{2+} can be readily oxidised.

$$2CuSO_4 + 4KCN \longrightarrow 2CuCN + 2K_2SO_4 + (CN)_2$$

$$CuCN + 3KCN \longrightarrow K_3[Cu(CN)_4]$$

36. Oxidation number of Cr is +5 in $[Cr(O_2)_4]^{3-}$. It is a tetraperoxo species and thus,

$$a + 8 \times (-1) = -3$$

$$a = +5$$

37. $2Ag^+ + S^{2-} \longrightarrow Ag_2S$

∴ Mass of Ag_2S required

$$= \frac{\text{molar mass of } Ag_2S \times 12}{2 \times 108}$$

$$= 13.8 \text{ g} \qquad [\because \text{Molar mass of } Ag_2S = 248]$$

38. MnO_4^- used $= 30.6 \times 0.1$ milimol $= 3.06 \times 10^{-3}$ mol

$2 \text{ mol } MnO_4^- = 5 \text{ mol } H_2C_2O_4 \cdot H_2O$

Thus, 3.06×10^{-3} mol $MnO_4^- = 7.65 \times 10^{-3}$ mol unreacted

$(H_2C_2O_4 \cdot H_2O)$ taken

$$\frac{1.651}{108} = 1.53 \times 10^{-2} \text{ mol}$$

Used $H_2C_2O_4 \cdot H_2O$ by

$$MnO_2 = (1.53 \times 10^{-2} - 7.65 \times 10^{-3})$$

$$= 7.650 \times 10^{-3} \text{ mol}$$

$1 \text{ mol } H_2C_2O_4 \cdot H_2O \equiv 1 \text{ mol } MnO_2$

∴ 7.65×10^{-3} mol $H_2C_2O_4 \cdot H_2O = 7.65 \times 10^{-3}$ mol MnO_2

$$= 7.65 \times 10^{-3} \times 87 \text{ g pure } MnO_2$$

$$= 0.6655\text{g in } 0.81\text{g impure } MnO_2$$

∴ Percentage of pure $MnO_2 = \dfrac{0.6655}{0.81} \times 100 = 82.16\%$

39. Magnetic moment $= \sqrt{n(n+2)}$ or $6.92 = \sqrt{n(n+2)}$

[Here, n = number of unpaired electrons.]

$$n = 6$$

Hence, metal = Cr = $3d^5 4s^1$

40.
$$\underset{\text{'A'}}{2FeSO_4} \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$$

$$\underset{\text{'A'}}{FeSO_4} + 2NaOH \longrightarrow \underset{\text{green}}{Fe(OH)_2} + Na_2SO_4$$

$$Fe(OH)_2 \xrightarrow{[O]} \underset{\text{brown}}{Fe(OH)_3}$$

41. (X) gives yellow ppt, insoluble in NH_4OH with Ag^+ solution, so contains I^- ions. It suggests it to be KI.

$$2CuSO_4 + \underset{(X)}{4KI} \longrightarrow 2CuI_2 + 2K_2SO_4$$

$$2CuI_2 \longrightarrow \underset{\text{yellow brown ppt.}}{Cu_2I_2\downarrow} + I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow \underset{\text{white}}{Na_2S_4O_6} + 2NaI$$

$$Ag^+ + \underset{(X)}{KI} \longrightarrow \underset{\substack{\text{yellow ppt.}\\ \text{(insoluble in } NH_4OH)}}{AgI\downarrow} + K^+$$

42. (a) V^{2+} = 3 unpaired electrons

Cr^{2+} = 4 unpaired electrons

Mn^{2+} = 5 unpaired electrons

Fe^{2+} = 4 unpaired electrons

Hence, the order of paramagnetic behaviour should be $V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$

(b) Ionic size decreases from left to right in the same period.

(c) (As per data from NCERT)

$Co^{3+}/Co^{2+} = 1.97$; $Fe^{3+}/Fe^{2+} = 0.77$;

$Cr^{3+}/Cr^{2+} = -0.41$

Sc^{3+} is highly stable (It does not show + 2).

(d) The oxidation states increases as we go from group 3 to group 7 in the same period.

43. When a small amount of $KMnO_4$ is added to concentrated H_2SO_4, manganese heptoxide is obtained, which on warming decomposes with a mild explosion into MnO_2 and O_2.

$$2KMnO_4 + H_2SO_4 \longrightarrow \underset{\text{green liquid}}{Mn_2O_7} + K_2SO_4 + H_2O$$

$$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$$

44. Cu_2O is not colourless, it is coloured because of the presence of one unpaired electron, which makes d - d transition possible.

$Cu^{2+} = [Ar]3d^9$

$$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$$

All other given statements are correct.

45. The half equations of the reaction are

$$MnO_4^- \longrightarrow Mn^{2+}$$
$$C_2O_4^{2-} \longrightarrow CO_2$$

The balanced half equations are

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

On equating number of electrons we get

$$2MnO_4^- + 16H^+ + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$$
$$5C_2O_4^{2-} \longrightarrow 10CO_2 + 10e^-$$

On adding both the equations we get

$$2MnO_4^- + 5C_2O_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 2 \times 5CO_2 + \frac{16}{2}H_2O$$

Thus x, y and z are 2, 5 and 16 respectively.

46. Although Cl^- is a weak field ligand but in case of $[PdCl_4]^{2-}$, it pair up the electrons of Pd and results in dsp^2-hybridisation because of the large size of Pd^{2+}.

In all other pairing is not possible, so hybridisation is sp^3 with tetrahedral structure.

47.
$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 \xrightarrow{\Delta} \underset{\substack{\text{chromyl chloride}\\ \text{(red vapours)}}}{2CrO_2Cl_2} + K_2SO_4 + 2Na_2SO_4 + 3H_2O$$

48. Due to the presence of maximum number of unpaired electrons, element having $3d^5$, $4s^2$, configuration may exhibit the largest number of oxidation states in its compounds.

49. $E^\circ_{\underset{M}{3+}}/M^{2+}$ is positive for Co^{3+}/Co^{2+} ion, therefore, Co would have highest $E^\circ_{M^{3+}}/M^{2+}$ value.

50. The hydration enthalpies of the trivalent cations are shown below

Sc^{3+} = 3960 kJ/mole

Fe^{3+} = 4429 kJ/mole

Co^{3+} = 4653 kJ/mole

Cr^{3+} = 4563 kJ/mole

The above values show that Sc^{3+} is less hydrated, therefore, it is least stable.

Since, Fe^{2+} contains 4 unpaired electrons while M^{2+} contains 5 unpaired electrons, hence (d) is the incorrect option.

51. The given reaction can be written as

$$2MnO^{-4} + 5C_2O_4^{2-} + 16\,H^+ \rightarrow 2M^{2+} + 10\,CO_2 + 8H_2O$$

$x = 2$, $y = 5$ and $z = 16$

52.
$$K_3[\overset{+3}{Fe}(CN)_6(CN)_6] + KI(\text{excess}) \longrightarrow K_4[Fe^{2+}(CN)_6] + \underset{\text{brownish yellow solution}}{[KI_3(\text{redox})]}$$

$K_4[Fe(CN)_6] + ZnSO_4 \longrightarrow K_2Zn_3[Fe(CN)_6]_2$

or $\underset{\text{white ppt.}}{K_2Zn\,[Fe(CN)_6]}$

$\underset{\text{brownish yellow filtrate}}{I_3^-} + Na_2S_2O_3 \longrightarrow \underset{\text{clear solution}}{Na_2S_4O_6} + 2NaI + \underset{\text{turns starch solution blue}}{I_2}$

$K_2Zn[Fe(CN)_6]$ reacts with NaOH as follows

$K_2Zn\,[Fe(CN)_6] + NaOH \longrightarrow [Zn(OH)_4]^{2-} + [Fe(CN)_6]^{4-}$

53. (a) $FeO > Fe_2O_3$ (basic character)

(b) $FeCl_2 > FeCl_3$ (ionic nature), larger the charge greater the polarizing power thus greater the covalent nature. thus correct.

(c) Fe^{2+} salts are more ionic thus less volatile than Fe^{3+} salts. Thus, correct.

(d) Greater the covalent nature, more easily they are hydrolysed. Thus, $FeCl_3$ is more hydrolysed than $FeCl_2$

Thus, incorrect

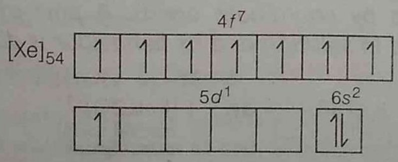
54. (a) There is a gradual decrease in the radii of the lanthanoids with increasing atomic number – a case of lanthanide contraction, thus true.

(b) Ionization potential for the formation of Lu^{3+} is comparatively low, hence, + 3 state is favourable, thus true.

(c) Due to lanthanide contraction – Zr and Hf; Nb and Ta, Mo and W have the same size and thus similar properties and thus separation is not easy, thus true.

(d) Formation of + 4 state requires very high energy, thus incorrect.

55. Gd (64)



All the electrons in 4*f*-orbital are unpaired, hence, stable.

Thus, Gd (64) has EC as $[Xe]_{54}\,4f^7\,5d^1\,6s^2$ instead of $[Xe]_{54}\,4f^8\,6s^2$.

56. The most common oxidation state of lanthanoid is +3. Lanthanoids in +3 oxidation state usually have unpaired electron in *f*-subshell and impart characteristic colour in solid as well as in solution state due to *f-f* transition. (Except lanthanum and lutetium).

57. As oxidation state increases, electronegativity increases thus acidic characteristic increases not basic.

58. Lanthanoids $[Xe]4f^{1-14}\,5d^{0-1}\,6s^2$

Actinoids $[Rn]\,5f^{1-14}\,6d^{0-1}\,7s^2$

Lanthanoids and actinoids use core *d* and *f* orbitals also to show higher oxidation state. As actinoids have comparatively low energy difference between *f* and *d* orbitals, thus shows more oxidation states.

59. In CuF_2, Cu^{2+} ions exist, having d^9 configuration. Unpaired electron causes colour (*d-d*) transition. In the crystalline form, CuF_2 is blue coloured.

60. 4*f* and 5*f* belongs to different shell, so experience different amount of shielding.

61. Lanthanoid contraction is due to ineffective shielding produced by larger *f*-subshell.

62. In $VOCl_2$, V is in +4 state $(3d^1)$ and in $CuCl_2$, Cu is in +2 state $(3d^9)$. Both have one unpaired electron hence, show similar colour.

63. $Hg_2Cl_2 + 2NH_3 \longrightarrow \underset{\text{white}}{HgNH_2Cl} + \underset{\text{black}}{Hg}\downarrow + NH_4Cl$

64. $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

$NH_4NO_2 \xrightarrow{\Delta} 2H_2O + N_2\uparrow$

65. +3 and +4 states are shown by Ce in aqueous solution.

66. $2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{purple colour}}{2K_2MnO_4} + 2H_2O$

67. $HgI_2 + 2KI \longrightarrow \underset{\text{(soluble)}}{K_2HgI_4}$

$HgI_2 \xrightarrow{\Delta} Hg + I_2$

Day 24

Coordination Compounds

Day 24

Outlines ...

- Complex or Coordination Compounds
- Isomerism in Coordination Compounds
- Bonding in Coordination compounds
- Crystal Field Theory
- Stability Constant and Stability of Complexes

Complex or Coordination Compounds

Complex compounds or coordination compounds are those molecular compounds which retain their identity in solid as well as in aqueous solution. In these compounds metal atoms are bound to a number of anions or neutral molecules by coordinate bonds. A part of these compounds is not dissociated in solution and its behaviour is different than its constituents.

e.g., $$\underset{\text{ionisable species}}{K_4}\ \underset{\text{non-ionisable coordination sphere}}{[Fe(CN)_6]} + H_2O \longrightarrow 4K^+ + \underset{\text{central metal atom ligands}}{[Fe(CN)_6]^{4-}}$$

The following are some terms related to coordination compounds given as

1. Complex Ion

It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or molecules

(i) **Anionic Complex** It is complex ion which carries negative charge.

$$K_3[Fe(C_2O_4)_3] \longrightarrow 3K^+ + \underset{\text{anionic complex}}{[Fe(C_2O_4)_3]^{3-}}$$

(ii) **Cationic Complex** It is complexion which carries positive charge

$$[CoCl_2(en)_2]Cl \longrightarrow \underset{\text{cationic complex}}{[CoCl_2(en)_2]^+} + Cl^-$$

(iii) **Neutral Complex** It is complexion which does not carry any charge.

$$\underset{\text{neutral complex}}{[Ni(CO)_4]}$$

2. Ligands

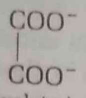
The ions or molecules bound to the central atom/ion in the coordination entity are called **ligands**

Types of Ligands

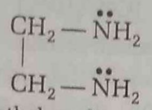
(i) **Unidentate Ligand** It is bound to a metal ion through a single donor atom. *e.g.*, $H_2O, NH_3, CO, Cl^-, NH_2^-$ etc.

(ii) **Didentate Ligand** It is bound to a metal ion through two donor atoms.

e.g.,


$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix}$$

oxalate ion


$$\begin{matrix} CH_2 - \ddot{N}H_2 \\ | \\ CH_2 - \ddot{N}H_2 \end{matrix}$$

ethylene diamine

(iii) **Polydentate** It is bound to a metal ion through several donor atoms. *e.g.*, ethylene diamine tetra acetate ion $[EDTA]^{4-}$.

(iv) **Ambidentate Ligands** It can ligate through two different atoms. *e.g.*, $—NO_2$, $—ONO$, $—SCN$, $—NCS$, etc.

(v) **Chelate ligands** may be di or polydentate ligands which form closed ring with central metal ion. Closed ring is known as chelate ring and this process is called chelation.

More the number of chelate rings in a complex, complex will be more stable. The number of such ligating groups is called the **denticity**.

3. Coordination Number

The number of chemical bonds formed by the ligands with central metal atom or ion is called the **coordination number** of that complex.

In case of monodentate ligand, it is equal to the number of ligands while in bidentate ligand it is equal to the 2× number of ligands present in the complex.

4. Coordination Sphere

The central ion and the ligands attached to it are enclosed in square bracket which is known as coordination sphere. The ionisable group written outside the bracket is known as counter ions.

5. Coordination Polyhedron

The spatial arrangement of the ligands which are directly attached to the central atom or ion, is called coordination polyhedron around the central atom or ion.

6. Oxidation Number of Central Atom

The charge of the complex if all the ligands are removed along with the electron pairs that are shared with the central atom, is called oxidation number of central atom.

Effective Atomic Number Rule

Effective atomic number EAN of a metal in a complex

- = atomic number of nearest inert gas.

or EAN = at. no. of metal ± valency + 2 × CN

where, CN = coordination number.

Homoleptic and Heteroleptic Complexes

Complexes in which a metal is bound to only one kind of donor groups *e.g.*, $[Co(NH_3)_6]^{3+}$ are known as **homoleptic**. Complexes in which a metal is bound to more than one kind of donor groups *e.g.*, $[Co(NH_3)_4Cl_2]^+$, are known as **heteroleptic**.

Nomenclature of Coordination Compounds

1. **Cationic Complex** $[\underset{2}{Co}(NH_3)_4\underset{1}{Cl}(NO_2)]\underset{3}{NO_3}$

Tetramminechloronitrocobalt (III) nitrate

- Prefixes mono, di, tri etc.,…… are used to indicate the number of the individual ligands and ligands are named in alphabetical order.
- Central metal atom and its oxidation state is indicated by Roman numeral in parenthesis.
- Name of ionisable anion.

2. **Anionic Complex** $\underset{1}{K_3}[\underset{3}{Fe}\underset{2}{(CN)_6}]$

potassiumhexacyanoferrate (III)

- Name of ionisable metal.
- Name of ligand in alphabetical order.
- Central metal atom + ate and oxidation state.

3. **Neutral Complex** $[\underset{2}{Pt}(NH_3)_2\underset{1}{Cl}(NO_2)]$

diamminechloronitrito-N-platinum (II)

- Name of ligands in alphabetical order.
- Central metal atom and its oxidation state.

The oxidation state of Fe is + 2 in sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ and it has the ligand nitrosonium ion, NO^+.

When $Fe^{2+}(aq)$ is added to $K_3[Fe(CN)_6]$, the product obtained is Turnbull's blue, but on addition of $Fe^{3+}(aq)$ to $K_4[Fe(CN)_6]$, the product Prussian blue is obtained.

Isomerism in Coordination Compounds

It is a phenomenon, in which compounds have the same molecular formula but different physical and chemical properties on account of different structures. These compounds are called ***isomers.***

1. Stereo Isomerism

It occurs due to different arrangements of ligands around central metal atom.

It is of two types; geometrical isomerism and optical isomerism.

(i) Geometrical Isomerism

It arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found in square planar and octahedral complexes.

(a) **Square planar complex of formula** $[MX_2L_2]$ (X and L are unidentate), the two X ligands may be arranged adjacent to each other in a *cis*-isomer or opposite to each other in a *trans*-isomer. *e.g.,* $[Pt(NH_3)_2Cl_2]$

(b) **Square planar complex of the type** $[MABXL]$ (where A, B, X, L are unidentate) shows three isomers, **two *cis*** and **one trans**. Such isomerism is not possible for tetrahedral geometry. *e.g.,* $[Pt(NH_3)(Br)(Cl)(Py)]$

(c) Square planar complex of type $M(XL)_2$, here, XL is unsymmetrical didentate ligand, *e.g.,* $[Pt(gly)_2]$

(d) **Octahedral complexes of formula** $[MX_2L_4]$ in which the two ligands X may be oriented *cis* or *trans* to each other, *e.g.,* $[Co(NH_3)_4Cl_2]^+$.

(e) **Octahedral complexes of formula** $[MX_2A_2]$ (where X are unidentate ligands and A are didentate ligands) form *cis* and *trans*-isomers. *e.g.,* $[CoCl_2(en)_2]$

(f) **Octahedral coordination entities of the type** $[Ma_3b_3]$ like $[Co(NH_3)_3(NO_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the *facial* (*fac*) isomer. When the positions are around the meridian of the octahedron, we get the *meridional* (*mer*) isomer.

Tetrahedral complexes do not show geometrical isomerism. Octahedral complexes of type $[M(AA)_3]$, MA_6 *and* MA_5B *do not show geometrical isomerism.* $MA_2X_2Y_2$ *shows both optical and geometrical isomerism.*

(ii) Optical Isomerism

It arises when mirror images cannot be superimposed on one another. These mirror images are called **enantiomers**. The two forms are called *dextro* (*d*) and *laevo* (*l*).

Optical isomerism is common in octahedral complexes having atleast one didentate ligand.

e.g., $[Co(en)_3]^{3+}$, $[PtCl_2(en)_2]^{2+}$ etc.

2. Structural Isomerism

In structural isomerism, isomers have different bonding pattern.

Different types of structural isomerism is as follows

(i) **Linkage isomerism** arises in a coordination compound containing ambidentate ligand.

e.g., $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$

(ii) **Coordination isomerism** arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

e.g., $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr[NH_3)_6][Co(CN)_6]$

(iii) **Ionisation isomerism** when the ionisable anion exchange with anion ligand.

e.g., $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

(iv) **Solvate isomerism** is also known as "hydrate isomerism". In this case water is involved as a solvent.

e.g., $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

Bonding in Coordination Compounds

The bonding formation in coordination compounds can be explained by using the two approaches as given below

Werner's Theory

(i) In complex compounds, metal atom exhibit two types of valencies—primary valency and secondary valency.

(ii) Primary valencies are satisfied by anions only while secondary valencies are satisfied by ligands. Primary valency depends upon oxidation number of central metal atom while secondary valency represents the coordination number of central metal atom.

(iii) Primary valencies are ionisable and are non-directional while secondary valencies are non-ionisable and directional. Therefore, geometry of complex is decided by secondary valencies.

e.g., $[Cr(H_2O)_6]Cl_3$ has primary valency = 3 (o S of Cr) and secondary valency = 6 (CN of Cr)

Valence Bond Theory

According to this theory, the metal atom or ion under the influence of ligands form inner orbital and outer orbital complex. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

1. Six Ligands (unidentate) Octahedral Entity

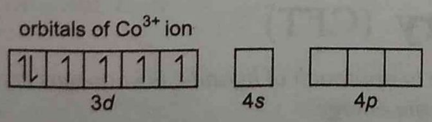
Generally, central atom belongs to 3*d* series and ligands can be monodentate or didentate but coordination number should be six. The shape of complexes will be octahedral. *Such complexes are of the following two types*

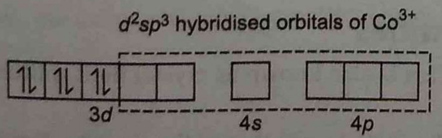
(i) **Inner Orbital Complexes** (hyperligated com- plexes) which are formed due to strong field ligands or low spin ligands, has hybridisation d^2sp^3 (where two orbitals are of 3*d*, one orbital of 4*s* and three orbitals of 4*p*) and shape of complex will be octahedral.

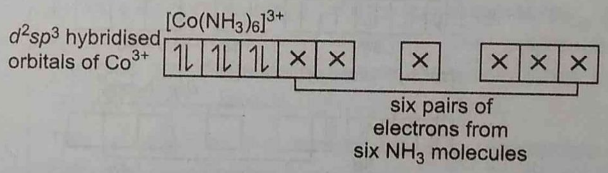
(ii) **Outer Orbital Complexes** (hypoligated complexes) which are formed due to weak field ligands or high spin ligands, has hybridisation sp^3d^2 (where one orbital is of 4*s*, three orbitals of 4*p* and two orbitals of 4*d*).

Generally halides (F^-, Cl^-, Br^-, I^-), SCN^-, S^{2-} form outer orbital complexes and other ligands form inner orbital complexes. *e.g.*,

(a) **Inner Orbital Complex** $[Co(NH_3)_6]^{3+}$

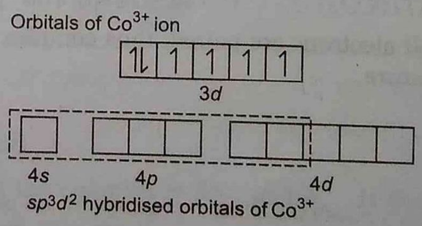


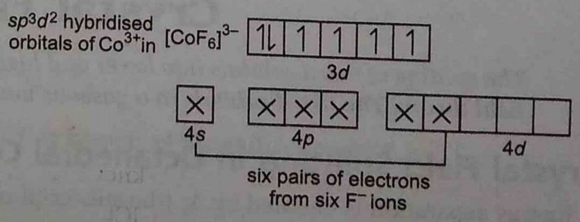




All electrons are paired, therefore complex will be diamagnetic in nature.

(b) **Outer Orbital Complex** $[CoF_6]^{3-}$





Complex has unpaired electrons, therefore it will be paramagnetic in nature.

2. Four-ligands (unidentate), Tetrahedral and Square Planar Entity

Tetrahedral complexes can also form inner orbital or outer orbital complexes, characteristics of which are shown below :

Tetrahedral complexes

Inner orbital

Outer orbital

Inner orbital complexes

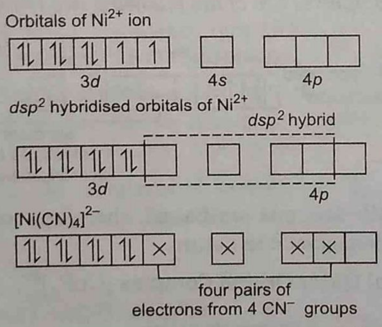
- strong field or low spin ligands
- hybridisation is dsp^2 (where one orbital is of $3d$, one orbital of $4s$ and two orbitals of $4p$).
- square planar shape

Outer orbital complexes

- weak field ligands or high spin ligands
- hybridisation is sp^3 (where one orbital is of 4snd three orbitals of $4p$).
- tetrahedral shape

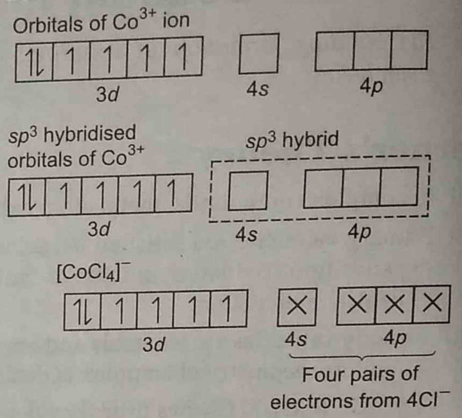
Generally, halide (F^-, Cl^-, Br^-, I^-) ligands, $[Ni(CO)_4]$, $[Co(CO)_4]$, $[Zn(NH_3)_4]^{2+}$ complexes form outer orbital complexes and other form inner orbital complexes. For example,

(i) Inner Orbital Complex $[Ni(CN)_4]^{2-}$



All electrons are paired, thus complex will be diamagnetic in nature.

(ii) Outer Orbital Complex $[CoCl_4]^-$



Complex has unpaired electrons, so it will be paramagnetic in nature.

Limitations of Valence Bond Theory

Although this theory described the formation, structure and magnetic behaviour of complexes sucessfully but it suffers from the following short comings.

- It involves a number of assumptions.
- It describes bonding in coordination compounds only qualitatively. It does not offer any explanation for the optical absorption spectra of complexes.
- It does not describe the detailed magnetic properties of coordination compounds.
- It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
- It does not distinguish between weak and strong ligands.

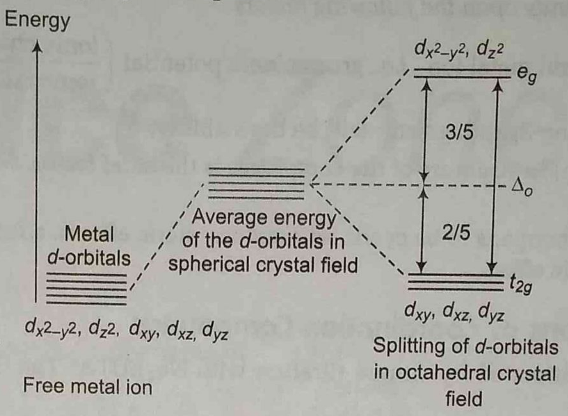
Crystal Field Theory (CFT)

The spliting of five d-orbitals into lower and higher energy levels due to approach of ligands, is known as crystal field theory. The five d-orbitals in a gaseous metal atom/ion have same energy.

Crystal Field Splitting in Octahedral Coordination Entities

- Energy separation is denoted by Δ_o (the subscript o is for octahedral). This is also known as crystal field splitting energy (CFSE).
- The energy of the two e_g orbitals (higher energy orbitals) will increase by (3/5) Δ_o and that of the three t_{2g} (lower energy orbitals) will decrease by (2/5) Δ_o.

- If $\Delta_o < P$, the fourth electron enters one of the e_g, orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.



- If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.
- Where, P represents the energy required for electron pairing in a single orbital. (Pairing energy)

Crystal Field Splitting in Tetrahedral Coordination Entities

In tetrahedral coordination entities, $\Delta_t = (4/9)\Delta_o$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and therefore, low spin configurations are rarely observed. Due to less crystal field stabilisation energy, it is not possible to pair electrons and so all the tetrahedral complexes are high spin.

Spectrochemical Series

An arrangement of ligands in order of increasing crystal field strength is spectrochemical series.

$I^- < Br^- < Cl^- < F^- < H_2O < C_2O_4^{2-} < NH_3 < en < NO_2^- < CN^- < CO$

Colour in Coordination Compounds

In complex compounds d-orbitals split in two sets t_{2g} and e_g. These have different energies. The difference in energies lies in visible region and electron jump from ground state t_{2g} level to higher state e_g level.

This is known as d–d transition and is responsible for colour of coordination compounds. d–d transition takes place in d^1 to d^9 ions, so the ions having d^1 to d^9 configuration are coloured.

On the other hand, the ions with d^0 and d^{10} configuration do not show d–d transition.

Stability Constants and Stability of Complexes

Stability of a complex can be expressed in terms of stability constant, k. If the complex is ML_n and β_n is the overall formation constant, then

$$M + nL \rightleftharpoons ML_n$$

$$\beta_n = \frac{[ML_n]}{[M][L]^n} = k_1 \times k_2 \times k_3 \dots k_n$$

$k_1, k_2, \dots k_n$ are called stepwise formation constants. [Alternatively $1/k$ is known as instability constant.

Factors Affecting Stability of Complexes

The strength of a complex ion depends upon the following factors

(i) **Higher charge** of the central metal ion *i.e.*, greater ionic potential $\left(\frac{\text{ionic charge}}{\text{ionic radius}}\right)$ and greater is the stability.

(ii) **Greater base strength** of the ligand, greater will be the stability.

(iii) **Ring formation** (chelation) in structure of the complexes is the chief factor, which **increases** the stability of the complexes in solution.

(iv) If a multidentate ligand happens to be cyclic without any steric effects, a further increase in stability occurs. This is called **macrocyclic effect.**

Importance and Applications of Coordination Compounds

(i) Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.

(ii) Some important extraction processes of metals, like those of silver and gold make use of complex formation.

(iii) Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel (Mond's process).

(iv) Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, Wilkinson catalyst, is used for the hydrogenation of alkenes.

(v) Metals present in toxic proportions in animals and plants are removed by chelate therapy, *e.g.*, Cu and Fe are removed by D-penicillamine and desferrioxime-B.

Organometallic Compounds

- Organometallic compounds contain atleast one metal-carbon bond. These are of three types, *viz*, σ-bond (*e.g.*, $(C_2H_5)_2Zn$, $(CH_3)_3Al$], π-bonded (Zeisse's salt, ferrocene) and mixed or σ-and π-bonded (*e.g.*, $Fe(CO)_5$, $[Ni(CO)_4]$).
- π-acid ligands have lone pair of electrons as well as π or $\overset{*}{\pi}$ molecular orbitals. They form σ coordinate bond through lone pair and also form π bond by accepting an appreciable amount of π electron density from metal atom into empty π or $\overset{*}{\pi}$ orbital. *e.g.*, CO is a good π-acceptor (Lewis acid).
- In Zeise's salt, ethylene acts as ligand but it does not have a lone pair of electrons.
- Oxidation state of Fe in ferrocene is Fe^{2+}. In this compound there are two cyclopentadienyl anion ($C_5H_5^-$) and iron is sandwiched between two aromatic rings.

Practice Zone

DAY 24

1. The coordination number of copper in cuprammonium sulphate is

(a) 2 (b) 3 (c) 4 (d) 6

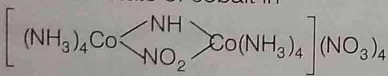
2. Which of the following is not expected to show paramagnetism ?

(a) $[Ni(H_2O)_6]^{2+}$ (b) $Ni(CO)_4$
(c) $[Ni(NH_3)_4]^{2+}$ (d) $[Co(NH_3)_6]^{2+}$

3. Which of the following ligands is bidentate?

(a) EDTA (b) Ethylenediamine
(c) Acetate (d) Pyridine

4. The oxidation state of cobalt in



$\left[(NH_3)_4Co\overset{NH}{\underset{NO_2}{\diamond}}Co(NH_3)_4\right](NO_3)_4$ is

(a) 2 (b) 3
(c) 4 (d) 6

5. The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)]^{3-}$, $[Co(NH_3)_6]^{3-} - [Co(H_2O)_6]^{3+}$ **[NCERT Exemplar]**

(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3+}$
(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$
(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$
(d) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

6. The effective atomic number of Cr (atomic no. 24) in $[Cr(NH_3)_6]Cl_3$ is

(a) 35 (b) 27 (c) 33 (d) 36

7. The number of *d*-electrons in $[Cr(H_2O)_6]^{3+}$ [atomic no. of Cr = 24] is

(a) 2 (b) 3
(c) 4 (d) 5

8. $[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4ClNO_2]Cl$ exhibit which type of isomerism?

(a) Geometrical (b) Optical
(c) Linkage (d) Ionisation

9. Ammonia will not form complex ions with

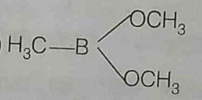
(a) Ag^+ (b) Cd^{2+}
(c) Cu^{2+} (d) Pb^{2+}

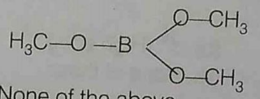
10. In the compound lithiumtetrahydroaluminate, the ligand is

(a) H^+ (b) H
(c) H^- (d) None of these

11. Which of the following is an organometallic compound ?

(a) $C_2H_5 - Zn - C_2H_5$

(b)


(c)


(d) None of the above

12. The number of geometrical isomers of the complex $[Co(NO_2)_3(NH_3)_3]$ is

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

13. According to EAN rule, how many CO groups should be attached to Fe?

(a) 4 (b) 5
(c) 6 (d) 8

14. The complex $CoCl_3 \cdot 3NH_3$ ionises to form

(a) 2 Cl^- ion (b) 1 Cl^- ion
(c) 3 Cl^- ion (d) no Cl^- ion

15. The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species? **[NCERT Exemplar]**

(a) $[Fe(CO)_5]$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Fe(C_2O_4)_3]^{3-}$ (d) $[Fe(H_2O)_6]^{3+}$

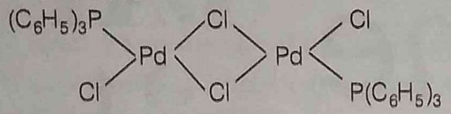
16. Which of the following complexes doesn't have d^2sp^3 hybridisation ?

(a) $[Cr(NH_3)_6]^{3+}$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Co(NH_3)_6]^{3+}$ (d) $[Co(H_2O)_6]^{3+}$

17. $CuSO_4$ reacts with KCN solution and forms

(a) $Cu(CN)$ (b) $Cu(CN)_2$
(c) $K_3[Cu(CN)_4]$ (d) $K_4[Cu(CN)_6]$

18. IUPAC name for



(a) chlorotriphenylphosphine palladium (II)-μ-dichloro chlorotriphenyl phosphine palladium (II)
(b) chlorotriphenylphosphine palladium(III)–μ – dichlorochlorotriphenyl phosphine palladium (II)
(c) triphenylphosphinechloro palladium (II) –μ – dichlorido triphenylphosphinechloro palladium (III)
(d) triphenylphosphinechloro palladium (III)–μ– dichlorotriphenylphosphinechloro palladium (III)

19. How many moles of AgCl would be obtained, when 100 mL of 0.1 M $Co(NH_3)_5Cl_3$ is treated with excess of $AgNO_3$?

(a) 0.01 (b) 0.02
(c) 0.03 (d) None of these

20. Which of the following liquids cannot show linkage isomerism?

(a) NO_2^- (b) SCN^- (c) CN^- (d) NH_3

21. Which of the following sub-shell form an octahedral complex?

(a) d^4 (Low spin) (b) d^8 (High spin)
(c) d^6 (High spin) (d) None of these

22. What is the ratio of uncomplexed to complexed Zn^{2+} ion in a solution that is 10 M in NH_3, if the stability constant of $[Zn(NH_3)_4]^{2+}$ is 3×10^9?

(a) 3.3×10^{-9} (b) 3.3×10^{-11}
(c) 3.3×10^{-14} (d) 3×10^{-13}

23. If excess of $AgNO_3$ is added to 100 mL of a 0.024 M solution of dichlorobis (ethylene diamine) cobalt (III) chloride how many moles of AgCl be precipitated?

(a) 0.0012 (b) 0.0016
(c) 0.0024 (d) 0.0048

24. Among the following which is not the π-bonded organometallic compound?

(a) $K[PtCl_3(\eta^2-C_2H_4)]$ (b) $Fe(\eta^5-C_5H_5)_2$
(c) $(CH_3)_4Sn$ (d) $Cr(\eta^6-C_6H_6)_2$

25. Consider the following complexes

1. K_2PtCl_6
2. $PtCl_4 \cdot 2NH_3$
3. $PtCl_4 \cdot 3NH_3$
4. $PtCl_4 \cdot 5NH_3$

Their respective electrical conductances in aqueous solutions are

(a) 256, 0, 97, 404 (b) 404, 0, 97, 256
(c) 256, 97, 0, 404 (d) 404, 97, 256, 0

26. The complex $[Fe(H_2O)_5NO]^{2+}$ is formed in the brown ring test for nitrates when freshly prepared $FeSO_4$ solution is added to aqueous solution of NO_3^- followed by addition of conc. H_2SO_4. Select the correct statement about this complex.

(a) Colour change is due to charge transfer
(b) It has iron in +1 oxidation state and nitrosyl as NO^+
(c) It has magnetic moment of 3.87 BM confirming three unpaired electrons in Fe
(d) All the above are correct statements.

27. Ferrocene is an example of

(a) sandwiched complex
(b) pi-bonded complex
(c) a complex in which all the five carbon atoms of cyclopentadiene anion are bonded to the metal
(d) All of the above

Directions (Q. Nos. 28 to 30) *The octahedral complex ions* $[FeCl_6]^{3-}$ *and* $[Fe(CN)_6]^{3-}$ *are both paramagnetic but the former is high spin and the latter is low spin.*

28. High spin complex $[FeCl_6]^{3-}$ has the *d*-configuration as

(a) $t_{2g}^3\ e_g^2$ (b) t_{2g}^5
(c) $t_{2g}^2\ e_g^3$ (d) e_g^5

29. Low spin complex $[Fe(CN)_6]^{3-}$ has the *d*-configuration as

(a) $t_{2g}^3\ e_g^2$ (b) t_{2g}^5
(c) $t_{2g}^2\ e_g^3$ (d) e_g^5

30. Unpaired electrons in $[FeCl_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ are respectively

(a) 5, 2 (b) 5, 1
(c) 3, 2 (d) 2, 3

Directions (Q. Nos. 31 and 32) *A research guide instructed his two students to synthesize complex*

$$[Co(NH_3)_5(NO_2)]Cl_2$$

They synthesised the complexes with identical molecular formula, molar mass, geometry, conductance and spin, but they differed in colour. Based on the above facts answer the following questions.

31. The difference in colour is due to

(a) optical isomerism
(b) geometrical isomerism
(c) linkage isomerism
(d) nuclear isomerism

32. Which of the ligands can show ambident property?

(a) NO_2^- (b) NH_3
(c) H_2O (d) CO_3^{2-}

Directions (Q. Nos. 33 to 36) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

33. Statement I $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.

Statement II The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons.

34. Statement I The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically inactive.

Statement II Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry.

35. Statement I The coordination number of complex in $[Zn(OH)_3]^-$, $[Fe(CO)_5]$ and $[TaF_8]^{3-}$ is three, five and eight respectively.

Statement II Coordination number always represents the number of ligands attached on central metal atom.

36. Statement I Complexes of type MA_6 and MA_5B do not show geometrical isomerism.

Statement II Geometrical isomerism is not shown by complexes of coordination number 2 and 3.

37. The value of CFSE for complex ion $[CoCl_6]^{4-}$ is 18000 cm^{-1}. The CFSE for $[CoCl_4]^{2-}$ complex ion will be

(a) 18000 cm^{-1} (b) 16000 cm^{-1}
(c) 8000 cm^{-1} (d) 2000 cm^{-1}

38. For an octahedral complex, which of the following *d*-electron configuration will give maximum CFSE ?

(a) High spin d^6 (b) Low spin d^4
(c) Low spin d^5 (d) High spin d^7

39. A complex is prepared by mixing $CoCl_3$ and NH_3 in the molar ratio 1 : 4. 0.1 M solution of this complex was found to freeze at −0. 372° C. What is the formula of the complex ?

$[K_f(\text{water}) = 1.86° \text{ C / m}]$

(a) $[Co(NH_3)_4Cl_2]Cl$ (b) $[Co(NH_3)_5Cl]Cl_2$
(c) $[Co(NH_3)_3Cl_3]$ (d) $[Co(NH_3)_6]Cl_3$

40. An aqueous solution of an inorganic salt (X), when added to an aqueous solution of barium chloride, a precipitate insoluble in dil HCl is obtained. Addition of excess of KI to X gives a brown precipitate which turns white on addition of excess of hypo. With an aqueous solution of potassium ferrocyanide, a chocolate coloured precipitate is formed. Xi s

(a) $Cu\,(NH_3)_4\,SO_4$ (b) $CuSO_4 \cdot 5H_2O$
(c) $ZnSO_4 \cdot 5H_2O$ (d) $AgNO_3$

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41. The magnetic moment of the complex anion $[Cr(NO)(NH_3)(CN)_4]^{2-}$ is **[JEE Main Online 2013]**

(a) 5.91 BM (b) 3.87 BM (c) 1.73 BM (d) 2.82 Bm

42. Which of the following complex species is not expected to exhibit optical isomerism? **[JEE Main Online 2013]**

(a) $[Co(en)_3]^{3+}$ (b) $[Co(en)_2\,Cl_2]^+$
(c) $[Co\,(NH_3)_3Cl_3]$ (d) $[Co(en)(NH_3)Cl_2]^+$

43. In which of the following octahedral complex species the magnitude of Δ_o will be maximum? **[JEE Main Online 2013]**

(a) $[Co(H_2O)_6]^{2+}$ (b) $[Co(CN)_6]^{3-}$
(c) $[Co(C_2O_4)_3]^{3-}$ (d) $[Co(NH_3)_6]^{3+}$

44. Which of the following is diamagnetic? **[JEE Main Online 2013]**

(a) $[Fe(CN)_6]^{3-}$ (b) $[Co(OX)_3]^{3-}$ (c) $[FeF_6]^{3-}$ (d) $[Co(F_6)]^{3-}$

45. Which of the following statements is incorrect ? **[JEE Main Online 2013]**

(a) Fe^{3+} ion also gives blood red colour with SCN^- ion
(b) Fe^{3+} ion gives red colour with SCN^- ion
(c) On passing H_2S into Na_2ZnO_2 solution, a white ppt of ZnS is formed
(d) Cupric ion reacts with excess of ammonia solution to give deep blue colour of $[Cu(NH_3)_4]^{2+}$ ion

46. Type of isomerism which exists between $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ is **[JEE Main Online 2013]**

(a) linkage isomerism (b) coordination isomerism
(c) ionisation isomerism (d) solvate isomerism

47. Which of the following complex species is not expected to exhibit optical isomerism? **[IIT JEE 2013]**

(a) $[Co[en]_2Cl_2]^+$ (b) $[Co[NH_3]_3Cl_3]$
(c) $[Co[Cn](NH_3)_2\,Cl_2]^+$ (d) $[Co(en)_3]^{3+}$

48. $NiCl_2[P(C_2H_5)_2(C_2H_5)]_2$ exhibit temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and damagnetic states are respectively **[IIT JEE 2012]**

(a) tetrahedral and tetrahedral
(b) square planar and square planar
(c) tetrahedral and square planar
(d) square planar and tetrahedral

49. Which among the following will be named as dibromidobis-(ethylenediamine) chromium (III) bromide? **[AIEEE 2012]**

(a) $[Cr(en)_3]Br_3$ (b) $[Cr(en)_2Br_2]Br$
(c) $[Cr(en)Br_4]^-$ (d) $[Cr(en)Br_2]Br$

50. The volume (in mL) of 0.1M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to **[IIT JEE 2011]**

(a) 3 (b) 4
(c) 5 (d) 6

51. Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is wrong? **[AIEEE 2011]**

(a) The complex involves d^2sp^3 hybridization and is octahedral in shape.
(b) The complex is paramagnetic.
(c) The complex is an outer orbital complex.
(d) The complex gives white precipitate with silver nitrate solution.

52. The magnetic moment (spin only) of $[NiCl_4]^{2-}$ is **[AIEEE 2011]**

(a) 1.82 BM (b) 5.46 BM
(c) 2.82 BM (d) 1.41 BM

53. Which one of the following has an optical isomer?
(en = ethylenediamine) **[AIEEE 2010]**

(a) $[Zn(en)(NH_3)_2]^{2+}$ (b) $[Co(en)_3]^{3+}$
(c) $[Co(H_2O)_4(en)]^{3+}$ (d) $[Zn(en)_2]^{2+}$

54. Which of the following pairs represents linkage isomers? **[AIEEE 2009]**

(a) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
(b) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$
(c) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$
(d) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

55. The coordination number and the oxidation state of the element '*E*' in the complex $[E(en)_2(C_2O_4)]NO_2$ are respectively, [where, en is ethylene diamine] **[AIEEE 2008]**

(a) 6 and 2 (b) 4 and 2
(c) 4 and 3 (d) 6 and 3

56. In which of the following octahedral complexes of Co(at. no. 27), will the magnitude of Δ_o be the highest? **[AIEEE 2008]**

(a) $[Co(CN)_6]^{3-}$ (b) $[Co(C_2O_4)_3]^{3-}$
(c) $[Co(H_2O)_6]^{3-}$ (d) $[Co(NH_3)_6]^{3+}$

57. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes are respectively, **[IIT JEE 2008]**

(a) sp^3, sp^3 (b) sp^3, dsp^2
(c) dsp^2, sp^3 (d) dsp^2, dsp^2

58. Which one of the following has a square planar geometry? **[AIEEE 2007]**

(At. no. Co = 27, Ni = 28, Fe = 26, Pt = 78)
(a) $[CoCl_4]^{2-}$ (b) $[FeCl_4]^{2-}$
(c) $[NiCl_4]^{2-}$ (d) $[PtCl_4]^{2-}$

59. Among the following metal carbonyls, the C—O bond order is lowest in **[IIT JEE 2007]**

(a) $[Mn(CO)_6]^+$ (b) $[Fe(CO)_5]$
(c) $[Cr(CO)_6]$ (d) $[V(CO)_6]^-$

60. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in the alkaline solutions but not in acidic solutions. What is the reason for it ? **[AIEEE 2003]**

(a) In acidic solutions hydration protects copper ions
(b) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available
(c) In alkaline solutions insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali
(d) Copper hydroxide is an amphoteric substance

Answers

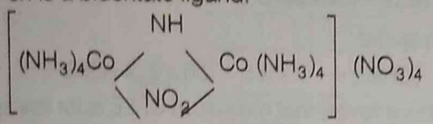
1. (c)	**2.** (b)	**3.** (c)	**4.** (b)	**5.** (b)	**6.** (c)	**7.** (b)	**8.** (d)	**9.** (d)	**10.** (c)
11. (a)	**12.** (a)	**13.** (b)	**14.** (d)	**15.** (c)	**16.** (d)	**17.** (c)	**18.** (a)	**19.** (b)	**20.** (d)
21. (a)	**22.** (c)	**23.** (c)	**24.** (c)	**25.** (a)	**26.** (d)	**27.** (d)	**28.** (a)	**29.** (b)	**30.** (b)
31. (c)	**32.** (a)	**33.** (a)	**34.** (a)	**35.** (c)	**36.** (b)	**37.** (c)	**38.** (c)	**39.** (a)	**40.** (b)
41. (c)	**42.** (c)	**43.** (a,b)	**44.** (b)	**45.** (a)	**46.** (a)	**47.** (b)	**48.** (c)	**49.** (b)	**50.** (d)
51. (c)	**52.** (c)	**53.** (b)	**54.** (b)	**55.** (d)	**56.** (a)	**57.** (b)	**58.** (d)	**59.** (b)	**60.** (b)

Hints & Solutions

1. Cuprammonium sulphate is $[Cu(NH_3)_4]SO_4$. CN of Cu is four.

2. $Ni(CO)_4$ is diamagnetic, all others are paramagnetic.

3. en is a bidentate ligand.

4. 

$$[(NH_3)_4Co(\mu\text{-}NH)(\mu\text{-}NO_2)Co(NH_3)_4](NO_3)_4$$

$\because \quad (4\times 0)+x+(1\times -1)+(1\times -1)\times x+(4\times 0)+(4\times -1)=0$

$\therefore \quad x=+3$

5. The CFSE of the ligands in the order $H_2O < NH_3 < CN^-$

Therefore, wavelengths absorbed will be in the opposite order as $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

6. EAN in $[Cr(NH_3)_6]Cl_3$ is EAN $= 24-3+2\times 6 = 33$

7. $[Cr(H_2O)_6]^{3+}$ has Cr^{3+} ion with 3 unpaired electrons in 3*d* orbitals.

8. Ionisation isomerism is shown.

9. NH_3 does not form complex with Pb^{2+} as it is not a *d*- block element.

10. In $Li[AlH_4]$, H^- is the ligand.

11. An organometallic compound is one, which contains atleast one metal-carbon bond. In $B(OCH_3)_3$ and $CH_3B(OCH_3)_2$ there is no carbon atom that linked directly to a metal.

12. Facial and meridonial the two geometrical isomers are possible.

13. Atomic number of Fe = 26

Atomic number of next noble gas = 36

$\therefore$ Number of electrons to be provided by ligands $= 36-26 = 10$

$\because$ Each CO group provides 2 electrons,

$\therefore$ Number of CO groups attached to Fe = 5

14. The coordination number of Co is 6, thus the complex is $[Co(NH_3)_3Cl_3]$. Since, no Cl^- ion is present outside the coordination sphere, no Cl^- ion is obtained after ionisation.

15. $C_2O_4^{2-}$ is didentate ligand that forms chlate.

16. H_2O provides a weak ligand field, hence unpaired electrons of 3*d* orbital can't be paired up, hence sp^3d^2 hybridisation.

17. $2CuSO_4 + 10KCN \longrightarrow 2K_3[Cu(CN)_4] + (CN)_2 + 2K_2SO_4$

18. The IUPAC name of the compound is chlorotriphenylphosphine palladium (II)- μ- dichloro chlorotriphenylphosphinepalladium (II).

19. $Co(NH_3)_5Cl_3$ is an octahedral complex ionising in aqueous solution as :

$$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$$

Moles of $[Co(NH_3)_5Cl]Cl_2 = \dfrac{0.1}{1000}\times 100 = 0.01$ mol

Moles of AgCl formed = 2 × moles of Cl^- in complex

$= 0.01\times 2 = 0.02$ mol

20. NH_3 cannot show linkage isomerism as it does not contain two donor atoms.

21. d^4 low spin complex will have two *d*-orbitals vacant required for d^2sp^3 hybridisation to give an octahedral complex.

22. $Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$

$$K_f = \frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}][NH_3]^4} = 3\times 10^9$$

$$\therefore \quad \frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}]} = [NH_3]^4 \times 3\times 10^9$$

$$\therefore \quad \frac{[Zn^{2+}]}{[Zn(NH_3)_4]^{2+}} = 3.3\times 10^{-14}$$

23. 100 mL of 0.024 M = 0.0024 mole of the complex.

Complex is $[Co(en)_2Cl_2]Cl$ and thus, one Cl^- is formed per mol of the complex which gives 1 mole of AgCl.

Hence, AgCl formed = 0.0024 mol.

24. $(CH_3)_4Sn$ is a σ-bonded organometallic compound.

25. Greater the number of ions produced greater the conductance.

1. $K_2[PtCl_6] = 2K^+ + [PtCl_6]^{2-}$ (3 ions)
2. $PtCl_4\cdot 2NH_3 \rightleftharpoons [Pt(NH_3)_2Cl_4] \longrightarrow$ no ions (least)
3. $[Pt(NH_3)_3Cl_3]Cl \rightleftharpoons [Pt(NH_3)_3Cl_3] + Cl^-$ (2 ions)
4. $[Pt(NH_3)_5Cl]Cl_3 \rightleftharpoons [Pt(NH_3)_5Cl] + 3Cl^-$

(4 four ions maximum)

26.

Fe^{2+} =

$3d^6$				
⇅	↑	↑	↑	↑

$$\left.\begin{aligned} NO &\longrightarrow NO^+ + e^- \\ Fe^{2+} + e^- &\longrightarrow Fe^+ \end{aligned}\right] \text{Charge transfer}$$

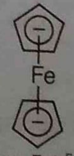
$\therefore$

Fe^+ =

$3d^7$				
⇅	⇅	↑	↑	↑

Thus, all the given options are correct.

27. Ferrocene is a sandwich complex compound in which all the five carbon atoms of ferropentadiene anions are linked to the metal (pi-bonds).



Ferrocene, $Fe(\eta^5\text{–}C_5H_5)$

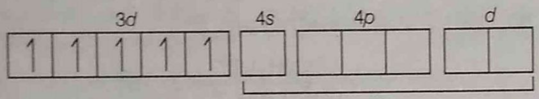
28. In $[FeCl_6]^{3-}$ complex, Cl^- is a weak field ligand. It do not cause pairing of electrons in 3*d* subshell of Fe^{3+}. Hence, configuration is $t_{2g}^3 e_g^2$.

29. In $[Fe(CN)_6]^{3-}$, Fe is also in Fe^{3+} oxidation state but CN^- is a strong field ligand. It causes pairing of electrons in 3*d* orbitals. Hence, configuration is t_{2g}^5.

30. ${}_{26}Fe = 1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6, 3d^6, 4s^2$

$Fe^{3+} = 1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6\, 3d^5, 4s^0$

In the formation of $FeCl_6^{3-}$



six sp^3d^2 hybrid orbitals

(Cl^- do not cause pairing because it is a weak field ligand; no. of unpaired electrons are five.

On the other hand, in $Fe(CN)_6^{3-}$ complex, CN^- is a strong field ligand, it causes pairing so the number of unpaired electron is one.

31. The difference in colour is due to the formation of linkage isomers.

32. NO_2^- is an ambidentate ligand. It can ligate to metal atom or ion either through –O– or –N– (nitro or nitrito respectively.)

33. $[Fe(H_2O)_5NO]SO_4$; oxidation state of Fe is

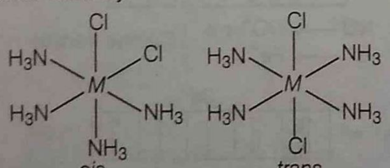
$$x + 5 \times (0) + 1 + (-2) = 0$$

$$x = +1$$

$$Fe^+ = [Ar]\, 3d^6 4s^1$$

NO^+ causes pairing of 4*s* electron inside. Thus, the configuration is $3d^7$ and number of unpaired electrons = 3.

34. The *cis* and *trans* both forms of complex $[M(NH_3)_4Cl_2]$ are optically inactive. There are plane of symmetry in addition to that there is alternate axis of symmetry which also causes their optical inactivity.



cis *trans*

35. In bidentate ligand, it represents number of coordinate bonds.

36. Both are facts.

37. $$\Delta_t = \frac{4}{9} \times \Delta_o = \frac{4}{9} \times 18000 = 8000 \text{ cm}^{-1}$$

38. $\Delta_o = -0.4 \times n_{t_{2g}} + 0.6 \times n_{e_g}$

[where, n = number of electrons]

(a) For high spin d^6

$$\Delta_o (\text{CFSE}) = -0.4 \times 4 + 0.6 \times 2 = -0.4$$

(b) For low spin d^4

$$\Delta_o (\text{CFSE}) = -0.4 \times 4 + 0.6 \times 0 = -1.6$$

(c) For low spin d^5

$$\Delta_o (\text{CFSE}) = -0.4 \times 5 + 0.6 \times 0 = -2.0$$

(d) For high spin d^7

$$\Delta_o (\text{CFSE}) = -0.4 \times 5 + 0.6 \times 2 = -0.8$$

The calculations reveal that maximum CFSE is for low spin d^5 configuration.

39. $$\Delta T_f = K_f \times m = 1.86 \times 0.1 = 0.186° \text{ C}$$

Observed value of $\Delta T_f = 0.372\ °\text{C}$

As observed value of ΔT_f is double the theoretical value, this shows that each molecule of the complex dissociates to form two ions. Hence, formula is $[Co(NH_3)_4Cl_2]Cl$

40. $CuSO_4 + BaCl_2 \longrightarrow \underset{\text{insoluble in HCl}}{BaSO_4} + CuCl_2$

$2[Ar] = \longrightarrow \underset{\text{brown ppt.}}{Cu_2I_2} + 2K_2SO_4 + I_2$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

$$2CuSO_4 + K_4\, [Fe(CN)_6 \longrightarrow \underset{\text{(chocolate ppt.)}}{Cu_2\, [Fe(CN)_6]} + 2K_2SO_4$$

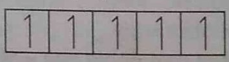
41. In $[Cr\,(NO)\,(NH_3)\,(CN)_4]^{2-}$,

Let the oxidation state of Cr is x.

$\therefore \quad x + (+1) + (0) + (-1)4 = -2$

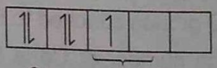
$x - 3 = -2$ or $x = 1$

$$Cr^+ = [Ar]\, 3d^5 4s^0$$



But CN^- and NO being strong field ligands pair up the unpaired electrons of Cr^+.

$$[Cr(NO)\,(NH_3)\,(CN)_4]^{2-}$$



One unpaired electron

$\therefore \quad n = 1$

Magnetic moment, $\mu = \sqrt{n\,(n+2)}$

$$= \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

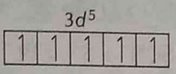
42. Optical isomerism is exhibited by only those complexes which lacks elements of symmetry.

$[Co(NH_3)_3Cl_3]$ shows facial as well as meridional isomerism. But both the forms contain plane of symmetry. Thus, this complex does not exhibit optical isomerism.

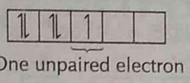
43. Δ_o magnitude depends upon the charge of central metal atom and strength of ligand. Among the given, CN^- is the strongest field ligand and in the complex $[Co\,(CN)_6]^{3-}$, Co is present as Co^{3+}. So, this complex will exhibit the maximum value of Δ_o.

44. If there is no unpaired electrons, the species is diamagnetic. Fe^{3+} and Co^{3+} both the ions have unpaired electrons in their ground state, but strong field ligands, like CN^-, OX if present, pair up the unpaired electrons resulting to reduce paramagnetism.

$Fe^{3+} = 3d^5 4s^0$

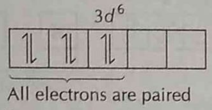


In $[Fe(CN^-)_6]^{3-}$,



$Co^{3+} = 3d^6 4s^0$

In $[Co(OX)_3]^{3-}$,

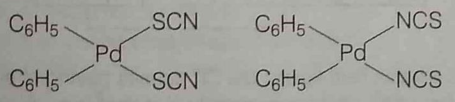


Thus, $[Co(OX)_3]^{3-}$ is a diamagnetic species as all the electrons are paired in it.

45. $Fe^{3+} + SCN^- \longrightarrow \underset{\text{red colour, not blood red colour}}{[Fe(SCN)]^{2+}}$

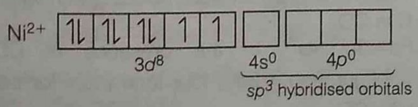
All other given statements are correct.

46. Given compound shows linkage isomerism.



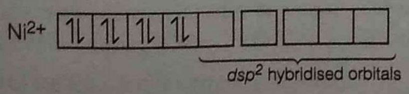
47. $[Co(NH_3)_3Cl_3]$ exists as facial and meridonial forms which are optical inactive.

48. In the given complex, $NiCl_2\{P(C_2H_5)_2(C_2H_5)\}_2$, nickel is in + 2 oxidation state.



For the given four-coordinated complex to be paramagnetic, it must possess unpaired electrons in the valence shell. Therefore, the four sp^3 hybrid orbitals of metal occupies four lone pairs. The geometry of paramagnetic complex must be tetrahedral.

On the other hand, for complex to be diamagnetic, there should not be any unpaired electrons in the valence shell. This condition can be fullfilled by pairing electrons of $3d$ orbitals.



The geometry of diamagnetic complex is square planar.

49. Two Br, two (en) and one Cr are parts of complex.

Charge on the complex is

$$\left.\begin{array}{l} 2\ (Br) = -2 \\ 2\ (en) = 0 \\ 1\ (Cr) = +3 \end{array}\right\} = +1$$

Thus, complex ion is $[Cr(en)_2Br_2]^+$.

Since, anion is bromide thus, complex is $[Cr(en)_2Br_2]$ Br.

50. m mol of complex = 30 × 0.01 = 0.3

1 mole of complex $[Cr(H_2O)_5Cl]\ Cl_2$ gives only two moles of chloride ion when dissolved in solution.

$$[Cr(H_2O)_5Cl]Cl_2 \longrightarrow [Cr(H_2O)_5Cl]^{2+} + 2Cl^-$$

mmol of Cl^- ion produced from its 0.3 mmol = 0.6

Hence, 0.6 mmol of Ag^+ would be required for precipitation.

$$0.6 \text{ mmol of } Ag^+ = 0.1\ M \times V \text{ (in mL)}$$

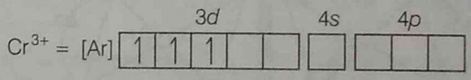
$$V = 6 \text{ mL}$$

51. $\underbrace{[Cr(NH_3)_6]}_{\text{coordinate sphere}} \cdot \underbrace{Cl_3}_{\text{ionisable}}$

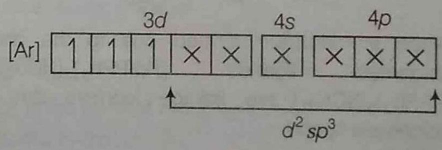
$$[Cr(NH_3)_6]^{3+} + 3Cl^- \xrightarrow{AgNO_3} \underset{\text{white precipitate}}{AgCl\downarrow}$$

$Cr(24) = [Ar]\ 3d^5\ 4s^1$

$Cr^{3+} = [Ar]3d^3\ 4s^0$



$[Cr(NH_3)_6]^{3+} =$



Indicates that lone-pair of NH_3 are donated to Cr.

(a) d^2sp^3-hybridisation, octahedral. Thus, correct.

(b) There are three unpaired electrons, hence paramagnetic. Thus, correct.

(c) d^2sp^3-inner orbital complex, thus incorrect.

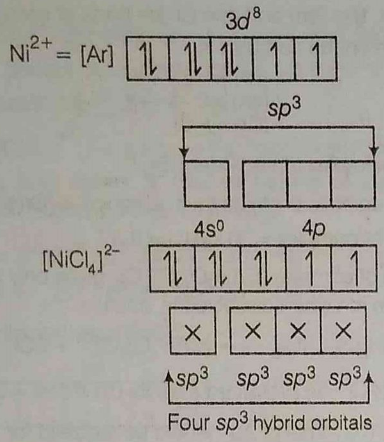
(d) Due to ionizable Cl^- ions, white precipitate with $AgNO_3$, thus correct.

52. $[NiCl_4]^{2-}$; oxidation number of Ni,

$$x - 4 = -2$$

$$\therefore \quad x = +2$$

$Ni_{(28)} = [Ar]\ 3d^8, 4s^2$



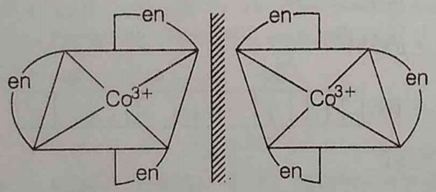
sp^3-hybrid orbitals, tetrahedral

Cl^- is a weak field ligand and thus unpaired electrons are not paired. Lone pairs from $4Cl^-$ are accommodated in four sp^3 hybrid orbitals. n = unpaired electrons = 2, paramagnetic

Magnetic moment (spin only)

$$= \sqrt{n(n+2)}\ \text{BM} = \sqrt{8}$$
$$= 2.828\ \text{BM}$$

53. Complex $[Co(en)_3]^{3+}$ has no plane of symmetry and centre of symmetry that's why it is optically active.



54. Linkage isomers are formed due to the presence of ambidentate ligands. $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$ are linkage isomers due to SCN, ambidentate ligand.

55. $\begin{matrix} CH_2{-}NH_2 \\ | \\ CH_2{-}NH_2 \end{matrix}$ is a bidentate ligand. $C_2O_4^{2-}$ is also a bidentate ligand. Hence, coordination number = 6

Complex can be ionised as

$$[E(en)_2(C_2O_4)]NO_2 \longrightarrow [E(en)_2(C_2O_4)]^+ + NO_2^-$$

Oxidation number $= x + 0 + (-2) = 1$

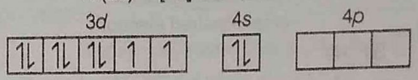
$\therefore \qquad x = 3$

56. CFSE (crystal field splitting energy) for octahedral complex, Δ_o depends on the strength of negative ligand. Spectrochemically, it has been found that the strength of splitting is as follows :

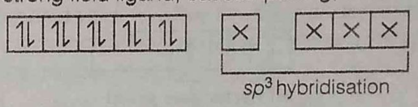
$$CO > \underline{CN^-} > \underline{NO_2^-} > en > \underline{NH_3} > py >$$
$$NCS^- > \underline{H_2O} > \underline{O^{2-}} > \underline{ox^{2-}} > OH^- > F^- >$$
$$Cl^- > SCN^- > S^{2-} > Br^- > I^-$$

57. In $[Ni(CO)_4]$, the oxidation state of Ni is zero.

$$Ni(28) = [Ar]\ 3d^8, 4s^2$$

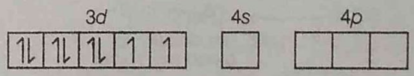


CO is strong field ligand, causes pairing, thus

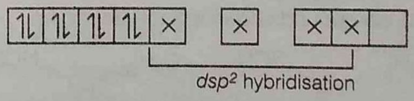


In $[Ni(CN)_4]^{2-}$, the oxidation state of Ni is +2.

$$Ni^{2+} = [Ar]\ 3d^8, 4s^0$$



CN^- is strong field ligand causes pairing, thus



58. Cl^- is a weak field ligand but Cl^- causes pairing of electrons with large Pt^{2+} and consequently give dsp^2 hybridisation and square planar geometry.

59. (a) $Mn^+ = 3d^5, 4s^1$; In the presence of CO, effective configuration $= 3d^6 4s^0$

Three lone pairs for back bonding with vacant orbital of C in CO.

(b) $Fe = 3d^6, 4s^2$; In the presence of CO, effective configuration $= 3d^8$, four lone pairs for back bonding with CO.

(c) $Cr = 3d^5, 4s^1$; effective configuration $= 3d^6$. Three lone pairs for back bonding with CO.

(d) $V^- = 3d^4, 4s^2$; effective configuration $= 3d^6$

Three lone pairs for back bonding with CO. Maximum back bonding in $Fe(CO)_5$, therefore, CO bond order is lowest here.

60. The pair of electrons present with nitrogen will not be available to be donated as H^+ will consume that one.

Unit Test 4
(Inorganic Chemistry)

DAY 25

1. Heating the pyrites in air for oxidation of sulphur is called
(a) slagging (b) smelting
(c) roasting (d) None of these

2. The process of isolation of metals by dissolving the ore in a suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called **[NCERT Exemplar]**
(a) Hydrometallurgy (b) Zone refining
(c) Electrorefining (d) Electrometallurgy

3. When a metal is to be extracted from its ore, if the gangue associated with the ore is silica, then
(a) a basic flux is needed
(b) an acidic flux is needed
(c) both basic and acidic flux are needed
(d) neither of them is needed

4. The final step for the extraction of copper from copper pyrite in Bessemer converter involves the reaction
(a) $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$
(b) $4Cu_2O + FeS \longrightarrow 8Cu + FeSO_4$
(c) $2Cu_2O + FeS \longrightarrow 4Cu + Fe + SO_2$
(d) $Cu_2S + 2FeO \longrightarrow 2Cu + 2Fe + SO_2$

5. van-Arkel method of purification of metals involves converting the metal to a
(a) volatile stable compound
(b) non-volatile stable compound
(c) volatile unstable compound
(d) None of the above

6. Wolframite ore is separated from tin stone ore by the process of
(a) calcination (b) electromagnetic process
(c) roasting (d) smelting

7. Slow acting nitrogenous fertiliser among the following is
(a) CaNCN (b) NH_2CONH_2 (c) KNO_3 (d) NH_4NO_3

8. Which of the following is correct for hydrogen?
(a) It has same electronegativity as halogens
(b) It has a very high ionisation potential
(c) It is always collected at cathode
(d) It can form bonds in +1 as well as −1 oxidation state

9. Which one of the following is a true peroxide?
(a) SO_2 (b) MnO_2 (c) NO_2 (d) BaO_2

10. Setting of plaster of paris is
(a) dehydration
(b) oxidation with atmospheric oxygen
(c) combination with atmospheric CO_2
(d) hydration to yield another hydrate

11. The most stable compound is **[NCERT Exemplar]**
(a) LiF (b) LiCl (c) LiI (d) LiBr

12. In which of the following processes fused sodium hydroxide is electrolysed at 330°C temperature for extraction of sodium?
(a) Castner's process (b) Cyanide process
(c) Down's process (d) Both (b) and (c)

13. The most acidic oxide is
(a) BeO (b) MgO
(c) CaO (d) BaO

14. Which is the poorest reducing agent?
(a) Atomic hydrogen
(b) Nascent hydrogen
(c) Dihydrogen
(d) All have same reducing strength

15. In Birkeland-Eyde process the raw material used is
(a) air (b) NO_2 (c) HNO_3 (d) NH_3

16. Which is used in the manufacture of safe matchsticks?
(a) Red phosphorus (b) Sulphur
(c) Selenium (d) White phosphorus

17. Action of conc. HNO_3 on metallic tin produces
(a) stannic nitrate (b) stannous nitrite
(c) metastannic acid (d) stannous nitrate

18. NH_3 on reaction with hypochlorite anion, can form
(a) NO (b) N_2H_4 (c) NH_4Cl (d) HNO_2

19. The pentavalency in phosphorus is more stable as compared to that of nitrogen even though they belong to the same group. It is due to

(a) inert nature of nitrogen
(b) reactivity of phosphorus
(c) larger size of phosphorus atom
(d) dissimilar electronic configuration

20. Oxygen is not evolved on reaction of ozone with

(a) H_2O_2 (b) Hg (c) SO_2 (d) KI

21. Conc. HNO_3 reacts with I_2 to give

(a) HI (b) HOI (c) HIO_3 (d) HIO_4

22. Which one of the following is formed by xenon?

(a) XeF_7 (b) XeF_4 (c) XeF_5 (d) XeF_3

23. Which one of the following oxides is ionic?

(a) MnO (b) CrO_3
(c) P_2O_5 (d) Mn_2O_7

24. What is the magnetic moment of $[FeF_6]^{3-}$?

(a) 4 (b) 5.49 (c) 2.32 (d) 5.92

25. Spiegeleisn is an alloy of

(a) Fe, Co and Cr (b) Fe, Co and Mg
(c) Fe, Mg and C (d) Fe, C and Mn

26. The number of moles of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate; $Fe(C_2O_4)$ in acidic solution is

(a) 1 (b) 2/5 (c) 3/5 (d) 4/5

27. Which of the following ions form most stable complex compound?

(a) Mn^{2+} (b) Ni^{2+}
(c) Fe^{2+} (d) Cu^{2+}

28. The electronic configuration of Cu (II) is $3d^9$ while that of Cu (I) is $3d^{10}$. Which of the following statement is correct? **[NCERT Exemplar]**

(a) Cu(II) is more stable
(b) Cu (II) is less stable
(c) Cu (I) and Cu (II) are equally stable
(d) Stability of Cu (I) and Cu (II) depends on the nature of Cu salts.

29. Which of the following is not true for ligand metal complex ?

(a) Highly charged ligand forms strong bonds.
(b) Greater the ionisation potential of central metal, the stronger is the bond.
(c) Larger the permanent dipole moment of ligand, the more stable is the bond.
(d) Larger the ligand, the more stable is the metal ligand bond.

30. The number of ions formed, when cuprammonium sulphate is dissolved in water, is

(a) zero (b) 1 (c) 2 (d) 4

31. Given the molecular formula of the hexa coordinated complexes
(A) $CoCl_3 \cdot 6NH_3$ (B) $CoCl_3 \cdot 5NH_3$ (C) $CoCl_3 \cdot 4NH_3$. If the number of coordinated NH_3 molecules in A, B and C respectively are 6, 5 and 4, primary valency in (A), (B) and (C) are

(a) 0, 1, 2 (b) 3, 2, 1 (c) 6, 5, 4 (d) 3, 3, 3

32. Ligands in complex compounds

(a) donate electron pair
(b) accept electron pair
(c) neither accept electron pair nor donate
(d) All of the above

33. Finely divided iron combines with CO to give

(a) $Fe(CO)_5$ (b) $Fe_2(CO)_6$ (c) $Fe(CO)_{12}$ (d) $Fe_2(CO)_9$

34. The IUPAC name of $K_2[Cr(CN)_2O_2(O)_2(NH_3)]$ is

(a) potassiumamminedicyanodioxoperoxo chromate (VI)
(b) potassiumamminecyanoperoxodioxo chromate (IV)
(c) potassiumamminecyanoperoxodioxo chromium (VI)
(d) potassiumamminecyanoperoxodioxo chromium (VI)

35. Change in composition of coordination sphere yields which type of isomer?

(a) Geometrical (b) Ionisation
(c) Optical (d) None of these

36. What mass of CaO will be required to remove the hardness of 1000 L of water containing 1.62 g of calcium bicarbonate per litre?

(a) 0.56 g (b) 560 g (c) 162 g (d) 56 g

37. In which of the following arrangements the order is not according to the property indicated against it?

(a) $Li < Mg < Ca$ (increasing reactivity with N_2)
(b) $Be < Mg < Ca < Sr$ (increasing basic nature)
(c) $BeO < MgO < CaO$ (increasing refractory properties)
(d) $BBr_3 > BCl_3 > BF_3$ (decreasing acidic nature)

38. The optically active compound of boron is

(a) borosalicylic acid (b) borax
(c) borazole (d) boron nitride

39. A black compound (*A*) in solid state is fused with KOH and $KClO_3$. The aqueous extract is green colour solution (*B*). On passing CO_2 gas through it, pink colour of (*C*) is noticed along with some black insoluble mass of *A*. The pink coloured solution is decolourised by Fe^{2+} in acidic medium. Identify *A*.

(a) MnO_2 (b) Fe_2O_3 (c) PbS (d) $ZnSO_4$

40. The dissociation of a complex may be expressed as $[ML_x]^{y+} \rightleftharpoons M^{y+} + xL$ and equilibrium constant of this dissociation equilibrium is known as instability constant, which is a measure of stability. Hence, identify which of the following complexes is most stable?

(a) $[Cu(CN)_2]^-$, $K_d = 1 \times 10^{-16}$ (b) $[Fe(CN)_6]^{4-}$, $K_d = 1 \times 10^{-37}$
(c) $[Fe(CN)_6]^{3-}$, $K_d = 1 \times 10^{-44}$ (d) $[Ag(CN)_2]^-$, $K_d = 1 \times 10^{-20}$

Directions (Q. Nos. 41 to 43) *The coordination number of* Ni^{2+} *is 4.*

$NiCl_2$ + KCN (excess) $\longrightarrow$ *A* (Cyano complex)

$NiCl_2$ + conc. HCl (excess) $\longrightarrow$ *B*(Chloro complex)

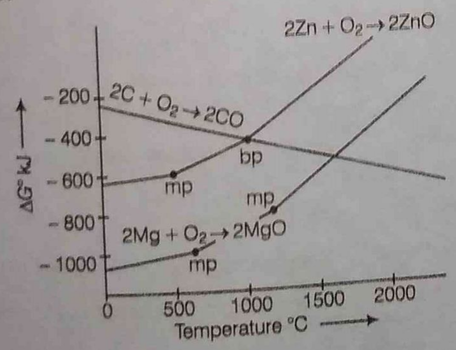
[IIT JEE 2006]

41. The IUPAC name of *A* and *B* are
(a) potassium tetracyanonickelate(II), potassium Tetrachloro nickelate (II)
(b) tetracyano potassiumnickelate(II), tetrachloro potassiumnickelate (II)
(c) tetracyanonickel (II), tetrachloronickel (II)
(d) potassiumtetracyanonickel (II), potassium tetrachloronickel (II)

42. Predict the magnetic nature of *A* and *B*.
(a) Both are diamagnetic
(b) *A* is diamagnetic and *B* is paramagnetic with one unpaired electron
(c) *A* is diamagnetic and *B* is paramagnetic with two unpaired electrons
(d) Both are paramagnetic

43. The hybridisation of *A* and *B* are
(a) dsp^2, sp^3 (b) sp^3, sp^3
(c) dsp^2, dsp^2 (d) sp^3d^2, d^2sp^3

Directions (Q. Nos. 44 to 46) *In the diagram points are melting and boiling points of the metal zinc and magnesium. $\Delta G°$ is a function of temperature for some reactions of extractive metallurgy.*



44. At what approximate temperature, zinc and carbon have equal affinity for oxygen?
(a) 1000°C (b) 1500°C
(c) 500°C (d) 1200°C

45. At this temperature, $\Delta G°$ of the reaction

$ZnO + C \longrightarrow Zn + CO$ is
(a) –ve (b) +ve
(c) zero (d) Nothing can be said

46. To make the following reduction process, spontaneous temperature should be

$ZnO + C \longrightarrow Zn + CO$
(a) <1000°C (b) >1100°C
(c) <500°C (d) >500°C but <1000°C

Directions (Q. Nos. 47 to 50) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I
(c) Statement I is true; Statement II is false
(d) Statement I is false; Statement II is true

47. Statement I $E°$ for Mn^{3+}/Mn^{2+} is more positive than Cr^{3+}/Cr^{2+}.
Statement II The third ionisation energy of Mn is larger than that of Cr.

48. Statement I $K_2Cr_2O_7$ is used as a primary standard in volumetric analysis.
Statement II It has a good solubility in water.

49. Statement I Silicones are hydrophobic in nature.
Statement II Si—O—Si linkages are moisture sensitive.

50. Statement I Potassium ferrocyanide and potassium ferricyanide both are diamagnetic.
Statement II The former does not have any unpaired electron.

Answers

1. (c)	**2.** (a)	**3.** (a)	**4.** (a)	**5.** (b)	**6.** (b)	**7.** (a)	**8.** (d)	**9.** (d)	**10.** (d)
11. (a)	**12.** (a)	**13.** (a)	**14.** (c)	**15.** (c)	**16.** (a)	**17.** (c)	**18.** (b)	**19.** (c)	**20.** (c)
21. (c)	**22.** (b)	**23.** (a)	**24.** (d)	**25.** (d)	**26.** (c)	**27.** (d)	**28.** (a)	**29.** (d)	**30.** (c)
31. (b)	**32.** (a)	**33.** (a)	**34.** (a)	**35.** (b)	**36.** (b)	**37.** (c)	**38.** (a)	**39.** (a)	**40.** (c)
41. (a)	**42.** (c)	**43.** (a)	**44.** (a)	**45.** (c)	**46.** (b)	**47.** (b)	**48.** (d)	**49.** (c)	**50.** (d)

Hints & Solutions

1. Heating the pyrites in air for oxidation of sulphur is called roasting. It is generally carried in a reverberatory furnace.

2. Hydrometallurgy is the technique used for the isolation of metals by dissolving the ore in a suitable reagent followed by the precipitation of the metal.

3. $$\underset{\text{acidic impurity}}{SiO_2} + \underset{\text{basic flux}}{CaO} \longrightarrow \underset{\text{slag}}{CaSiO_3}$$

4. In Bessemer converter, copper sulphide is partially oxidised to cuprous oxide which further reacts with remaining copper sulphide to form copper and SO_2.

$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$

5. $$Ti + 2I_2 \xrightarrow{500\,K} \underset{\substack{\text{volatile stable}\\ \text{compound}}}{TiI_4} \xrightarrow{1700\,K} \underset{\substack{\text{pure}\\ \text{metal}}}{Ti} + 2I_2$$

6. Wolframite ore $[FeWO_4]$ is present in tin stone as impurity and it has same mass per unit volume as that of tin stone, so it is separated by electromagnetic separation because wolframite is magnetic in nature, hence it gets attracted by magnet while tin stone does not.

7. CaNCN decomposes very slowly.

$$CaNCN + 2H_2O \longrightarrow CaCO_3 + NH_2CONH_2$$
$$NH_2CONH_2 + H_2O \longrightarrow CO_2 + 2NH_3$$
$$NH_3 \xrightarrow[\text{bacteria}]{\text{Nitrifying}} \text{Soluble nitrates} \longrightarrow \text{Plants}$$

8. Hydrogen forms bonds in +1 and –1 oxidation states.

9. BaO_2 is a true peroxide.

10. It is exothermic process.

$$CaSO_4 \cdot \frac{1}{2}H_2O \xrightarrow{H_2O} \underset{\text{orthorhombic}}{CaSO_4 \cdot 2H_2O} \xrightarrow{\text{Hardening}} \underset{\substack{\text{monoclinic}\\ \text{(gypsum)}}}{CaSO_4 \cdot 2H_2O}$$

11. Due to the small size of Li and F, LiF has highest lattice enthalpy and hence, most stable compound.

12. Castner's process is used to obtain Na by electrolysis of fused sodium hydroxide.

13. On moving down the group, basic character of oxides increases.

14. Because dihydrogen is less reactive.

15. In Birkeland-Eyde process NO is prepared commercially from air by liquification and fractional distillation which finally gives HNO_3.

16. Due to less reactivity, red phosphorus is used in the manufacture of safe matchsticks.

17. $$Sn + \text{conc. } 4HNO_3 \longrightarrow \underset{\substack{\text{metastannic}\\ \text{acid}}}{H_2SnO_3} + 4NO_2$$

18. $$\underset{\text{(excess)}}{2NH_3} + OCl^- \longrightarrow NH_2{-}NH_2 + NH_4Cl + OH^-$$

19. Pentavalency in P is more stable than N due to larger size of phosphorus atom.

20. $$3SO_2 + O_3 \longrightarrow 3SO_3$$

Whole oxygen of ozone is used up for oxidation.

21. $$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

22. XeF_2, XeF_4, XeF_6 are formed by xenon.

23. MnO is ionic due to lower oxidation state.

24. Fe^{3+} ion has five unpaired electrons.

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

25. Spiegeleisn is an alloy of Fe, C and Mn.

26. $$3MnO_4^- + 5\,[Fe^{2+} + C_2O_4^{2-}] + 24H^+ \longrightarrow 3Mn^{2+} + 5Fe^{3+} + 10CO_2 + 12H_2O$$

Thus, 5 moles of FeC_2O_4 are oxidised by 3 moles of $KMnO_4$, therefore 1 mole of FeC_2O_4 is oxidised by 3/5 mole of $KMnO_4$.

27. The magnitude of stability constants for some divalent metal ions of the first transition series with oxygen or nitrogen donor ligands increases in the order

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$$

28. Though Cu(I) possess $3d^{10}$ electronic configuration while that of Cu(I) has $3d^9$ configuration yet Cu (II) is more stable than Cu (I) due to greater effective nuclear change of Cu (II).

29. Higher the charge and smaller the size of ligand, more stable is the complex formed.

30. Cuprammonium salt is $[Cu(NH_3)_4]SO_4$

$$[Cu(NH_3)_4]SO_4 \rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

31. The complexes can be written as follows

$$[Co(NH_3)_6]Cl_3,\ [Co(NH_3)_5Cl]Cl_2,\ [Co(NH_3)_4Cl_2]\,Cl$$

32. Ligands in complex compounds donate electron pair.

33. $$Fe + 5\,CO \xrightarrow[\text{pressure}]{\text{Heat}} \underset{\text{iron penta carbonyl}}{[Fe(CO)_5]}$$

34. It is potassiumamminedicyanodiooxoperoxo chromate (VI).

35. Change in composition of coordination sphere yields ionisation isomers.

36. $$CaO + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + H_2O$$

For one litre water,

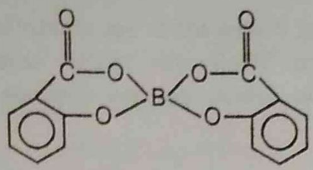
$$\text{Meq. of } CaO = \text{Meq. of } Ca(HCO_3)_2$$
$$\frac{w \times 1000}{56/2} = \frac{1.62 \times 1000}{162/2}$$
$$\therefore \quad w_{CaO} = 0.56\ g$$

Thus, CaO required for 10^3 L $H_2O = 0.56 \times 10^3 = 560$ g

37. Refractory property of alkaline earth metal oxides decreases on moving down the group. Thus, the correct order is

$$BeO > MgO > CaO$$

38. Borosalicylic acid is an optically active compound of boron.



39. $\underset{\text{(A) (black)}}{3MnO_2} + 6KOH + KClO_3 \xrightarrow{\Delta} \underset{\text{(B) (green)}}{3K_2MnO_4} + KCl + 3H_2O$

In the presence of CO_2, the medium becomes acidic.

$$\underset{(B)\ \text{(green)}}{3\,MnO_4^{2-}} + 4H^+ \longrightarrow \underset{(A)}{MnO_2} + \underset{(C)}{2MnO_4^-} + 2H_2O$$

$$\underset{(C)\ \text{(pink)}}{MnO_4^-} + 5Fe^{2+} + 8H^+ \xrightarrow{\Delta} Mn^{2+} + 5Fe^{3+} + 4H_2O$$

40. As dissociation constants of complexes are inversely proportional to their stability constants, their stability constants are given as

$[Cu(CN)_2]^-$ $K_S = \frac{1}{K_d} = 1\times10^{16}$

$[Fe(CN)_6]^{4-}$ $K_S = 1\times10^{37}$

$[Fe(CN)_6]^{3-}$ $K_S = 1\times10^{44}$

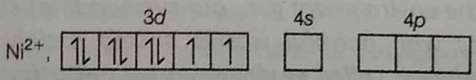
$[Ag(CN)_2]^-$ $K_S = 1\times10^{20}$

41. (i) $NiCl_2 + \underset{\text{excess}}{4KCN} \longrightarrow \underset{\substack{\text{potassium tetra}\\ \text{cyanonickelate (II)}\\ (A)\\ \text{(cyano complex)}}}{K_2[Ni(CN)_4]} + 2KCl$

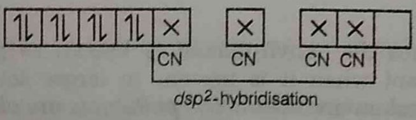
(ii) $NiCl_2 + \underset{\text{excess}}{4HCl}\ \text{(conc)} \longrightarrow \underset{\substack{\text{potassium tetra}\\ \text{chloronickelate (II)}\\ (B)\\ \text{(chloro complex)}}}{K_2[NiCl_4]} + 4HCN$

42. In cyano complex $K_2[Ni(CN)_4]$, complex ion is $[Ni(CN)_4]^{2-}$ and Ni is present as Ni^{2+} or Ni (II), so

$$Ni^{2+} = 1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^8, 4s^0$$



In $[Ni(CN)_4]^{2-}$ ion

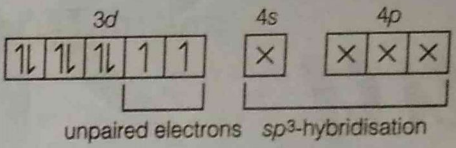


In it, unpaired electron is not present, so it is diamagnetic in character (square planar shape).

In chloro complex $K_2[Ni(Cl)_4]$, complex ion is $[Ni(Cl)_4]^{2-}$ and Ni is present as Ni^{2+} or Ni(II), so

$$Ni^{2+} = 1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^8, 4s^0$$

In $[Ni(Cl)_4]^{2-}$ ion, Ni^{2+} is present as such due to weaker ligand character of Cl^- ion. (Cl^- is weak field ligand). So, it is unable to pair up the electron and Ni^{2+} needs four empty orbitals to accomodate four Cl^- ligand. Thus, $[NiCl_4]^{2-}$ shows sp^3-hybridisation (tetrahedral shape).



Hence, due to presence of two unpaired electrons, it is paramagnetic in character.

45.

$$ZnO \longrightarrow Zn + \frac{1}{2}O_2;\ \Delta G°_1 = x$$

$$C + \frac{1}{2}O_2 \longrightarrow CO\ ;\ \Delta G°_2 = -x$$

$$ZnO + C \longrightarrow Zn + CO;\ \Delta G°_3 = 0$$

System is at equilibrium; $\Delta G_1^\circ = -\Delta G_2^\circ$

Hence, $\Delta G^\circ = 0$

46. This will be above a temperature when two curve intersect. Hence, > 1100°C.

47. Mn has more oxidation potential than Cr. It is present below Cr in electrochemical series. So, its reduction potential is less than that of Cr. The third ionisation energy for Mn is 3258 kJ mol^{-1} and for Cr is 2994 kJ mol^{-1}. So, both the statements are true but statement II is not a correct explanation of statement I.

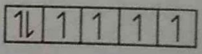
48. Potassium dichromate is used in volumetric analysis mostly in oxidation titration because it is not deliquescent. It forms compound with other elements and precipitate out. It is water soluble. So, the statement I and II both are true but statement II is not the explanation of statement I.

49. Silicones are insoluble in water and does not react with it. So, they are hydrophobic in nature. The crystal structure of silica has Si—O—Si linkage and it is extremely stable and considerable energy is required to break the silicon oxygen bonds in it. So, silicones are hard and have high melting point. Thus the statement I is true but statement II is false.

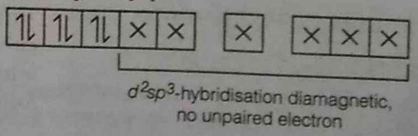
50. Potassium ferrocyanide is $K_4[Fe(CN)_6]$.

In it, Fe is present as Fe^{2+}.

$$Fe^{2+} = [Ar]\,3d^6$$

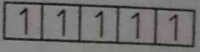


In $[Fe(CN)_6]^{4-}$ = [Ar]



Potassium ferricyanide is $K_3[Fe(CN)_6]$.
Fe is as Fe^{3+}.

$$Fe^{3+} = [Ar]\,3d^5$$



In $[Fe(CN)_6]^{3-}$ = [Ar]