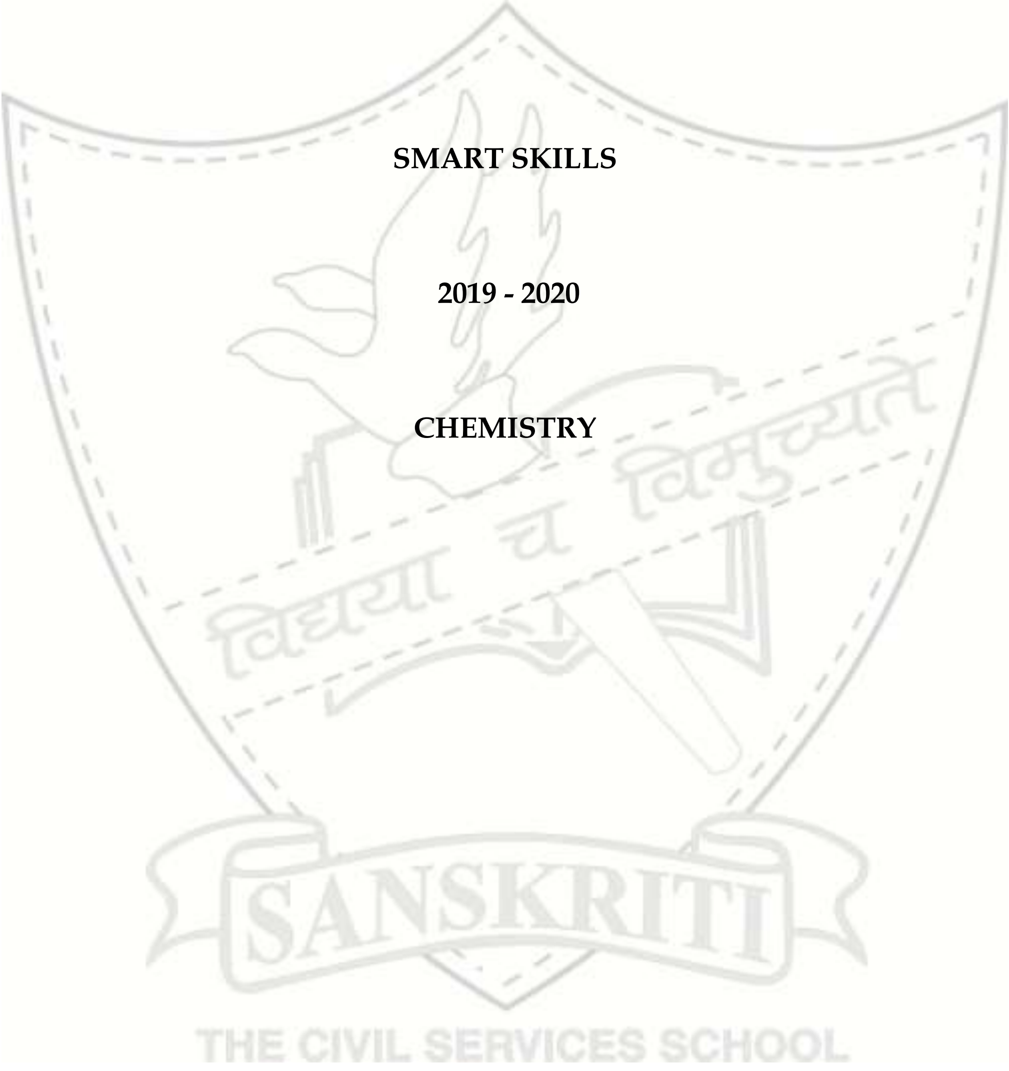


# SMART SKILLS

2019 - 2020

## CHEMISTRY

# INDEX

**CLASS XII (2019-20)**

**(THEORY)**

**Total Periods (For Theory -150 + For Practical -60)**

**Time: 3 Hours** **70 Marks**

| Unit No. | Title | No. of Periods | Marks |
|---|---|---|---|
| Unit I | Solutions | 10 | |
| Unit II | Electrochemistry | 12 | 23 |
| Unit III | Chemical Kinetics | 10 | |
| Unit IV | Surface Chemistry | 08 | |
| Unit V | General Principles and Processes of Isolation of Elements | 08 | |
| Unit VI | p -Block Elements | 12 | 19 |
| Unit VII | d -and f -Block Elements | 12 | |
| Unit VIII | Coordination Compounds | 12 | |
| Unit IX | Haloalkanes and Haloarenes | 10 | |
| Unit X | Alcohols, Phenols and Ethers | 10 | |
| Unit XI | Aldehydes, Ketones and Carboxylic Acids | 10 | |
| Unit XII | Organic Compounds containing Nitrogen | 10 | 28 |
| Unit XIII | Biomolecules | 12 | |
| Unit XIV | Polymers | 08 | |
| Unit XV | Chemistry in Everyday Life | 06 | |
| | **Total** | **150** | **70** |

**Unit I: Solutions** **10 Periods**

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, colligative properties - relative lowering of vapour pressure, Raoult's law, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, Van't Hoff factor.

**Unit II: Electrochemistry** **12 Periods**

Redox reactions, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell -electrolytic cells and Galvanic cells, lead accumulator, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibb’s energy change and EMF of a cell, fuel cells, corrosion.

**Unit III: Chemical Kinetics** **10 Periods**

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half life (only for zero and first order reactions), concept of collision theory (elementary idea, no mathematical treatment). Activation energy, Arrhenius equation.

**Unit IV: Surface Chemistry** **08 Periods**

Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, catalysis, homogenous and heterogenous activity and selectivity; enzyme catalysis colloidal state distinction between true solutions, colloids and suspension; lyophilic, lyophobic multimolecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation, emulsion - types of emulsions.

**Unit V: General Principles and Processes of Isolation of Elements** **08 Periods**

Principles and methods of extraction - concentration, oxidation, reduction - electrolytic method and refining; occurrence and principles of extraction of aluminium, copper, zinc and iron.

**Unit VI: p-Block Elements** **12 Periods**

**Group 16 Elements:** General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties, dioxygen: Preparation, Properties and uses, classification of Oxides, Ozone, Sulphur -allotropic forms; compounds of Sulphur: Preparation Properties and uses of Sulphur-dioxide, Sulphuric Acid: industrial process of manufacture, properties and uses; Oxoacids of Sulphur (Structures only).

**Group 17 Elements:** General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties; compounds of halogens, Preparation, properties and uses of Chlorine and Hydrochloric acid, interhalogen compounds, Oxoacids of halogens (structures only).

**Group 18 Elements:** General introduction, electronic configuration, occurrence, trends in physical and chemical properties, uses.

### Unit VII: "d" and "f" Block Elements 12 Periods

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first row transition metals - metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.

**Lanthanoids -** Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences.

**Actinoids -** Electronic configuration, oxidation states and comparison with lanthanoids.

### Unit VIII: Coordination Compounds 12 Periods

Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT; structure and stereoisomerism, importance of coordination compounds (in qualitative inclusion, extraction of metals and biological system).

### Unit IX: Haloalkanes and Haloarenes. 10 Periods

**Haloalkanes:** Nomenclature, nature of C -X bond, physical and chemical properties, mechanism of substitution reactions, optical rotation.

**Haloarenes:** Nature of C -X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only).

Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

### Unit X: Alcohols, Phenols and Ethers 10 Periods

**Alcohols:** Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol.

**Phenols:** Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols.

**Ethers:** Nomenclature, methods of preparation, physical and chemical properties, uses.

**Unit XI: Aldehydes, Ketones and Carboxylic Acids** **10 Periods**

**Aldehydes and Ketones:** Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes: uses.

**Carboxylic Acids:** Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

**Unit XII: Organic compounds containing Nitrogen** **10 Periods**

**Amines:** Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

**Cyanides and Isocyanides -** will be mentioned at relevant places in text.

**Diazonium salts:** Preparation, chemical reactions and importance in synthetic organic chemistry.

**Unit XIII: Biomolecules** **12 Periods**

**Carbohydrates -** Classification (aldoses and ketoses), monosaccahrides (glucose and fructose), D-L configuration oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose,glycogen); Importance of carbohydrates.

**Proteins -**Elementary idea of - amino acids, peptide bond, polypeptides, proteins, structure ofproteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only),denaturation of proteins; enzymes. Hormones - Elementary idea excluding structure.

**Vitamins -** Classification and functions.

**Nucleic Acids:** DNA and RNA.

**Unit XIV: Polymers** **08 Periods**

Classification - natural and synthetic, methods of polymerization (addition and condensation), copolymerization, some important polymers: natural and synthetic like polythene, nylon polyesters, bakelite, rubber. Biodegradable and non-biodegradable polymers.

**Unit XVI Chemistry in Everyday life** **06 Periods**

**Chemicals in medicines -** analgesics, tranquilizers antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistamines.

**Chemicals in food –** preservatives, artificial sweetening agents, elementary idea of antioxidants.

**Cleansing agents-** soaps and detergents, cleansing action.

## CHEMISTRY (CODE-043)

## QUESTION PAPER DESIGN
## CLASS - XII (2019-20)

**Time 3 Hours** **Max. Marks: 70**

| **S. No.** | **Typology of Questions** | **Very Short Answer (VSA) (1 mark)** | **Short Answer-I (SA-I) (2 marks)** | **Short Answer –II (SA-II) (3 marks)** | **Long Answer (L.A.) (5 marks)** | **Total Marks** | **% Weigh-tage** |
|---|---|---|---|---|---|---|---|
| 1 | Remembering (Knowledge based Simple recall questions, to know specific facts, terms, concepts, principles, or theories, Identify, define, or recite, information) | 2 | 1 | 1 | - | 7 | 10% |
| 2 | Understanding- (Comprehension -to be familiar with meaning and to understandconceptually, interpret, compare, contrast, explain,paraphrase information) | - | 3 | 4 | 1 | 21 | 30% |
| 3 | Application (Use abstract information in concrete situation, to apply knowledge to new situations, Use given content to interpret asituation, provide an | - | 3 | 4 | 1 | 21 | 30% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | example, or solve a problem) | | | | | | |
| 4 | High Order Thinking Skills ( Analysis &Synthesis- Classify,compare, contrast, or differentiate between different pieces of information, Organize and/or integrate unique pieces of information from a variety of sources) | 2 | - | 1 | 1 | 10 | 14% |
| 5 | **Evaluation and Multi Disciplinary-** (Appraise, judge, and/or justify the value or worth of a decision or outcome, or to predict outcomes based on values) | 1 | - | 2 | - | 11 | 16% |
| | **TOTAL** | **5x1=5** | **7x2=14** | **12x3=36** | **3x5=15** | **70(27)** | **100%** |

## QUESTION WISE BREAK UP

| Type of Question(s) | Mark(s) per Question | Total No. of Questions | Total Marks |
|---|---|---|---|
| VSA | 1 | 5 | 05 |
| SA-I | 2 | 7 | 14 |
| SA-II | 3 | 12 | 36 |
| LA | 5 | 3 | 15 |
| **Total** | | **27** | **70** |

1. **Internal Choice:** *There is no overall choice in the paper. However, there is an internal choice in two question of 1 mark weightage, two questions of 2 marks weightage, four questions of 3 marks weightage and all the three questions of 5 marks weightage.*

2. *The above template is only a sample. Suitable internal variations may be made for generating similar templates keeping the overall weightage to different form of questions and typology of questions same.*

## PRACTICALS

| **Evaluation Scheme for Examination** | **Marks** |
|---|---|
| Volumetric Analysis | 08 |
| Salt Analysis | 08 |
| Content Based Experiment | 06 |
| Project work | 04 |
| Class record and viva | 04 |
| **Total** | **30** |

## PRACTICALS SYLLABUS 60 Periods

**Micro-chemical methods are available for several of the practical experiments. Wherever possible, such techniques should be used.**

### A. Surface Chemistry

(a) Preparation of one lyophilic and one lyophobic sol
  Lyophilic sol - starch, egg albumin and gum
  Lyophobic sol - aluminium hydroxide, ferric hydroxide, arsenous sulphide.
(b) Dialysis of sol-prepared in (a) above.
(c) Study of the role of emulsifying agents in stabilizing the emulsion of different oils.

### B. Chemical Kinetics

(a) Effect of concentration and temperature on the rate of reaction between Sodium Thiosulphate and Hydrochloric acid.
(b) Study of reaction rates of any one of the following:
  (i) Reaction of Iodide ion with Hydrogen Peroxide at room temperature using different concentration of Iodide ions.
  (ii) Reaction between Potassium Iodate, (KIO3) and Sodium Sulphite: (Na2SO3) using starch solution asindicator (clock reaction).

### C. Thermochemistry

Any one of the following experiments
i) Enthalpy of dissolution of Copper Sulphate or Potassium Nitrate.
ii) Enthalpy of neutralization of strong acid (HCI) and strong base (NaOH).
iii) Determination of enthaply change during interaction (Hydrogen bond formation) between Acetone and Chloroform.

### D. Electrochemistry

Variation of cell potential in $Zn/Zn^{2+}||Cu^{2+}/Cu$ with change in concentration of electrolytes ($CuSO_4$ or$ZnSO_4$) at room temperature.

**E. Chromatography**

i) Separation of pigments from extracts of leaves and flowers by paper chromatography and determinationof $R_f$ values.

ii) Separation of constituents present in an inorganic mixture containing two cations only (constituents having large difference in $R_f$ values to be provided).

**F. Preparation of Inorganic Compounds**

i) Preparation of double salt of Ferrous Ammonium Sulphate or Potash Alum.

ii) Preparation of Potassium Ferric Oxalate.

**G. Preparation of Organic Compounds**

Preparation of any one of the following compounds

i) Acetanilide

ii) Di -benzal Acetone

iii) p-Nitroacetanilide

iv) Aniline yellow or 2 - Naphthol Aniline dye.

**H. Tests for the functional groups present in organic compounds:**

Unsaturation, alcoholic, phenolic, aldehydic, ketonic, carboxylic and amino (Primary) groups.

**I. Characteristic tests of carbohydrates, fats and proteins in pure samples and their detection in givenfood stuffs.**

**J. Determination of concentration/ molarity of $KMnO_4$ solution by titrating it against a standard solution of:**

i) Oxalic acid,

ii) Ferrous Ammonium Sulphate

(Students will be required to prepare standard solutions by weighing themselves).

**K. Qualitative analysis**

Determination of one cation and one anion in a given salt.

**Cation-** $NH_4^+$, $Pb^{2+}$, $Cu^{2+}$ $As^{3+}$, $Al^{3+}$, $Fe^{3+}$, $Mn^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Mg^{2+}$

**Anions-**$CO_3^{2-}$, $S^{2-}$, $SO_3^{2-}$, $SO_4^{2-}$, $NO_2^-$, $NO_3^-$, $Cl^-$, $Br^-$, $I^-$, $PO_4^{3-}$; $CH_3COO^-$

(Note: Insoluble salts excluded)

## PROJECT

**Scientific investigations involving laboratory testing and collecting information from other sources.**

**A few suggested Projects.**

- Study of the presence of oxalate ions in guava fruit at different stages of ripening.
- Study of quantity of casein present in different samples of milk.
- Preparation of soybean milk and its comparison with the natural milk with respect to curd formation, effect of temperature, etc.
- Study of the effect of Potassium Bisulphate as food preservative under various conditions (temperature, concentration, time, etc.)
- Study of digestion of starch by salivary amylase and effect of pH and temperature on it.
- Comparative study of the rate of fermentation of following materials: wheat flour, gram flour, potato juice, carrot juice, etc.
- Extraction of essential oils present in Saunf (aniseed), Ajwain (carum), Illaichi (cardamom).
- Study of common food adulterants in fat, oil, butter, sugar, turmeric power, chilli powder and pepper.

**Note:** Any other investigatory project, which involves about 10 periods of work, can be chosen with the approval of the teacher.

## MONTHWISE SYLLABUS DISTRIBUTION

### MONTHS: March, April, May

**Unit II: Electrochemistry** **(Periods 14)**

Redox reactions, conductance in electrolytic solutions, specific and molar conductivity variations of conductivity with concentration, Kohlrausch's Law, electrolysis and laws of electrolysis (elementary idea), dry cell- electrolytic cells and Galvanic cells; lead accumulator, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, fuel cells; corrosion.

**Unit III: Chemical Kinetics** **(Periods 12)**

Rate of a reaction (average and instantaneous), factors affecting rate of reaction; concentration, temperature, catalyst; order and molecularity of a reaction; rate law and specific rate constant, integrated rate equations and half life (only for zero and first order reactions); concept of collision theory (elementary idea, no mathematical treatment), Activation energy, Arrhenious equation

**Unit I: Solutions** **(Periods 12)**

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, colligative properties - relative lowering of vapour pressure, elevation of Boiling Point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, Van’t Hoff factor.

**Unit VI: p-Block Elements** **(Periods 14)**

**Group16 elements:** General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties; dioxygen: preparation, properties and uses; simple oxides; Ozone. Sulphur - allotropic forms; compounds of sulphur: preparation, properties and uses of sulphur dioxide; sulphuric acid: industrial process of manufacture, properties and uses, oxoacids of sulphur (structures only).

**Group 17 elements**: General introduction, electronic configuration, oxidation states, trends in physical and chemical properties; compounds of halogens: preparation, properties and uses of chlorine and hydrochloric acid, interhalogen compounds, oxoacids of halogens I (structures only).

**Group 18 elements**: General introduction, electronic configuration. Occurence, trends in physical and chemical properties, uses.

**Practicals:**

**EXPERIMENT- 1-6**

Qualitative analysis
Determination of one cation and one anion in a given salt.

Cations - $Pb^{2+}$ $Cu^{2+}$ $As^{3+}$ $Al^{3+}$ $Fe^{3+}$ $Mn^{2+}$ $Zn^{2+}$ $Co^{2+}$ $Ni^{2+}$ $Ca^{2+}$ $Sr^{2+}$ $Ba^{2+}$ $Mg^{2+}$ $NH_4^+$
Anions – $CO_3^{2-}$, $S^{2-}$, $SO_3^{2-}$, $SO_4^{2-}$, $NO_2^-$, $NO_3^-$, $Cl^-$, $Br^-$, $I^-$, $PO_4^{3-}$; $CH_3COO^-$
(Note: Insoluble salts excluded)

**PROJECT WORK**

## MONTH : JULY

### Unit IX: Haloalkanes and Haloarenes (Periods 12)

**Haloalkanes:** Nomenclature, nature of C-X bond, physical and chemical properties, mechanism of substitution reactions.
**Haloarenes:**Nature of C-X bond, substitution reactions (directive influence of halogen for monosubstituted compounds only). Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

### Unit X: Alcohols, Phenols and Ethers (Periods 12)

**Alcohols:** Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only); identification of primary, secondary and tertiary alcohols; mechanism of dehydration, uses of methanol and ethanol
**Phenols:** Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophillic substitution reactions, uses of phenols.
**Ethers**: Nomenclature, methods of preparation, physical and chemical properties, uses.

### Unit XI: Aldehydes, Ketones and Carboxylic Acids (Periods 12)

**Aldehydes and Ketones:** Nomenclature, nature of carbonyl group, methods of preparation. physical and chemical properties mechanism of nucleophilic addition.
**EXPERIMENT No.: 7-8**

Determination of concentration/molarity of $KMnO_4$ solution by titrating it against a standard solution of:
i) Oxalic acid,
ii) Ferrous ammonium sulphate
(Students will be required to prepare standard solutions by weighing themselves).

**EXPERIMENT No.: 9-10**

Preparation of one lyophilic and one lyophobic sol.
(a) Lyophilic sol- starch
(b) Lyophobic sol- ferric hydroxide.

## MONTH : AUGUST

**Unit XI: Aldehydes, Ketones and Carboxylic Acids (Continued) (Periods 12)**

**Aldehydes and Ketones : R**eactivity of alpha hydrogen in aldehydes, chemical reactivity; uses.
**Carboxylic Acids**: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

**Unit XII: Organic compounds containing Nitrogen (Period 10)**

**Amines:** Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.
**Cyanides and Isocyanides** - will be mentioned at relevant places in context.
**Diazonium salts:** Preparation, chemical reactions and importance in synthetic organic chemistry.

**Unit XIV: Polymers (Periods 8)**

Classification - natural and synthetic, methods of polymerization (addition and condensation), copolymerization. Some important polymers: natural and synthetic like polythene, nylon, polyesters, bakelite, rubber. Biodegradable and non- biodegradable polymers.

**EXPERIMENT No.: 11, 12**

Effect of concentration on the rate of reaction between sodium thiosulphate and hydrochloric acid

Effect of temperature on the rate of reaction between sodium thiosulphate and hydrochloric acid

**EXPERIMENT No.: 13-18**

**Tests for the functional groups present in organic compounds:**
Alcoholic, phenolic, aldehydic, ketonic, carboxylic and amino (primary) groups.

## MONTH: SEPTEMBER- OCTOBER

**Unit XIII: Biomolecules (Periods 12)**

**Carbohydrates** - Classification (aldoses and ketoses), monosaccal1rides (glucose and tfuctose), oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose, glycogen); importance.
**Proteins** - Elementary idea of a - amino acids, peptide bond, polypeptides, proteins, structure of amines-primary, secondary, tertiary structure and quaternary structures ( qualitative idea only), denaturation of proteins; enzymes.
**Vitamins** -Classification and functions. Nucleic Acids: DNA and RNA.

**Unit VIII: Coordination Compounds (Period 12)**

Coordination 'Compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds.bonding; isomerism, importance of coordination compounds (in qualitative analysis, extraction of metals and biological systems).

**Unit VII: d and f Block Elements (Period 14)**

General introduction ,electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first row transition metals - metallic character, ionization enthalpy, oxidation states, ionic radii, colour catalytic property, magnetic properties, interstitial compounds, alloy formation preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.

Lanthanoids - electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction.
Actinoids - Electronic configuration, oxidation states.

**EXPERIMENT No.: 19-20**
**Preparation of lnorganic Compounds:**
i) Preparation of double salt of ferrous ammonium sulphate
ii) Preparation of double salt of potash alum.

**EXPERIMENT No.: 21-23**
Characteristic tests of carbohydrates, fats and proteins in pure samples and their detection in given food stuffs.

## MONTH: NOVEMBER

**Unit V: General Principles and Processes of Isolation of Elements (Periods 8)**

Principles and methods of extraction - concentration, oxidation, reduction electrolytic method and refining; occurrence and principles of extraction of aluminium, copper, zinc and iron.

### Unit IV: Surface Chemistry

Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, colloids distinction between true solutions,colloids and suspension; lyophilic, lyophobic multi molecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation, emulsion - types of emulsions.

### Unit XV: Chemistry in Everyday life (Period 8)

**Chemicals in medicines** - analgesics, tranquilizers, antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistanlines.

**Chemicals in food** - preservatives, artificial sweetening agents.

**Cleansing agents** - soaps and detergents, cleansing action

### EXPERIMENT No.: 24

**Chromatography**

To separate the constituents present in an inorganic mixture containing Fe3+ and Cu2+ using paper chromatography and determination of their $R_f$ values.

### EXPERIMENT No.: 25

Preparation of Di-benzal Acetone

## Assignment

## Chapter 1: Solutions

1. Calculate the freezing point of a solution containing 60 g of glucose . (Molar mass = 180 g mol$^{-1}$) in 250 g of water. ( $K_f$ of water = 1.86 K kg mol$^{-1}$) (-2.48$^{o}$C)

2. Give reasons for the following:
   (i)Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers.
   (ii)Aquatic animals are more comfortable in cold water than in warm water.
   (iii)Elevation of boiling point of 1M KCl solution is nearly double than that of 1 M sugar solution.
3. A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if freezing point of pure water is 273.15 K. Given : (Molar mass of sucrose = 342 g mol$^{-1}$ , Molar mass of glucose = 180 g mol$^{-1}$)

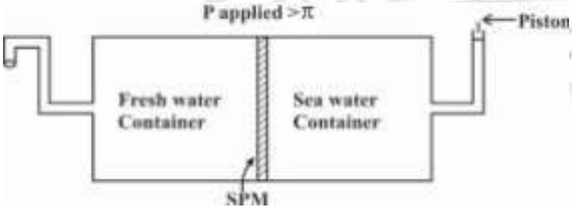
4. State the formula relating pressure of a gas with its mole fraction in a liquid solution in contact with it. Name the law and mention its two applications.

5. Two liquids A and B boil at 145$^{0}$C and 190$^{0}$C respectively. Which of them has a higher vapour pressure at 80$^{0}$C?

6. (a) Why is the vapour pressure of a solution of glucose in water lower than that of water?
   (b) A 6.90 M solution of KOH in water contains 30% by mass of KOH. Calculate the density of the KOH solution? ( molar mass of KOH = 56 g/mol)
   (1.288 g/ml)
7. Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example.

8. Explain with suitable examples in each case why the molar masses of some substances determined with the help of colligative properties are (i) higher (ii) lower than actual values.

9. Given below is the sketch of a plant for carrying out a process.



   (i) Name the process occurring in the above plant.
   (ii) To which container does the net flow of solvent take place?
   (iii) Name one SPM which can be used in this plant.
   (iv) Give one practical use of the plant.
10. Calculate the freezing point of solution when 1.9 g of $MgCl_2$(M=95 g mol–1) was dissolved in 50 g of water, assuming $MgCl_2$ undergoes complete ionization. ($K_f$ for water = 1.86 K kg mol$^{-1}$)

11. a) Out of 1 M glucose and 2 M glucose, which one has a higher boiling point and why?
    b) What happens when the external pressure applied becomes more than the osmotic pressure of solution ?

12. State Raoult's law for solutions of volatile liquids. Taking suitable examples explain the meaning of positive and negative deviations from Raoult's law. What is the sign of $\Delta H_{mix}$ for positive deviation?

13. a) Define the term osmotic pressure. Describe how the molecular mass of a substance can be determined by a method based on measurement of osmotic pressure.
    b) Determine the osmotic pressure of a solution prepared by dissolving 0.025g of $K_2SO_4$ in 2L of water at $25^{\circ}C$, assuming that is completely dissociated.
    (R=0.0821 L atm/K/mol, molar mass of $K_2SO_4$= 174g/mol)

14. 15 g of an unknown molecular material was dissolved in 450 g of water. The resulting solution was found to freeze at $-0.34^{\circ}C$. What is the molar mass of this material? $K_f$ for water = 1.86 K Kg $mol^{-1}$). (182 g $mol^{-1}$)
15. A solution is prepared by dissolving 1.25g of oil of winter green (methyl salicylate) in 99.0g of benzene has a boiling point of $80.31^{0}C$. Determine the molar mass of this compound. (B.P. of pure benzene = $80.10^{0}C$ and $K_b$ for benzene = $2.53^{0}C$ kg $mol^{-1}$) (152.21 g/mol)
16. A 1.00 molal aqueous solution of trichloroacetic acid ( $CCl_3COOH$) is heated to its boiling point. The solution has the boiling point of $100.18^{0}C$. Determine the van't Hoff factor for trichloroacteic acid ($K_b$ for water = 0.512 K Kg $mol^{-1}$). (i= 0.35)

## More Practice
## Chapter 1: Solutions

1. Calculate the temperature at which a solution containing 54 g of glucose, ($C_6H_{12}O_6$), in 250g of water will freeze ($k_f$ for water = 1.86 k $mol^{-1}$ Kg).

2. Why it is better to find molality of a solution than its molarity?

3. The Henry law constant for oxygen dissolved in water is 4.34 x $10^4$ atm at $25^0$C. If the partial pressure of oxygen in air is 0.2 atm. under ordinary atmospheric conditions. Calculate the concentration (in moles per litre) of dissolved oxygen in water in equilibrium with air at $25^0$C.
4. Define the following terms:
   a ) Mole fraction
   b) Isotonic solutions
   c) Van't Hoff factor
   d) ideal solution.
   e) Colligative properties
   f) molality

5. What is the Van't Hoff factor for a compound which undergoes tetramerization in an organic solvent?

6. Benzoic acid completely dimerizes in benzene. What will be the vapour pressure of a solution containing 61 g of benzoic acid per 500 g benzene when the vapour pressure of pure benzene at the temperature of experiment is 66.6 torr? What would have been the vapour pressure in the absence of dimerisation?

7. Two elements A and B form compounds having molecular formulae $AB_2$ and $AB_4$. When dissolved in 20 g of benzene, 1 g of $AB_2$ lowers the freezing point by 2.3 K whereas 1g of $AB_4$ lowers it by 1.3 K. The molar depression constant for benzene is 5.1 K Kg $mol^{-1}$. Calculate the atomic masses of A and B.

8. Phenol associates in benzene to a certain extent to form a dimer. A solution containing 20 X $10^{-3}$ kg of phenol in 1 kg of benzene has its freezing point lowered by 0.69K. Calculate the fraction of phenol that has dimerised ($K_f$ = 5.1 KKg $mol^{-1}$)

9. 100 g of a protein is dissolved in just enough water to make 10.0 ml of solution. If this solution has an ostomic pressure of 13.3 mm Hg at $25^0$C, what is the molar mass of the protein?

10. Calculate the amount of KCl which must be added to 1 Kg of water so that the freezing point is depressed by 2K. (Kf for water = 1.86 /K Kg $mol^{-1}$) (40.05 g)

11. A decimolar solution of $K_4[Fe(CN)_6]$ is 50% dissociated at 300K. Calculate the osmotic pressure of the solution in atm.
12. Heptane and Octane form an ideal solution at 373 K. The vapour pressures of the pure liquids at this temperature are 105.2 KPa and 46.8 KPa respectively. If the solution contains 25 g of heptane and 28.5 g of octane, calculate
   (i) vapour pressure exerted by heptane.

(ii) vapour pressure exerted by solution.

(i) mole fraction of octane in the vapour phase.

13. A solution is made by dissolving 30 g of a nonvolatile solute in 90 g of water. It has a vapour pressure 2.8 KPa at 298 K. At 298 K, vapour pressure of pure water is 3.64 KPa. Calculate the molar mass of the solute.

14. What type of azeotrope is formed on mixing nitric acid and water?

15 An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_4(OH)_2$) and 200 g of water. Calculate the molality of the solution. If the density of this solution be 1.072 g $ml^{-1}$, what will be the molarity of the solution?

(9.1 M; 17.95 m)

## Assignment
## Chapter 2: Electrochemistry

1. Write the cell reaction and calculate the e.m.f of the following cell at 298 K.
   $Sn(s)|Sn^{2+}(0.004\ M)||H^{+}(0.020\ M)\ |\ H_2(g)\ (1\ bar)\ |\ Pt\ (s)$
   (Given : $E^{o}_{Sn^{2+}/Sn} = -0.14$ V) (0.11 V)

2. For the reaction
   $2AgCl\ (s) + H_2\ (g)\ (1\ atm) \longrightarrow 2Ag(s) + 2\ H^{+}(0.1M) + 2Cl^{-}\ (0.1M)$
   $\Delta G^{0} = -43600$ J at 25°C. Calculate the emf of the cell.
   (0.344 V)

3. Give reasons:
   a) On the basis of $E^{0}$ values, $O_2$ gas should be liberated at anode but it is $Cl_2$ gas which is liberated in the electrolysis of aqueous NaCl.
   b) Conductivity of $CH_3COOH$ decreases on dilution.

4. (a) Calculate the mass of Ag deposited at cathode when a current of 2 amperes was passed through a solution of $AgNO_3$ for 15 minutes.
   (Given : Molar mass of Ag = 108 g $mol^{-1}$ 1F = 96500 C $mol^{-1}$)
   (b) Define fuel cell.
5. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity ($\Lambda_m$) is 39.05 S $cm^2mol^{-1}$. Given $\lambda^{o}(H^{+}) = 349.6$ S $cm^2$ $mol^{-1}$ and $\lambda^{o}(CH_3COO^{-}) = 40.9$ S $cm^2$ $mol^{-1}$

6. i. Define molar conductivity of a solution and write their units and the relation between the two. How does molar conductivity changes with change in concentration of solution for weak and strong electrolyte.
   ii. Define limiting molar conductivity. Why is the conductivity of an electrolyte solution decrease with the decrease in concentration?

7. Define fuel cells? Give electrode reactions of $H_2$-$O_2$ fuel cell. Name any other fuel which can be used instead of $H_2$. Write its two advantages.
8. From the given cells :
   Lead storage cell, Mercury cell, Fuel cell and Dry cell
   Answer the following :
   (i) Which cell is used in hearing aids ?
   (ii) Which cell was used in Apollo Space Programme ?
   (iii) Which cell is used in automobiles and inverters ?
   (iv) Which cell does not have long life ?

9. The resistance of a conductivity cell containing 0.001 M KCl solution is 1500 Ω at 298K. What is the cell constant, if the conductivity of 0.001 M KCl solution at 298K is $0.146 \times 10^{-3}$ $Scm^{-1}$? ($0.219\ cm^{-1}$)
10. Account for the following :
    1. Alkaline medium inhibits the rusting of iron.
    2. Iron does not rust even if the zinc coating is broken in a galvanized iron pipe.
11. Three iron sheets have been coated separately with three metals ( A, B and C) whose standard electrode potentials are given below:

| Metal | A | B | C | Iron |
|---|---|---|---|---|
| $E^{o}$ values | -0.46 V | -0.66 V | -0.20 V | - 0.44 V |

Identify in which case rusting will take place faster when coating is damaged.

12. Write the reactions occurring during the electrolysis of ;
    a) Solution of dil. Sulphuric acid using platinum electrodes.
    b) Aqueous Silver Nitrate solution using Silver electrodes.
    c) Aqueous Sodium Chloride solution.
13.

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad E^\circ = +0.34\ V$$

$$Ag^+ + e^- \longrightarrow Ag \qquad E^\circ = +0.80\ V$$

a. Construct a galvanic cell using the above data.
b. For what concentration of $Ag^+$ ions will the emf of the cell be zero at 25°C, if the concentration of $Cu^{2+}$ is 0.01 M ? [ log 3.919 = 0.593] (calc. not reqd.)

14. (i) State Kohlaursch law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlaursch law.
    (ii) Calculate $\Lambda^0_m$ for acetic acid. ( Given that $\Lambda^0$m HCl = 426 $Scm^2\ mol^{-1}$ $\Lambda^0$m NaCl = 126 $Scm^2\ mol^{-1}$ $\Lambda^0$m $CH_3COONa$ = 91 $Scm^2\ mol^{-1}$ ) (391 $Scm^2 mol^{-1}$)

15. What type of battery is lead storage battery? Write the anode and the cathode reactions and overall reaction occurring in a lead storage battery when current is drawn from it.
16. Following reactions occur at the cathode during the electrolysis of aqueous silver chloride solution:

$$Ag^+ + e^- \longrightarrow Ag \qquad E^\circ = +0.80\ V$$

$$H^+ + e^- \longrightarrow \tfrac{1}{2} H_2 \qquad E^\circ = +0.00\ V$$

On the basis of standard reduction potential values, which reaction is feasible at the cathode and why?

**Hands –on / IT Enabled work**:

1) working of Cu-Zn daneill cell
   https://www.youtube.com/watch?v=LahawEMMvvY
2) batteries:
   https://drive.google.com/open?id=0B7-07wgSVzqTek0yQ2tOWG5MZW8
3) Demonstration of electrochemical cell.

## More Practice
## Chapter 2: Electrochemistry

1. Conductivity of 0.00241 M acetic acid is 7.896 X $10^{-5}$ $Scm^{-1}$. Calculate its molar conductivity. If $\Lambda o$ for acetic acid is 390.5 $Scm^2mol^{-1}$, what is its dissociation constant?

2. Explain with examples the terms weak and strong electrolytes? How can these be distinguished? With the help of a diagram explain the difference in the variation of molar conductivity with concentration for strong and weak electrolytes

3. Calculate the emf of the cell Mg | $Mg^{2+}$(0.1 M) | | $Cu^{2+}$(0.0001 M) | Cu at 298 K. Given $E^o_{Mg2+/Mg}$ = -2. 37 V and $E^o_{Cu2+/Cu}$ = + 0. 34 V.

4. A voltaic cell is set up at 25°C with the following half –cells;
   Al | $Al^{3+}$ (0.001 M) and Ni | $Ni^{2+}$ (0.50 M)
   Calculate the cell voltage [$E^0_{Ni2+|Ni}$ = -0.25 V, $E^0_{Al3+|Al}$= -1.66 V] (1.45 V)
5. The following chemical reaction is occuring in an electrochemical cell
   Mg(s) + $2Ag^+$(0.0001 M) $Mg^{2+}$( 0.10 M) + 2Ag(s)

   The $E^o$ values are Mg $^{+2}$ /Mg = -2.36 V and $Ag^+$ / Ag = 0.80V
   For this cell calculate / write
   (a) The carriers of current within this cell.
   (b) $E^o$ value for the electrode 2 $Ag^+$ /2 Ag .
   (c) Standard cell potential $E^o_{cell}$ .
   (d) Cell potential E $_{cell}$
   (e) How will the value of $E_{cell}$ change if the concentration of $Ag^+$ (aq.) is increased?
   (f) Symbolic representation of the above cell.
   (g) Will the above cell reaction be spontaneous?

6. In the button cell , widely used in watches , the following reaction takes place
   $Zn_{(s)}$ + $Ag_2O_{(s)}$ + $H_2O_{(l)}$ $Zn^{2+}_{(aq)}$ + 2 $Ag_{(s)}$ + $2OH^-$
   Determine $E^0$ and $\Delta G^0$ for the reaction.
   ( given: $E^0_{Ag+/Ag}$ = 0.80 V , $E^0_{Zn2+/Zn}$ = -0.76 V) (E=1.56 V, $\Delta G^o$ = -301.08 KJ $mol^{-1}$)
7. Three electrolytic cells A, B and C containing solutions of zinc sulphate, silver nitrate and copper sulphate, respectively are connected in series. A steady current of 1.5 ampere was passed through them until 1.45 g of silver were deposited at the cathode of cell B. How long did the current flow? What mass of copper and what mass of zinc were deposited in the concerned cells? ( Atomic masses of Ag = 108, Zn = 65.4, Cu = 63.5)
8. Calculate the emf of the following cell at 298K:
   Fe(s) | $Fe^{2+}$(0.001M) | | $H^+$(1M) | $H_2$(g)(1bar), Pt(s)
   Given $E^o_{cell}$=0.44V
9. How many coulombs of electric charge must be passed through a solution of silver nitrate to coat a silver sheet of area 100 $cm^2$ on both the sides with a 0.005 mm thick layer. Density of silver is 10.5 $g/cm^3$. Relative atomic mass of silver is 108. ( 938.2 C)

## Assignment
## Chapter 3: Chemical Kinetics

1. For the rection:

   $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

   The rate of formation of $NO_2$ (g) is 2.8 X $10^{-3}$ M $s^{-1}$. Calculate the rate of disappearance of $N_2O_5$ (g). (1.4 X 10-3 M/s)

2. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction. (Given: log 2 = 0.3010, log 4 =0.6021, R = 8.314 $JK^{-1}mol^{-1}$) (27.66 kJ/mol)

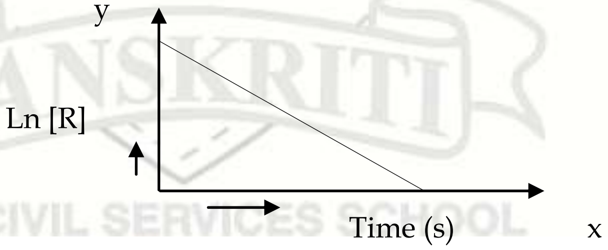
3. For a reaction R --> P, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction ?

4. For a reaction :
   $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$
   Rate = k
   (i) Write the order and molecularity of this reaction.
   (ii) Write the unit of k.

5. Explain the following terms:
   (i) Rate constant (k)
   (ii) Half life period of a reaction($t_{1/2}$)
   (iii) Order of the reaction
   (iv) pseudo first order reaction.

6. The rate of a particular reaction triples when temperature changes from $50^0$C to $100^0$C. Calculate the activation energy of the reaction.
   [log 3 = 0.4771, R = 8.314 $JK^{-1}$ $mol^{-1}$] ( 22.01 kJ/mol)

7. A reaction, reactant $\longrightarrow$ product is represented by the graph below. predict



   (i)The order of the reaction in this case.
   (ii)What does the slope of the graph represent?
   (iii)What are the units of rate constant k?
   (iv)Give the relationship between k and $t_{1/2}$ (half life period).
   (v) Draw the plot of log [R]o/[R] vs. time (s)

8. For the reaction
   $2\,NO_{(g)} + Cl_2(g) \longrightarrow 2NOCl\,(g)$
   The followingdata were collected . All the measurements were taken at 263 K:

| Experiment No. | Initial(NO) (M) | Initial($Cl_2$) (M) | Intial rate of disappearance of $Cl_2$ (M/min) |
|---|---|---|---|
| 1 | 0.15 | 0.15 | 0.60 |
| 2 | 0.15 | 0.30 | 1.20 |
| 3 | 0.30 | 0.15 | 2.40 |
| 4 | 0.25 | 0.25 | ? |

Write the expression for the rate law.

(a) Calculate the value of rate constant and specify in units.
(b) What is initial rate of disappearance of $Cl_2$ in exp.4 ?

[(a) k= 177,7 $M^{-2}$ $min^{-1}$; (b) Rate = 2.8 M $min^{-1}$]

9. For a certain chemical reaction:

$$2A + 2B \longrightarrow 2C + D$$

The experimentally obtained information is tabulated below.

| Experiment | [A]o | [B]o | Initial rate of reaction |
|---|---|---|---|
| 1. | 0.30 | 0.30 | 0.096 |
| 2. | 0.60 | 0.30 | 0.384 |
| 3. | 0.30 | 0.60 | 0.192 |
| 4. | 0.60 | 0.60 | 0.768 |

For this reaction

(i) derive the order of reaction w.r.t both the reactants A and B.
(ii) write the rate law.
(iii) calculate the value of rate constant k. (k = 3.5 $l^2mol^{-2}$ $s^{-1}$)
(iv) write the expression for the rate of reaction in terms of A and C.

10. For an elementary reaction

$$2A + B \longrightarrow 3C$$

the rate of appearance of C at time 't' is $1.3 \times 10^{-4}$ mol $l^{-1}s^{-1}$

Calculate at this time

i) rate of the reaction.
ii) Rate of disappearance of A.

{ (i) 4.33 x 10-5 mo/l/s, (ii) 8.66 x $10^{-5}$ mol/l/s) }

11. The following data were obtained during the first order thermal decomposition of $SO_2Cl_2$ at a constant volume:

$$SO_2Cl_2 (g) \longrightarrow SO_2 (g) + Cl_2(g)$$

| Experiment | Time/$s^{-1}$ | Total pressure/atm |
|---|---|---|
| 1 | 0 | 0.4 |
| 2 | 100 | 0.7 |

Calculate the rate constant. (Given log 4 = 0.6021, log 2 = 0.3010)

12. For a reaction, A+ B → P, the reaction is of first order in reactant A and second order in reactant B.

(i) How is the rate of this reaction affected when the concentration of B doubled.
(ii) What is the overall order of rection if A is present in large excess.

13. The rate constant for the first order decomposition of $H_2O_2$ is given by the following equation:

$$\text{Log } k = 14.2 - \frac{1.0 \times 10^4}{T} \text{ K}$$

Calculate Ea for this reaction and rate constant k if its half-life period be 200 minutes. (Given: R = 8.314 J $K^{-1}mol^{-1}$)

14. The rate constant for a reaction of zero order in A is 0.0030 mol $L^{-1}$ $s^{-1}$. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M.

(t= 8.33 sec)

15. The half life for decay of radioactive $^{14}C$ is 5730 years. An archaeological arttefact containing wood has only 80% of the $^{14}C$ activity as found in living trees. Calculate the age of the artefact.

16. For hydrolysis of methyl acetate, the following data were obtained

| Time/$s^{-1}$ | 0 | 30 | 60 |
|---|---|---|---|
| [$CH_3COOCH_3$]/mol $L^{-1}$ | 0.60 | 0.30 | 0.15 |

(i) Show that it follows pseudo first order reaction, as concentration of water remains constant.

(ii) Calculate the average rate between the time interval 30 to 60 seconds.
[log2=0.3010, log4=0.6020]

**Hands-on/ IT Enabled work:**

1) Collision theory https://www.youtube.com/watch?v=wbGgIfHsx-I

## More Practice

## Chapter 3: Chemical Kinetics

1. Following data are obtained for the reaction :
   $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$

   | t/s | 0 | 300 | 600 |
   |---|---|---|---|
   | $[N_2O_5]$/mol $L^{-1}$ | $1.6 \times 10^{-2}$ | $0.8 \times 10^{-2}$ | $0.4 \times 10^{-2}$ |

   (a) Show that it follows first order reaction.

   (b) Calculate the half-life.

   ( c) calculate its concentration after 2 min, if rate costant is $5 \times 10^{-4}$ $s^{-1}$

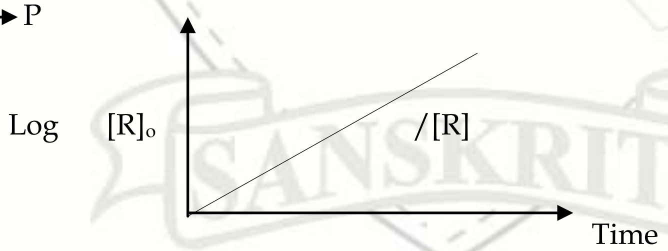
   (Given log 2 = 0.3010 log 4 = 0.6021)

2. The decomposition of $NH_3$ on platinum surface, $2NH_3\,(g) \xrightarrow{Pt} N_2\,(g) + 3H_2(g)$ is a zero order reaction with $k = 2.5 \times 10^{-4}$ $MS^{-1}$. What are the rates of production of $N_2$ and $H_2$ ? ( $2.5 \times 10^{-4}$ $Ms^{-1}$, $7.5 \times 10^{-4}$ $Ms^{-1}$)

3. A first order reaction takes 69.3 minutes for 50% completion. Set up an equation for the determining the time needed for 80% completion of this reaction.
   (Calculation of result is not required).

4. For the reaction :
   $Cl_2\,(g) + 2\,NO\,(g) \longrightarrow 2NOCl\,(g)$
   The rate law is expressed as rate $= k\,[Cl_2][NO]^2$
   What is the overall order of the reaction?

5. Answer the following questions on the basis of the curve for a first order reaction
   $A \longrightarrow P$



   a) What is the relation between slope of this line and rate constant?
   b) Calculate the rate constant of the above reaction if the slope is $2 \times 10^{-4}$ $S^{-1}$

6. A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value.

7. For the reaction $A \longrightarrow B$ , the rate of reaction becomes 27 times when the concentration of A is increased three times. What is the order of the reaction?

8. At elevated temperatures, HI decomposes according to the chemical equation;
   $2HI\,(g) \longrightarrow H_2(g) + I_2(g)$ at 443°C. The rate of the reaction increases with concentration of HI, as shown in the following table:

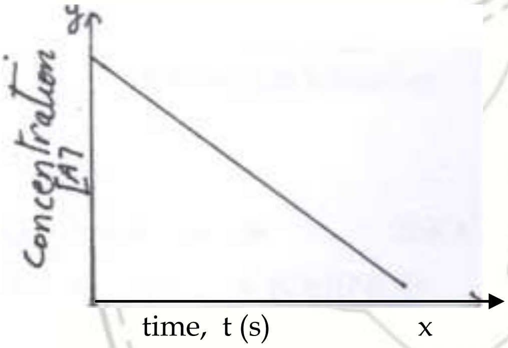
| | | | |
|---|---|---|---|
| HI (mol/ l) | 0.005 | 0.01 | 0.02 |
| Rate (mol/l/s) | $7.5 \times 10^{-4}$ | $3.0 \times 10^{-3}$ | $1.2 \times 10^{-2}$ |

(a) Determine (i) order of this reaction and
(ii) write the rate expression

(b) Calculate the rate constant and give its units.

9. A first order reaction has a rate constant of 0.0051 $\text{min}^{-1}$. If we begin with 0.10 M concentration of the rectant, what concentration of reactant will remain in solution after 3 hours?

10 Consider the reaction $A \xrightarrow{k} P$. The change in concentration of A with time is shown in the following plot.



(i) Predict the order of the reaction.

(ii) Derive the expression for the time required for the completion of the reaction.

# Notes :Chapter 4: Surface Chemistry

- **Adsorption:**
  (i) The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed as adsorption.
  (ii) It is a surface phenomenon.
  (iii) The concentration of adsorbate increases only at the surface of the adsorbent.
- **Adsorbate:** It is the substance which is being adsorbed on the surface of another substance.
- **Adsorbent:** It is the substance present in bulk, on the surface of which adsorption is taking place.
- **Desorption:** It is the process of removing an adsorbed substance from a surface on which it is adsorbed.
- **Absorption:**
  (i) It is the phenomenon in which a substance is uniformly distributed throughout the bulk of the solid.
  (ii) It is a bulk phenomenon.
  (iii) The concentration is uniform throughout the bulk of solid.
- **Sorption:** When adsorption and absorption take place simultaneously, it is called sorption.
- **Enthalpy or heat of adsorption:** Since, adsorption occurs with release in energy, i.e., it is exothermic in nature. The enthalpy change for the adsorption of one mole of an adsorbate on the surface of adsorbent is called enthalpy or heat of adsorption.

## Mechanism of Adsorption

Inside the Adsorbent (in bulk) the force acting between the particles are mutually balanced but on the surface, the particles are not surrounded by atoms or molecules of their kind on all sides and hence they posses attraction force so particle stick on the surface of the Adsorbent.

The extent of adsorption increases with increase in surface area per unit mass of the adsorbent at a given temperature and pressure.

**Heat of adsorption: -** With increase in heat Adsorption process decreases.

**Adsorption equilibrium: -** As the molecules of the adsorb ate are held on the surface of the solid adsorbent.

Entropy decreases, i.e. $\Delta$S is negative

- $\Delta G = \Delta H - T\Delta S$

For the process of adsorption to occur, $\Delta$G must be negative which is possible only when, $\Delta$S keeps on decreasing and T$\Delta$S keeps on increasing till ultimately $\Delta$H becomes equal.

To T$\Delta$S so that $\Delta$G = 0, this state is called ***adsorption equilibrium***.

- **Types of adsorption:** There are different types of adsorption namely,

1. Physical adsorption
2. Chemical adsorption

- **Physical adsorption**
  **(i)** If the adsorbate is held on a surface of adsorbent by weak van der Waals' forces, the adsorption is called physical adsorption or physisorption.
  **(ii)** It is non-specific.
  **(iii)** It is reversible.
  **(iv)** The amount of gas depends upon nature of gas, i.e., easily liquefiable gases like $NH_3$, $CO_2$, gas adsorbed to greater extent than $H_2$ and He. Higher the critical temperature of gas, more will be the extent of adsorption.
  **(v)** The extent of adsorption increases with increase in surface area, e.g. porous and finely divided metals are good adsorbents.
  **(vi)** There are weak van der Waals' forces of attraction between adsorbate and adsorbent.
  **(vii)** It has low enthalpy of adsorption (20 – 40 kJ mol-1).
  **(viii)** Low temperature is favourable.
  **(ix)** No appreciable activation energy is needed.
  **(x)** It forms multimolecular layers.
- **Chemical adsorption or chemisorption:**

**(i)** If the forces holding the adsorbate are as strong as in chemical bonds, the adsorption process is known as chemical adsorption of chemisorption.
**(ii)** It is highly specific.
**(iii)** It is irreversible.
**(iv)** The amount of gas adsorbed is not related to critical temperature of the gas.
**(v)** It also increases with increase in surface area.
**(vi)** There is strong force of attraction similar to chemical bond.
**(vii)** It has enthalpy heat of adsorption (180 – 240 kJ mol-1).
**(viii)** High temperature is favourable.
**(ix)** High activation energy is sometimes needed.
**(x)** It forms unimolecular layers.

- **Factors affecting adsorption of gases on solids:**

**a. Nature of adsorbate:** Physical adsorption is non-specific in nature and therefore every gas gets adsorbed on the surface of any solid to a lesser or greater extent. However, easily liquefiable gases like $NH_3$,HCl, $CO_2$, etc. which have higher critical temperatures are absorbed to greater extent whereas $H_2$, $O_2$, $N_2$ etc. are adsorbed to lesser extent. The chemical adsorption being highly specific, therefore, a gas gets adsorbed on specific solid only if it enters into chemical combination with it.

**b. Nature of adsorbent:** Activated carbon, metal oxides like aluminum oxide, silica gel and clay are commonly used adsorbents. They have their specific adsorption properties depending upon pores.

**c. Specific area of the adsorbent:** The greater the specific area, more will be the extent of adsorption. That is why porous or finely divided forms of adsorbents adsorb larger quantities of adsorbate. The pores should be large enough to allow the gas molecules to enter.

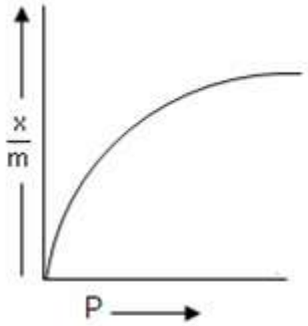
**d. Pressure of the gas:** Physical adsorption increases with increase in pressure.

- Adsorption isotherm:
- The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve is termed as adsorption isotherm.

- Freundlich Adsorption isotherm: The relationship between  and pressure of the gas at constant temperature is called adsorption isotherm and is given by

Where x- mass of the gas adsorbed on mass m of the adsorbent and the gas at a particular temperature k and n depends upon the nature of gas

- The adsorption first increases with increase in pressure at low pressure but becomes independent of pressure at high pressure.

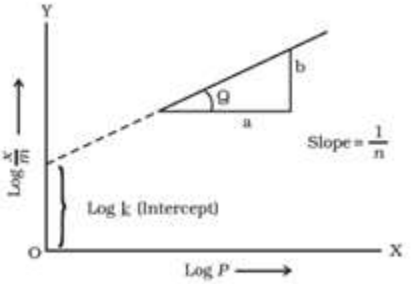


Taking logarithm on both sides, we get,

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

Taking logarithm on both sides, we get,

- If we plot a graph between log x/m and log P, we get a straight line.



The slope of the line isand intercept will be equal to log k.

## Applications of Adsorption

1) **Production of high vacuum**
2) **Gas masks**
3) **Control of humidity**
4) **Removal of coloring matter from solution**
5) **Separation of inert gases**
6) **Froth floatation process**
7) **Chromatographic analysis**

- Catalyst: These are substances which alter the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reactionand the phenomenon is known as catalysis.

- Promoters: These are the substances which increase the activity of catalyst. Example – Mo is promoter whereas Fe is catalyst in Haber's Process.

- Catalytic poisons (Inhibitors): These are the substances which decrease the activity of catalyst. Example -Arsenic acts as catalytic poison in the manufacture of sulphuric acid by 'contact process.'

- Types of catalysis:
- There are two types of catalysis namely,

1. Homogeneous catalysis: When the catalyst and the reactants are in the same phase, this kind of catalytic process is known as homogeneous catalysis.

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

$$C_{12}H_{22}O_{11}\ (aq.) + H_2O\ (l) \xrightarrow{H2SO4\ (l)} C_6H_{12}O_6\ (aq.) + C_6H_{12}O_6\ (aq.)$$

2.Heterogeneous catalysis: When the catalyst and the reactants are in different phases, the catalytic process is said to be heterogeneous catalysis.

$$2SO_2(g) \xrightarrow{Pt\ (s)} 2SO_3(g)$$

$$\text{Vegetable oils (l)} + H_2\ (g) \xrightarrow{Ni\ (s)} \text{vegetable ghee (s)}$$

3. **Activity of catalyst**:

It is the ability of a catalyst to increase the rate of a chemical reaction.Catalyst has an ability to increase the rate of reaction. This ability of catalyst is known as the activity of catalyst. It depends upon adsorption of reactants on the surface of catalyst. Chemisorption is the main factor governing the activity of catalysts. The bond formed during adsorption between the catalytic surface and the reactants must not be too strong or too weak.

It must be strong enough to make the catalyst active whereas, not so strong that the reactant molecules get immobilized on the catalytic surface leaving no further space for the new reactants to get adsorbed. Generally for the hydrogenation reaction, from Group 5 to Group 11 metals, the catalytic activity increases. The catalytic activity is found to be highest for group 7-9 elements of the periodic table.

$$H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(l)$$

### 4. *Selectivity of Catalyst*

Catalysts are highly specific compounds. They have an ability to direct the reaction to yield a particular product. The reaction with same reactants but different catalyst may yield different products. This is termed as the selectivity of catalyst. Catalysts are highly selective in nature. They can accelerate a particular reaction while inhibit another reaction. Hence, we can say a particular catalyst can catalyse one particular reaction only. It may fail to catalyse another reaction of the same type. For example: reaction of hydrogen and carbon monoxide yields methane when nickel is used as catalyst, methanol when a mixture of zinc oxide and chromium oxide is used as catalyst and methanal when only copper is used as catalyst.

**For example:** CO and $H_2$ react to form different products in presence of different catalysts as follows:

(i) $CO(g) + 3H2(g) \xrightarrow{Ni} CH4(g) + H2O(g)$
(ii) $CO(g) + 2H2(g) \xrightarrow{Cu/ZnO\_Cr2O3} CH3OH(g)$
(iii) $CO(g) + H2(g) \xrightarrow{Cu} HCHO(g)$

- Shape – selective catalysis: It is the catalysis which depends upon the pore structure of the catalyst and molecular size of reactant and product molecules. Example – Zeolites are shape – selective catalysts due to their honey- comb structure. They are alumino silicates with Al-O-Si network. Example- ZSM-5 is a shape selective catalyst which catalysis dehydration of alcohols to for gasoline.
- Enzymes: These are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass. They are biochemical

$$C_6H_{12}O_6(aq.) \xrightarrow{zymase} C_2H_5OH(aq.) + 2CO_2$$

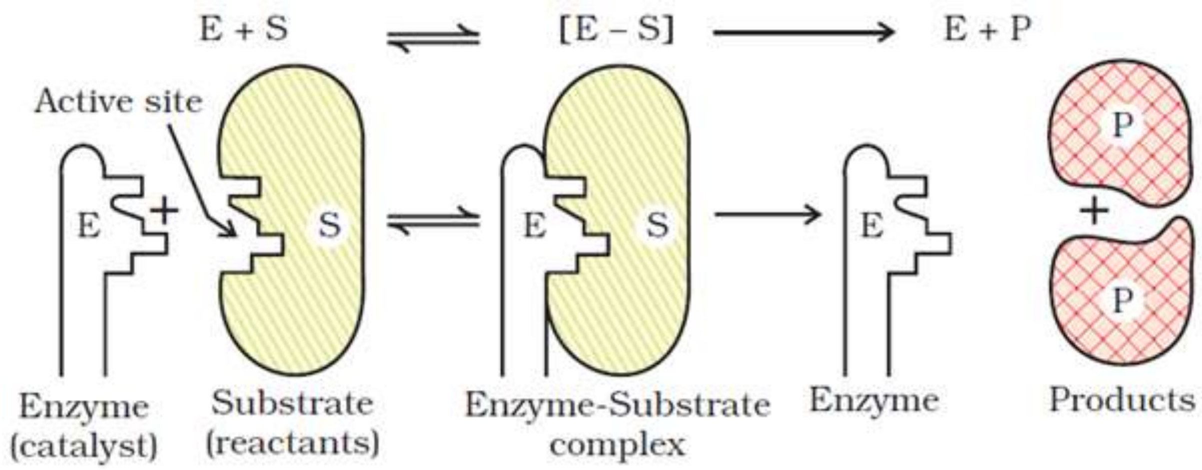
Glucose ethyl alcohol + gas

$$NH_2CONH_2(aq.) + H_2O(l) \xrightarrow{urease} NH_3(g) + CO_2(g)$$

catalysts Urea water ammonia carbon dioxide

- **Steps of enzyme catalysis:**

(i) Binding of enzyme to substrate to form an activated complex.
(ii) Decomposition of the activated complex to form product.



- **Characteristics of enzyme catalysis:**

(i) They are highly efficient. One molecule of an enzyme can transform 106 molecules of reactants per minute.
(ii) They are highly specific in nature. Example – Urease catalysis hydrolysis of urea only.
(iii) They are active at optimum temperature (298 – 310 K). The rate of enzyme catalysed reaction becomes maximum at a definite temperature called the optimum temperature.
(iv) They are highly active at a specific pH called optimum pH.
(v) Enzymatic activity can be increased in presence of coenzymes which can be called as promoters.
(vi) Activators are generally metal ions Na$^+$, Co$^{2+}$ and Cu$^{2+}$ etc. They weakly bind to enzyme and increase its activity.
(vii) Influence of inhibitors (poison): Enzymes can also be inhibited or poisoned by the presence of certain substances.

- **True solution:**

(i) It is homogeneous.
(ii) The diameter of the particles is less than 1 nm.
(iii) It passes through filter paper.
(iv) Its particles cannot be seen under a microscope.

- **Colloids:**

(i) It appears to be homogeneous but is actually heterogeneous.
(ii) The diameter of the particles is 1 nm to 1000 nm.
(iii) It passes through ordinary filter paper but not through ultra-filters.
(iv) Its particles can be seen by a powerful microscope due to scattering of light.

- **Suspension:**

(i) It is heterogeneous.
(ii) The diameter of the particles are larger than 1000 nm.
(iii) It does not pass through filter paper.
(iv) Its particles can be seen even with naked eye.

- Dispersed phase: It is the substance which is dispersed as very fine particles.
- Dispersion medium: It is the substance present in larger quantity.
- Classification of colloids on the basis of the physical state of dispersed phase and dispersion medium:

| Name | Dispersed phase | Dispersed medium | Examples |
|---|---|---|---|
| Solid sol | solid | Solid | Coloured gem stones |
| Sol | Solid | Liquid | Paints |
| Aerosol | Solid | Gas | Smoke, dust |
| Gel | Liquid | Solid | Cheese, jellies |
| Emulsion | Liquid | Liquid | Hair cream, milk |
| Aerosol | Liquid | Gas | Mist, fog, cloud |
| Solid sol | Gas | Solid | Foam rubber, pumice stone |
| Foam | Gas | Liquid | Whipped cream |

- Classification of colloids on the basis of nature of interaction between dispersed phase and dispersion medium, the colloids are classified into two types namely,

1. Lyophobic sols
2. Lyophilic sols

- **Lyophobic sols:**

(i) These colloids are liquid hating.
(ii) In these colloids the particles of dispersed phase have no affinity for the dispersion medium.
(iii) They are not stable.
(iv) They can be prepared by mixing substances directly.
(v) They need stabilizing agents for their preservation.
(vi) They are irreversible sols.

- **Lyophilic sols:**

(i) These colloids are liquid loving.
(ii) In these colloids, the particles of dispersed phase have great affinity for the dispersion medium.
(iii) They are stable.
(iv) They cannot be prepared by mixing substances directly. They are prepared only by special methods.
(v) They do not need stabilizing agents for their preservation.
(vi) They are reversible sols.

- Classification of colloids on the basis of types of particles of the dispersed phase:

There are three types of colloids based on the type of dispersed phase, namely,

1. Multimolecular colloids: The colloids in which the colloidal particles consist of aggregates of atoms or small molecules. The diameter of the colloidal particle formed is less than 1 nm.
2. Macromolecular colloids: These are the colloids in which the dispersed particles are themselves large molecules (usually polymers). Since these molecules have dimensions comparable to those of colloids particles, their dispersions are called macromolecular colloids, e.g., proteins, starch and cellulose form macromolecular colloids.
3. Associated colloids (Micelles): Those colloids which behave as normal, strong electrolytes at low concentrations, but show colloidal properties at higherconcentrations due to the formation of aggregated particles of colloidal dimensions. Such substances are also referred to as associated colloids.

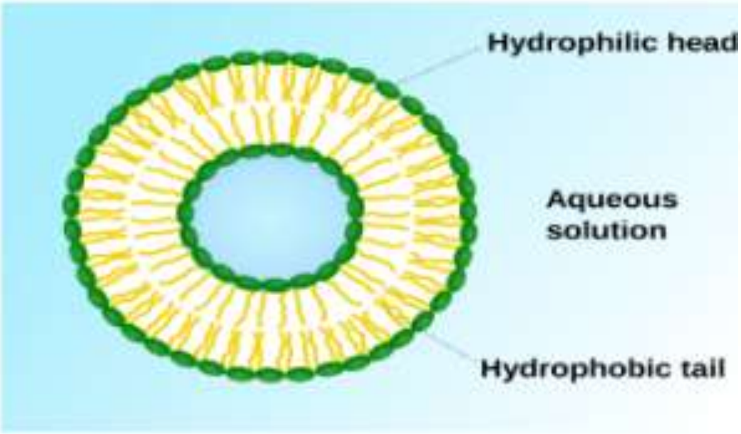
- Kraft Temperature (Tk):Micelles are formed only above a certain temperature called Kraft temperature.

- Critical Micelle Concentration (CMC): Micelles are formed only above a particular concentration called critical micelle concentration.

- Soaps: These are are sodium or potassium salts of higher fatty acids e.g., sodium stearate $CH_3(CH_2)_{16}COO\text{-}Na^+$
- **Cleansing action of soap:**

  When **soap** is dissolved in water, its hydrophobic ends attach themselves to dirt and remove it from the cloth.First, the molecules of **soap** arrange themselves in micelle formation and trap the dirt at the centre of the cluster. These micelles remain suspended in water like particles in a colloidal solution.

## Micelles



## Methods of preparation of colloids

### Chemical Methods:

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decompostion}} As_2S_3(sol) + 3H_2O$$

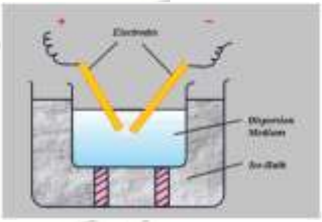
$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S(sol) + 2H_2O$$

$$2\ AuCl_3 + 3\ HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au(sol) + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\ (sol) + 3HCl$$

### Bredig's method:

An electric arc is struck between two metallic electrodes immersed in dispersion medium. The arc produced vapourises the metal which onfurther condensation produces particles of colloidal size.



### Peptization:

Process of converting a freshly prepared precipitate into colloidal sol by shaking it with electrolyte in dispersion medium is called as peptization. The electrolyte used for this purpose is called peptizing agent.

- **Purification of colloids:**

1. Dialysis: It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane.
2. Electro dialysis. The process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte.
3. Ultrafiltration: It is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles. Ultra filter paper is made by dipping filter paper in 4% solution of nitro cellulose in alcohol and ether. This filter paper is hardened by dipping in formaldehyde.
4. Ultracentrifugation: In this process, the colloidal solution is taken in a tube which is placed in ultracentrifuge. On rotating the tube at very high speed, the colloidal particles settle down at the bottom of the tube and the impurities remain in solution. The settled particles are mixed with dispersion medium to regenerate the sol.

- **Properties of colloids:**
    1. **Colour**: The colour of colloidal solution depends upon the wavelength of light scattered by the colloidal particles which in turn depends upon the nature and size of particles. The colour also depends upon the manner in which light is received by the observer. Example- Finest gold sol is red in colour and as the size of the particle keeps increasing its colour changes to blue, then purple and finally gold.
    2. **Brownian movement**: Colloidal particles move in zig – zag path. This type of motion is due to colliding molecules of dispersion medium constantly with colloidal particles.
    3. **Colligative properties**: The values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling

point) are of small order as compared to values shown by true solutions at the same concentrations.

4. **Tyndall effect**: The scattering of a beam of light by colloidal particles is called Tyndall effect. The bright cone of light is called the Tyndall cone.
5. **Charge on colloidal particles**: Colloidal particles always carry an electric charge. The nature of this charge is the same on all the particles in a given colloidal solution and may be either positive or negative.

**Positively charged colloidal particles**

(i) These include hydrated metallic oxides such as $Fe_2O_3.H_2O$, $Cr_2O_3.H_2O$, $Al_2O_3.H_2O$
(ii) Basic dye stuff like malachite green, methylene blue sols.
(iii) Example – Haemoglobin (blood).

**Negatively charged colloidal particles**:

(i) Metallic sulphides like $As_2S_3$, $Sb_2S_3$ sols.
(ii) Acid dye stuff like eosin, methyl orange, Congo red sols.
(iii) Examples – Starch sol, gum, gelatin, clay, charcoal, egg albumin, etc.

6. **Helmholtz electrical double layer**: When the colloidal particles acquire negative or positive charge by selective adsorption of one of the ions, it attracts counter ions from the medium forming a second layer. The combination of these two layers of opposite charges around colloidal particles is called Helmholtz electrical double layer.
7. **Electrokinetic potential or zeta potential**: The potential difference between the fixed layer and the diffused layer of opposite charges is called electrokinetic potential or zeta potential.
8. **Electrophoresis**: The movement of colloidal particles under an applied electric potential is called electrophoresis.

9. **Coagulation-** It is process of settling of colloidal particles. Also called precipitation of sol

## Coagulation of Lyophobic Sols-

Coagulation of lyophobic sols can be done by the following methods:

- By electrophoresis - The colloidal particles move towards oppositely changed electrodes get discharged and precipitate.
- By mixing two oppositely charged sols - Oppositely charged sols when mixed together in almost equal proportion, neutralise their charges and get partially or completely precipitated.
- By Boiling- When a sol is boiled the adsorbed layer is disturbed due to increased number of collisions with the molecules of the dispersion medium. This reduces the charge on the particles and they ultimately settle down in the form of a precipitate.
- By Persistent dialysis - On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely. Colloids become unstable and coagulate.

- By addition of electrolyte - When excess of electrolyte is added, colloidal particles precipitate as colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation.

Example- A negatively charged ion when added to a positively charged sol causes coagulation. The negatively charged ion is called coagulating ion/flocculative ion as it neutralises the colloid to cause coagulation.

## Coagulation of Lyophillic Sols-

Lyophilic sols are stable because of charge and solvation of colloidal particles. So we remove these two factors to coagulate them. This is done by

- Addition of an electrolyte
- Addition of a suitable solvent

## Protection of colloids -

- Lyophilic sols are more stable than lyophobic sols
- Lyophilic colloids have a unique ability to protect lyophobic colloids from electrolytes
- When a lyophilic sol is added to lyophobic sol, the lyophilic particles (colloids) form a layer around the particles of lyophobic sol
- Lyophilic colloids are also called protective colloids

## Hardy-Schulze Rule-

- The greater the valency of the flocculating ion added, the greater is its precipitation.
- For negative sols, when positive ions are added

  $Al^{3+} > Ba^{2+} > Na^{+}$ is the order in terms of flocculating power

- For positive sols, when negative ions are added

  $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$ is the order in terms of flocculating power

**Coagulation Value/ Flocculation value**: The number of millimoles of an electrolyte required to bring about the **coagulation** of one litre of a colloidal solution is called its flocculation **value**.

**Emulsions:** Emulsions are colloidal solutions where the dispersed phase and dispersion medium, both , are in liquid state.

- Types of emulsions:
  1. Water dispersed in oil (W/O): When water is the dispersed phase and oil is the dispersion medium. E.g. butter
  2. Oil dispersed in water (O/W): When oil is the dispersed phase and water is the dispersion medium. E.g. milk
- Emulsification: It is the process of stabilizing an emulsion by means of an emulsifier.

- Emulsifying agent or emulsifier: These are the substances which are added to stabilize the emulsions. They form an interfacial layer between the dispersed phase and dispersion medium. Examples – soaps, gum for O/W type emulsion and lamp black and long chain alcohols act as emulsifying agents for W/O type

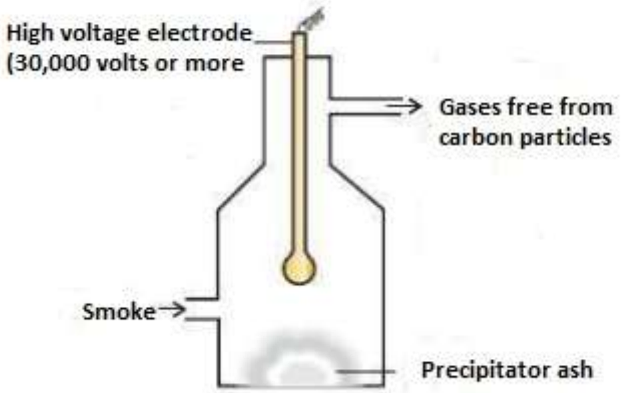
- Demulsification: It is the process of breaking an emulsion into its constituent liquids by freezing, boiling, centrifugation or some chemical methods.

  Certain reasons related to colloids around us:

  - Sky appears blue due to scattering of light by air molecules, water droplets, and other colloidal particles in the sky. Blue colour scatters the most.
  - Deltas are formed when river carrying silt, clay colloidal particles meets sea, as there a lot many salts dissolved in sea water, they neutralize the charge on colloidal particles leading to the coagulation of clay and silt forming deltas.
  - Albimunoids in blood are negatively charged colloids. If there is bleeding happening from a cut in the body, rubbing with alum (phikari), FeCl3 salt leads to coagulation of blood due to neutralization of charged albimunoid colloidal particles.
  - Artificial rain can be produced by spraying oppositely charged sol on the clouds which are colloids leading to their precipitation.

**Applications of Colloids**

1. Electro precipitation of smoke – The smoke is led through a chamber containing plates having a charged opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles settle down on the floor of the chamber. The precipitator is called Cottrell precipitator.



Cottrell Smoke precipitator

2. Purification drinking water – Alum is added to impure water to coagulate the suspended impurities and make water fit for drinking.

3. Medicines – Most of the medicines are colloidal in nature. Colloidal medicines are more effective because they have a larger surface area and are more easily absorbed by the body. Eg- Argyrol is a silver sol used as an eye lotion, milk of magnesia is used to cure stomach disorders, Antimony sol is used to cure Kalazaar, Gold sol is used in intramuscular injections.

4. Tanning – Animal hides are colloidal in nature. When a hide that has positively charged particles is soaked in tannin/chromium salts, which contains negatively charged particles ,

mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning.

5. Cleansing action of soaps- already explained
6. Photographic plates and films – Photographic plates and films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.

7. Rubber industry- Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.

8. Industrial products- Paints inks, synthetic plastics, rubber, cement, graphite lubricants are all colloids.

**Hands-on/ IT Enabled work:**

Whole chapter will be done with the help of power point presentation.

## Assignment

### Chapter 4: Surface Chemistry

1. CO(g) and $H_2$(g) react to give different products in the presence of different catalysts. Which ability of the catalyst is shown by these reactions?

2. What happens when
   (i) a freshly prepared precipitate of $Fe(OH)_3$ is shaken with a small amount of $FeCl_3$ solution?
   (ii) persistent dialysis of a colloidal solution is carried out?
   (iii)size of dispersed phase changes in gold sol.

3. (a) Define adsorption. Write any two features which distinguish physisorption and chemisorption. Which has higher enthalpy of adsorption?
   (b) Write one similarity between Physisorption and Chemisorption.
   (c) List four applications of adsorption.

4. Write one difference in each of the following :
   (i) Lyophobic sol and Lyophilic sol
   (ii) Solution and Colloid

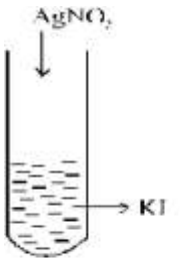
5. (a) How can a colloidal solution and true solution of the same colour be distinguished from each other?
   (b) Why is ferric chloride preferred over potassium chloride in case of a cut leading to bleeding?
   (c)Name the physical states of dispersed phase and dispersion medium of froth?

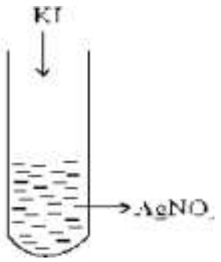
6. How does an increase in temperature affect both physical and chemical adsorption?

7. What causes Brownian movement in a colloidal solution?

8. Explain the following observations:
   a) Lyophilic colloid is more stable than lyophobic colloid.
   b) Coagulation takes place when sodium chloride solution is added to a colloidal solution of ferric hydroxide.
   c) Sky appears blue in colour.
   d) Adsorption of a gas on the surface of solid is generally accompanied by a decrease in entrop, still it is a spontaneous process.
   e) Enzyme catalysts are highly specific in their action.
   f) The enthalpy in case of chemisorption is usually higher than that of physisorption.
   g) Cottrell's smoke precipitator is fitted at the mouth of the chimney used in factories.
   h) Physical adsorption is multilayered, while chemisorption is monolayered.

9. (i) Differentiate between adsorbtion and absorption.
   (ii) Out of $MgCl_2$ and $AlCl_3$, which one is more effective in causing coagulation of negatively charged sol and why?
   (iii) Out of sulphur sol and proteins, which one forms multimolecular colloids ?
10. A colloidal solution of AgI is prepared by two different methods shown below:-
    (A) (B)



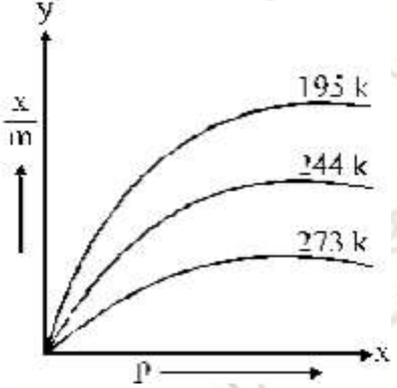


(a) What is the charge of AgI colloidal particles in the two test tubes (A) and (B)?
(b) Give reasons for the origin of charge.

11. What are the two classes of emulsion? Give one example of each class. State one activity to test the type of emulsion.

12. Describe the following giving an example each:
a) Mechanism of heterogeneous catalysis. Give a point of difference between Homogeneous catalysis and Heterogeneous catalysis.
b) Hardy Schulze Rule
c)Emulsification

13. Consider the adsorption isotherms given below and interpret the variation in the extent of adsorption ( x/m) when:



(a) (i) temperature increases at constant pressure.
(ii) pressure increases at constant temperature.
(b) Name the catalyst and the promoter used in Haber's process for manufacture of ammonia.

14. In reference to Freundlich adsorption isotherm write the expression for adsorption of gases on solids in the form of an equation.
Based on type of particles of dispersed phase, give one example each of associated colloid and multimolecular colloid.

15. Give reason for the following observations;
(i) Leather gets hardened after tanning.
(ii) It is necessary to remove CO when ammonia is prepared by Haber's process.

## Notes- Chapter -5

## PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

**Minerals:** These are naturally occurring chemical substances which are obtained from earth's crust by mining. In minerals metals are present in either native state or combined state.
**Ores**: The mineral from which metal can be economically and conveniently extracted is called ore.
**Metallurgy:** The entire scientific and technological process used for isolation of the metal from the ores is known as metallurgy. The major steps for extraction and isolation of metals are:--

- Concentration of the ore
- Isolation of metal from the concentrated ore
- Purification of metal

### I) CONCENTRATION OF ORES

Removal of unwanted materials (ie; clay, sand etc.) from ores is known as concentration. These earthly or undesirable impurities are called GANGUE. Some important procedures are:-

1) Hydraulic washing: This is based on the difference in gravities of the ore and the gangue particles. In this an upward stream of running water is used to wash the powdered on. The lighter gangue particles are washed away and heavier ores are left behind.

2) Magnetic Separation: This is base on the differences in the magnetic properties of the ore components. One of the two, ore or gangue is capable of being attracted by magnetic field.

3) Froth Floatation process: This method is used to remove gangue from sulphide ores. A suspension of powdered ore is made with water. To it collectors (E.g- Pine oil) and Froth stabilizers (e.g., cresol, aniline) are added. Collectors enhance wettability of pine oil and froth stabilizers froth. Mineral particles wetted by oil are carried away with froth and gangue particles move into water.

   Two sulphide ores can be separated using **depressants.** For eg. NaCN is used to separate ZnS and PbS present in a ore.

4) Chemical Methods(Leaching):
   a) Leaching of Alumina from Bauxite: Bauxite contains $SiO_2$, iron oxides and titanium oxide as impurities. Powdered ore is treated with concentrated solution of NaOH at 478-523 K and 35-36 bar pressure.

$$Al_2O_3(s) + 2NaOH(aq.) + 3H_2O(l) \longrightarrow 2Na[Al(OH)_4]\ (aq.)$$

   The aluminate solution is neutralized by passing $CO_2$ gas and hydrated $Al_2O_3$ separated out.

$$2Na[Al(OH)_4](aq.) + CO_2(g) \longrightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3g)$$

   The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give pure $Al_2O_3$.

$$Al_2O_3.xH_2O\ (S) \longrightarrow Al_2O_3\ (s) + x\ H_2O\ (g)$$

   b) Other example: In metallurgy of silver and gold, the respective metal is leached with dilute solution of NaCN or KCN in presence of air (Or $O_2$)

$$4M(S) + 8\ CN^-(aq.) + 2H_2O(aq.) + O_2(g) \longrightarrow 4[M(CN)_2]^-(aq.) + 4\ OH^-(aq.)$$

$$2[M(CN)_2]^-\ (aq.) + Zn(s) \longrightarrow [Zn(CN)_4]^{2-} + 2\ M(s) \qquad (M=Ag\ or\ Au)$$

II) **CALCINATION/ROASTING**: The concentrated ore is then converted to its oxide form by heating .

If the concentrated ore is heting strongly in the absence of air to get rid of impurities, and the ore changes to oxide form, it is called calcination. It is generally observed for carbonate ore.

$CaCO_3 \longrightarrow CaO + CO_2$

If the concentrated ore is heated in the presence of oxygen, ore gets converted to oxide form and small molecules like $SO_2$ are released. It generally takes place for sulphide ore. $ZnS + O_2 \longrightarrow ZnO + SO_2$

## III) REDUCTION

**Reduction of oxide to metal**:

This involves heating of the oxide with a reducing agent like C or CO or even another metal based on reactivity of the metal to be extracted.

$MxOy + yC \longrightarrow xM + yCO$

Extraction of iron from its oxides

$FeO(S) + C(s) \longrightarrow Fe(S/l) + CO(g)$

(Discussed later under extraction of Iron)

Extraction of copper from cuprous oxide:

The sulphide ores are roasted/smelted to give oxides (Most sulphide ores contain iron)

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

The oxide is then reduced to metallic copper using coke.

$Cu_2O + C \longrightarrow 2Cu + CO$

In actual process, the ore is heated in a reverberatory furnace after mixing with silica. The iron oxide slags off as iron silicate and **copper is produced in the form of copper matte. This contains $Cu_2S$ and FeS.**

$FeO + SiO_2 \longrightarrow FeSiO_3$ (slag)

Copper matte is then charged into silica lined convertor. Some silica is also added and hot air blast is blown to convert the remaining FeS, FeO and $Cu_2S/Cu_2O$ to metallic copper.

The reactions taking place are:

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

$FeO + SiO_2 \longrightarrow FeSiO_3$

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$

The solidified copper obtained has blistered appearance due to evaluation of $SO_2$& so is called blister copper.

Extraction of zinc from zinc oxide:

The reduction of zinc oxide is done using coke. For the purpose of heating, the oxide is made into brickettes with coke and clay.

$ZnO + C \xrightarrow{\text{coke, 673K}} Zn + CO$

The metal is distilled off and collected by rapid chilling.

**Thermodynamic principles of metallurgy**:

Gibb's energy is described by the equation $\Delta G = \Delta H - T\Delta S$.

For any reaction, this change can be described by $\Delta G = -RT\ln K$

Negative ΔG implies positive K and this can happen when reaction proceeds towards products.

(i) If ΔS is positive, on increasing T the value of TΔS would increase (ΔH < TΔS) and ΔH<TΔS) and ΔG becomes negative.

(ii) If reactants and products of two reactions are put together in a system and net ΔG is negative, overall reaction would occur. So the process involves coupling of two reactions and getting sum of their ΔG as negative.

For eg: In reduction of FeO

$$FeO\,(s) \longrightarrow Fe(s) + \tfrac{1}{2} O_2\,(g) \quad [\Delta G_{(FeO,\ Fe)}]$$

$$C\,(s) + \tfrac{1}{2} O_2\,(g) \longrightarrow CO\,(g) \quad [\Delta G_{(C,\ CO)}]$$

We couple the two so that net Gibb's energy change becomes

$$\Delta G_{(C,CO)} + \Delta G_{(FeO,\ Fe)} = \Delta G$$

The resultant will have ΔG as negative.

According to Ellingham diagram, the $\Delta G^o$ Vs. T plot representing the reaction goes upward and that representing C CO goes downward. At temp.above 1073 K the (C,CO) line come below the Fe, FeO line [ ΔG(C, CO) < ΔG( Fe, FeO)]. So coke will be reducing FeO and is itself oxidized to CO.

## IV) REFINING

A metal extracted by any method is usually contaminated with some impurity. Some methods are

a) **Distillation**: The impure metal is evaporated to obtain pure metal as distillate. Used for low boiling metals like **Zn and mercury**.

b) **Liquation:** The low melting metal, like **tin** is separated from high melting impurities by this method. The metal is made to flow on sloping surface.

c) **Electrolytic refining**: In this method impure metal is made to act as anode. A strip of same metal in pure form is made cathode. The electrolyte used contains soluble salt of the same metal. The more basic metals remain in the solution and less basic form anode mud.

For e.g**.** **Copper** is refined by electrolytic method. Anode is impure copper and pure copper strips are taken as cathode and electrolyte is acidified solution of copper sulphate.

Anode: $Cu \longrightarrow Cu^{2+} + 2e^-$

Cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

d) **Zone refining**: It is based on the fact that melting point of a substance is lowered by the presence of impurities. Consequently when an impure metal in molten state is cooled, crystals of pure metal are solidified first and impurities remain behind in the molten metal which crystallizes later. The semiconductors –silicon and germanium are purified by this method.

e) **Vapour Phase refining**: This method is used for preparing ultrapure metals by forming vapours of the compound of metal and later decomposition to get pure metal.

Eg- 1) **Mond process for refining Ni**

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

volatile complex- nickel tetracarbonyl

At higher temperature,

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

2) **Van Arkel method for refining of Zr or Ti** : This method is useful for removing all oxygen and nitrogen present as impurity. Crude metal is heated in evacuated vessel with iodine.

$$Zr + 2I_2 \longrightarrow ZrI_4$$

Metal iodide is then heated on a tungsten filament to about 1800 K.

$$ZrI_4 \xrightarrow{\Delta} Zr + 2I_2$$

f) **Chromatographic methods**: This method is based on the principle that different components are differently adsorbed on adsorbent. The mixture is put in a suitable solvent and applied on top of the column. The adsorbent is packed in a glass column. The adsorbed components are removed (eluted) out using suitable solvent (eluent). The weakly adsorbed component is eluted first followed by the more strongly adsorbed and so on. This is called column chromatography. This method is used for purification of elements available in minute quantities and impurities not very different in chemical properties.

## EXTRACTION OF ALUMINIUM:

Aluminium is extracted from bauxite ore, $Al_2O_3.2H_20$. It involves two steps:

1. **Concentration (by Baeyer's Process) :** Purification of Bauxite ore is done by Baeyer's process. This Chemical method is called leaching.
   (Explained under methods of concentration)
2. **Reduction { byElectrolysis of fused alumina (Hall-Heroult process)}**: The purified alumina is dissolved in molten cryolite and is electrolyse in an iron tank lined inside with carbon. The molten cryolite decreases the melting point to about 1173 K and also increases conductivity. The anode consists of a number of carbon rods which dip in fused electrolyte. The electrolyte is covered with a layer of powdered coke.

$$\mathbf{2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2}$$

Reactions at electrodes are:

At Cathode: $Al^{3+} (melt) + 3e^- \longrightarrow Al(l)$

At Anode: $C(s) + O^{2-} (melt) \longrightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-} (melt) \longrightarrow CO_2 (g) + 4e^-$

Therefore, aluminium is liberated at the cathode and gets collected at the bottom of the tank from where it is removed. The oxygen evolved combines with carbon of anode to form CO or $CO_2$ and escapes out. Because of reaction at carbon anodes, these need to be replaced periodically.

**3. Refininig of Aluminium:**

The aluminium metal obtained above is 99% pure, which is further purified by **Hoop's electrolytic method**. The process is carried out in an iron tank lined with carbon. It has 3 layers of molten liquid having different densities.

(i) The top layer consists of pure Al having carbon electrodes dipping in it. The carbon electrodes act as cathode.

(ii) The middle layer has fluorides of sodium, barium and Aluminium in molten state. This acts as an electrolyte.

(iii) The bottom layer consists of impure Al along with the carbon lining acts as anode.

On passing electric current aluminium ions from the middle layer are discharged at cathode as pure Al. The pure Al is removed from the tapping hole. An equivalent amount of Al from bottom layer moves into the middle layer leaving behind impurities.

## EXTRACTION OF IRON

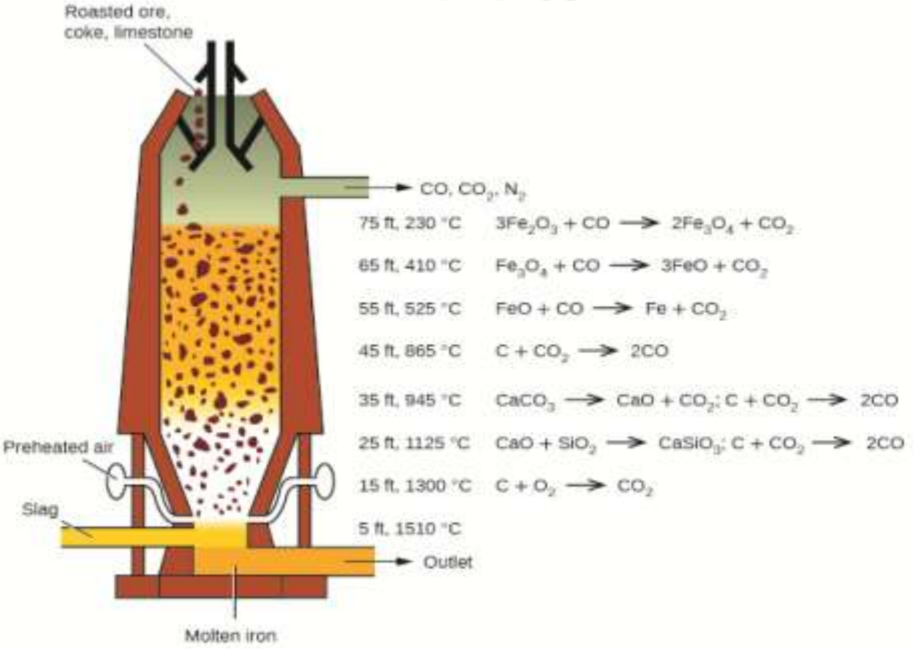
Iron is the second most abundant element occurring in earth's crust. The common ores are:

Haemite $Fe_2O_3$
Magnetite $Fe_3O_4$
Limonite $Fe_2O_3.3H_2O$
Iron Pyrites $FeS_2$
Siderite $FeCO_3$

Cast Iron is usually extracted from its oxide ore (haematite). It involves the following steps---

1) **Concentration**: The ore is first crushed and crushed ore is concentrated by gravity separation; ie hydraulic washing
2) **Calcination**: The concentrated ore is calcined, ie, heated strongly in limited supply of air in a reverberatoryfurnance. The following changes take place:
   i) Moisture is removed
   ii) Impurities of S, $P_4$ and As are converted to their gaseous oxides; sO2 , As2O3 and P4O10 which are volatile and escape out.
3) **Reduction (by Smelting)** : The calcined ore is reduced with carbon, ie smelted in a blast furnance. It is a tall cylindrical furnance made of steel llined with fire bricks. It is narrow at the top and has cup and cone arrangement for the introduction of charge and outlet for waste gases. At the base of furnace, it is provided with ---
   i) Tuyeres arrangement for introduction of hot air
   ii) A tapping hole for withdrawing molten iron and
   iii) An outlet through which slag is flown out.

The calcined ore ( 8 parts ) is mixed with coke (4 parts) and limestone (1part) is introduced from top. At the same time a blast of hot air preheated at 1000 K is blown upwards with the help of tuyers arrangement. The added coke acts as a reducing agent and lime serves as flux. The burning of coke to carbon monoxide supplies most of the heat required for working temperature of furnace and give temp. upto 2200 K at the bottom of furnace. As the gases move up, they meet the descending charge and temp. falls. At the bottom reducing agent is carbon but at the top the reducing agent is CO.



The reactions occurring are:---

1) Combustion zone: At the base coke burns to produce $CO_2$ which starts rising upward. The reaction is exothermic and heat produced raises the temperature to about 2200 K.

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = -393.4\ KJ$$

2) Fusion zone: As $CO_2$ rises upward, it comes in contact with coke and gets reduced to CO.

$$CO_2 + C \longrightarrow 2CO \qquad \Delta H = +63.2\ KJ$$

The reaction is endothermic , the temperature is lowered to 1570 K. The iron produced in the upper region melts. Any $Fe_2O_3$ if present is reduced by hot coke to iron.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO + heat$$

3) Slag formation zone; In the middle temperature is about 1270K. In this region limestone decomposes.

$$CaCO_3 \longrightarrow CaO + CO_2$$

The lime acts as flux and combines with silica (present as an impurity) to produce slag.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

The molten slag forms a separate layer above molten iron.

4) Reduction Zone: The temperature near the top of furnace is 875 K. The oxide is reduced by carbon monoxide to iron.

$$FeO + CO \longrightarrow Fe + CO_2$$
$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$
$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

The spongy iron produced moves down slowly and melts in fusion zone.

At lower hotter part, reaction is

$$FeO + C \longrightarrow Fe + CO.$$

It dissolves some carbon, silicon, phosphorus and manganese and forms a layer at the bottom. The iron obtained is called **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 less carbon content (about 3%) . It is extremely hard but brittle.

**Wrought iron** is purest form of iron and is prepared from cast iron by oxidizing impurities in reverberatory furnace lined with haematite. Haematite oxidizes carbon.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

Limestone is added as flux and S, Si and P are oxidized and passed into slag. The metal is then removed.

## EXTRACTION OF COPPER:

Copper is mainly extracted from copper pyrites ($CuFeS_2$). The various steps are:

1) **Crushing and concentration**: The ore is crushed in haw crushers and is finally powdered. It is concentrated by froth floatation process.

2) **Roasting**: The concentrated ore is roasted ,i.e, heated strongly in the presence of excess of air in a reverberatory furnace.

   a) Moisture is removed from ore and it becomes dry.

   b) The impurities of S, $P_4$, As and Sb are removed as their volatile oxides.

$$S + O_2 \longrightarrow SO_2$$
$$P_4 + 5O_2 \longrightarrow 2P_2O_5$$
$$4As + 3O_2 \longrightarrow 2As_2O_3$$
$$4Sb + 3O_2 \longrightarrow 2Sb_2O_3$$

   c) Copper pyrites is converted to ferrous sulphide (FeS) and cuprous sulphide ($Cu_2S$)

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + FeS + SO_2$$
$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

3) **Smelting**: The roasted ore is mixed with powdered coke and sand and is strongly heated in a blast furnace . The blast furnace is made of steel and is lined with fire bricks. A blast of hot air is introduced at the lower part of the furnace and changes occurring are:

**a)** Ferrous sulphide is oxidized to ferrous oxide which combines with silica to form slag.

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

$FeO + SiO_2 \longrightarrow FeSiO_3$ (slag)

The slag being lighter forms the upper layer and is removed from time to time.

**b)** During roasting if any oxide of copper is formed, it combines with FeS and is changed back into its sulphide

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$Cu_2O + FeS \longrightarrow Cu_2S + FeO$ (This changes to slag by combining with $SiO_2$)

As a result two separate layers are formed at the bottom of furnace. Upper layer is slag which is removed as waste. The lower layer of molten mass contains mostly cuprous sulphide and some traces of ferrous sulphide. It is called matte and is taken out from tapping hole at bottom.

4) **Bessemerisation**: The molten matte from Blast-furnace is transferred to Bessemer converter. The vessel is silica lined from inside. A blast of hot air is mixed with sand is blown into molten matte. During this process ….

a) Traces of ferrous sulphide present in matte are oxidized to FeO which combines with silica to form slag.

$2\,FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

$FeO + SiO_2 \longrightarrow FeSiO_3$ (slag)

b) Copper sulphide is oxidized to cuprous oxide which further reacts with remaining copper sulphide to form copper and sulphur dioxide.

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$

After the reaction has been completed, the converter is tilted and molten copper is put in moulds. The copper thus obtained is 99% pure and is known as blister copper. The name blister is given because as metal solidifies, the dissolved $SO_2$ escapes out producing blisters on metal surface.

5) **Refining**: Blister copper is purified by:

**a)** **Poling**: Heating strongly in a reverberatory furnace in the presence of excess of air. Impurities are either converted to oxides or converted to slag. Some copper also changes to cuprous oxide. This is reduced back to copper by stirring the molten metal with green poles of wood. This gives 99.5 % pure Cu, which is then purified by electrolytic refining.

**b)** **Electrolytic refining**: A thin sheet of metal is made cathode and block of crude metal is made as anode. Both the electrodes are placed in an acidified CuSO4 solution when electric current is passed through the solution, impure Cu from anode goes into the solution and pure Cu from the solution gets deposited on the cathode.

At anode: $Cu \longrightarrow Cu^{2+} + 2e^-$

At Cathode $Cu^{2+} + 2e^- \longrightarrow Cu$

The impurities of Zn, Ni, Fe etc. gets collected below as anode mud.

## EXTRACTION OF ZINC

Principal ore of Zinc is Zinc Blende. Extraction is carried out in the following steps:-

1) **Concentration**: Ore is concentrated by froth floatation process.
2) **Roasting**: Concentrated ore is roasted in excess of air at about 1200 K andZnS is converted to ZnO.

   $$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

3) **Reduction**: ZnO is reduced by heating with crushed coke at 673 K. For the purpose of heating, the oxide is made into brickettes with coke and clay.

   $$ZnO + C \xrightarrow{\text{coke, 673K}} Zn + CO$$

   The metal is distilled off and collected by rapid chilling.
4) **Refining**: Impure metal is refined by electrolysis. In this process, impure zinc is made the anode and a plate of pure zinc is made the cathode. The electrolyte is zinc sulphate with little dil. H2SO4. On passing current zinc is deposited at cathode while equal amount of zinc from anode goes into electrolyte. Thus, pure zinc is obtained on cathode.

**Some extractions based on oxidation:**

1) **EXTRACTION OF CHLORINE FROM BRINE**

   Chlorine is abundant in sea water and hence is obtained from electrolysis of brine solution.

   $$2Cl^- (aq.) + 2H_2O (l) \longrightarrow 2OH^- (aq.) + H_2(g) + Cl_2(g)$$

   $\Delta G^o = +422$ KJ and using $\Delta G^o = -nFE^oCell$ , $E^o = -2.2$ V .

   So it requires emf greater than 2.2 V. But electrolysis requires an excess potential to overcome some hindering reaction. Thus, $Cl_2$ is obtained by electrolysis giving out $H_2$ and aqueous NaOH as by products.

2) **EXTRACTION OF GOLD AND SILVER**:

   Extraction of Gold involves leaching the metal with $CN^-$ (OXIDATION)

   $4Au(s) + 8CN^-(aq.) + 2\,H_2O\,(aq.) + O_2\,(g) \longrightarrow 4[Au(CN)_2]^-(aq.) + 4OH^-\,(aq.)$[oxidation, NaCN here acts as a leaching agent or complexing agent.

   $2[Au(CN)_2]^-(aq.) + Zn\,(s) \longrightarrow 2Au(s) + [Zn(CN)_4]^{2-}\,(aq.)$ [ Reduction , Zn acts as a reducing agent]

   Similarly for Silver

   $4Ag(s) + 8CN^-(aq.) + 2\,H_2O\,(aq.) + O_2\,(g) \longrightarrow 4[Ag(CN)_2]^-(aq.) + 4OH^-\,(aq.)$

   $2[Ag(CN)_2]^-(aq.) + Zn\,(s) \longrightarrow 2Ag(s) + [Zn(CN)_4]^{2-}\,(aq.)$

**<u>Hands-on/ IT Enabled work</u>**

Whole chapter is taught with the help of a presentation with animations.

# Assignment
## Chapter 5: General Principles and Processes of Isolation of Elements

1. Write the chemical reactions involved in the process of extraction of Gold. Explain the role of dilute NaCN and Zn in this process.

2. (a) Write the principle of method used for the refining of germanium.
   (b) Out of PbS and $PbCO_3$ (ores of lead), which one is concentrated by froth floatation process preferably?
   (c) What is the significance of leaching in the extraction of aluminium?

3. What do you understand by the following terms?
   (a) Roasting (b) Flux (c) Calcination (d) Smelting (e) Slag

4. a) In the extraction of A*l*, impure $Al_2O_3$ is dissolved in conc. NaOH to form sodium aluminate and leaving impurities behind. What is the name of this process? also write the reactions involved
   b) What is the role of coke in the extraction of iron from its oxides?

5. Write the reactions occurring in the different zones of blast furnance during extraction of iron from concentrated Haemetite ore.
6. Explain Hall Heroult process of reduction of aluminium oxide. What is the role of graphite and cryolite in electrometallurgy of aluminium?

7. (a) Why is the froth floatation method selected for the concentration of Sulphide ores? Write reactions taking place in the extractions of zinc from zinc blende.
   (b) An ore sample of galena (PbS) is contaminated with zinc blende (ZnS). Name one chemical compound which can be used to concentrate galena selectively by froth floatation method. What are such substances called?

8. (a) What is the role of silica in the extraction of copper?
   (b) Explain electrorefining of copper. Name the common metals present as anode mud in electrorefining of copper.

9. Account for the following facts :
   a) The reduction of a metal oxide is easier if the metal formed is in liquid state at the temperature of reduction.
   b) The reduction of $Cr_2O_3$ with Al is thermodynamically feasible, yet it does not occur at room temperature.
   c) Pine oil is used in froth floatation method

10. a) Indicate the principle behind the method used for refining of zinc.
    b) Out of C and CO, which is a better reducing agent at the lower temperature range in the blast furnace to extract iron from the oxide ore?
    c) Which form of iron is the purest form of iron?

## p Block Elements

General Configuration: $ns^2 np^{1-6}$
Maximum oxidation state = Group 10

Across a period: Covalent radii and metallic character decreases, but electro negativity, electron affinity, oxidizing power and ionization energy increases.

Down the group: Covalent radii and metallic character increases, but electro negativity, electron affinity, oxidizing power and ionization energy decreases.

Inert pair effect: While going down the group, the $ns^2$ electrons become more and more reluctant to participate in bond formation. This is because down the group bond energy decreases and so the energy required to un-pair $ns^2$ electrons is not compensated by the energy released in forming two additional bonds.

## Group 16

Elements in group 16 are Oxygen (O), Sulphur (S), Selenium (Se), Tellurium (Te) and Polonium (Po). Also called Chalcogens.

**Occurrence**:

1. Oxygen is the most abundant element.
2. Sulphur exists as gypsum $CaSO_4.2H_2O$, Epsom salt $MgSO_4.7H_2O$ or galena PbS, Zinc blende ZnS etc.
3. Selenium and Tellurium as Selenides and Tellurides in sulphur ores.
4. Polonium exists as decay product of thorium and uranium minerals.

**Electronic Configuration**:
General electronic config – $ns^2np^4$

**Atomic and Ionic Radii**:
Due to increase in number of shells, atomic and ionic radii increase from top to bottom in the group.

**Ionization Enthalpy**:

1. Decreases down the group due to increase in size.
2. Group 16 elements have lower ionization enthalpy than corresponding elements of group 15 due to stability of half filled p-orbital electronic configuration in group 15.

**Electron Gain Enthalpy**:

1. Oxygen has less negative electron gain enthalpy due to its compact nature.
2. Sulphur onwards the value again becomes negative upto Po.

**Electronegativity**:
Oxygen is the second most electronegative element, next to fluorine. Within a group electro negativity decreases with increase in atomic number.

**Metallic Character**:
Increase from oxygen to polonium.

**Physical Properties**:

| | |
|---|---|
| **O,S - Non-Metals**<br>**Se, Te - Metalloids**<br>**Po - Metal** | **1. All of them exhibit Allotropy.**<br>**2. M.P and B.P increases with increase in atomic number but there is large difference in m.p of O and S due to its atomicity – $O_2$ and $S_8$.** |

**Chemical Properties**:
1. Stability of -2 oxidation state decreases down the group.
2. Oxygen shows only negative oxidation state of -2 and in case of $OF_2$, oxidation state of +2.
3. Other elements of the group easily show +2, +4, and +6 oxidation state.
4. Stability of +4 oxidation state increase down the group due to inert pair effect.

**Reactivity with Hydrogen**:
All the elements form hydrides of the formula $H_2E$ (E = S, Se, Te, Po).

| | |
|---|---|
| **$H_2O$**<br>**$H_2S$**<br>**$H_2Se$**<br>**$H_2Te$**<br>**$H_2Po$** | **1. Acidic nature increases from $H_2O$ to $H_2Te$ due to decrease in bond dissociation enthalpy.**<br>**2. Thermal Stability decreases from $H_2O$ to $H_2Po$.**<br>**3. All hydrides except water posses reducing property and this characteristic increases from $H_2S$ to $H_2Te$.** |

**Reactivity with Oxygen**:
All these elements form oxides of the formula $EO_2$ and $EO_3$ where E = S, Se, Te or Po.
1. $SO_2$ is gas but $SeO_2$ is solid.
2. Reducing property decreases from $SO_2$ and $TeO_2$. $SO_2$ is reducing and $TeO_2$ is an oxidising agent.
3. Also form $EO_3$ type oxides. Both types are acidic.

**Reactivity towards halogens**:
1. Form halides of the formula $EX_6$, $EX_4$ and $EX_2$.
2. Stability of halides decrease in the order $F^- > Cl^- > Br^- > I^-$.
3. Among hexahalides, hexafluorides are only stable. They (hexafluorides) are gaseous octahedral in nature. Most stable is $SF_6$ due to steric reasons.
4. Amongst tetrafluorides, $SF_4$ is gas, $SeF_4$ is liquid and $TeF_4$ a solid. They have $Sp^3d$ hybridization and have trigonal bipyramidal structures and are regarded as see-saw geometry.
5. All elements except Se form dichlorides and dibromides. Dihalides have $Sp^3$ hybridisation.
6. Monohalides are dimeric in nature. E.g – $S_2Fe$, $S_2Cl_2$, $S_2Br_2$, $Se_2Cl_2$ and $Se_2Br_2$. Dimeric halides undergo disproportionation as:- $2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$

## DIOXYGEN

**Methods of Preparation**:

1. By heating chlorates, nitrates and permanganates.
   $2KClO_3 \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$
2. Thermal decomposition of oxides.
   $2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g)$;  $2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$
   $2HgO(s) \rightarrow 2Hg(l) + O_2(g)$ :  $2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$
3. $2H_2O_2 \rightarrow 2H_2O + O_2$ Catalyst used – finely divided metals and manganese dioxide.
4. On large scale, prepared by electrolysis of water.
5. Industrially, from air → first carbon dioxide and water vapour are removed and remaining gases liquefied are fractionally distilled.

**Properties of DIOXYGEN**:

1. Colourless and odourless gas.
2. Directly reacts with nearly all metals and non metals except Au, Pt and some noble gases. Its combination with other elements is exothermic.

3. Some reactions with metals and non-metals are :
   $2Ca + O_2 \longrightarrow 2CaO$
   $4Al + 2O_2 \longrightarrow 2Al_2O_3$
   $P_4 + 5O_2 \longrightarrow P_4O_{10}$
   $C + O_2 \longrightarrow CO_2$
   $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$
   $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
4. Some compounds are catalytically oxidized.
   $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$
   $4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O$

**Uses**:

1. Importance in normal respiration and combustion.
2. Oxyacetylene welding.
3. Manufacture of steel.
4. Oxygen cylinders are used in hospitals, high altitude flying and in mountaineering.
5. Combustion of fuels, e.g, hydrazine in liquid oxygen provides thrust in rockets.

## OXIDES

A binary compound of oxygen with another element is called oxide.

Oxides can be simple (MgO, $Al_2O_3$) or mixed ($Pb_3O_4$, $Fe_3O_4$). Simple oxides can be acidic, basic or amphoteric oxides.

An oxide which combines with water to give an acid is termed as acidic oxide. (e.g $SO_2$, $CO_2$, $N_2O_5$)

$SO_2 + H_2O \longrightarrow H_2SO_3$ (Non metal oxides are acidic)

The oxide which gives a base with water is called basic oxides. Metal oxides are basic (e.g- $Na_2O$, $CaO$, $BaO$)

$CaO + H_2O \longrightarrow Ca(OH)_2$

Some metal oxides exhibit dual behavior. They show characteristics of both acidic as well as basic oxides. They are known as amphoteric oxides. E.g $Al_2O_3$

$Al_2O_3 + 6HCl + 9H_2O \longrightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^-$

$Al_2O_3 + 6NaOH + 3H_2O \longrightarrow 2Na_3[Al(OH)_6]$

Some oxides are neither acidic nor basic. E.g CO, NO and $N_2O$

## OZONE

Ozone is an allotrope of oxygen. It is too reactive to remain at sea level. At a height of 20km above sea level it is formed from atmospheric oxygen in the presence of sunlight. The ozone layer protects earth's surface from excessive concentration of UV radiation.

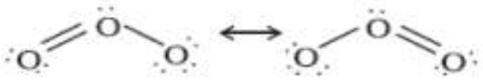
**Preparation**:

When silent electric discharge is passed through dry oxygen, ozonised oxygen (10%) is produced.

$3O_2$ $2O_3$ ($\Delta H$=142KJMol-1)

**Properties**:

1. Pale blue gas, dark blue liquid and violet black solid.
2. In small concentrations, it is harmless and if concentration rises above 100ppm breathing becomes uncomfortable.
3. Ozone is thermodynamically unstable. Its decomposition to oxygen results in liberation of heat and increase in entropy. The two effects results in negative Gibb's energy change for conversion into oxygen. High concentration of ozone can be dangerously explosive.
4. Acts as good oxidising agent because [$O_3 \rightarrow O_2 + O$] due to liberation of nascent oxygen.
   $PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$
   $2I^- + H_2O + O_3 \longrightarrow 2OH^- + I_2 + O_2$
   This reaction can be used for estimating $O_3$ gas. $I_2$ liberated titrated against standard $Na_2S_2O_3$ solution helps in estimation.
5. Nitrogen oxides emitted from exhaust system of supersonic aeroplanes might be slowly depleting ozone layer in upper atmosphere.
   $NO + O_3 \longrightarrow NO_2 + O_2$
6. Ozone layer is also depleted by refrigerants and aerosol sprays.
7.



Bond length is 128pm and bond angle is 117°.

**Uses**:

1. Used as germicide, disinfectant and sterilizing water.
2. Used for bleaching oils, ivory, flour and starch.
3. Acts as oxidising agent in manufacture of $KMnO_4$.

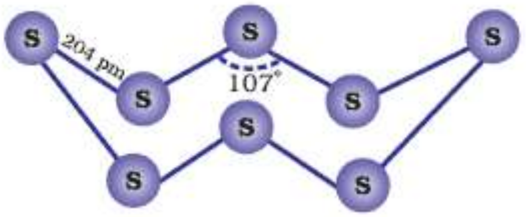
## SULPHUR

### Allotropic forms of Sulphur:

1. Yellow rhombic sulphur (α-sulphur)
2. Monoclinic sulphur (β-sulphur)

Rhombic is stable at room temperature which transforms to monoclinic when heated above 369k. Rhombic sulphur is yellow in colour, insoluble in water and dissolves to some extent in benzene, alcohol and ether. It is readily soluble in $CS_2$.

Monoclinic sulphur is stable above 369K and α-sulphur below 369K, called transition temperature, both forms are stable. Both exist as $S_8$ molecules. At high temperature (~1000k), $S_2$ is dominant and it is para magnetic.



## SULPHUR DIOXIDE

**Preparation**:

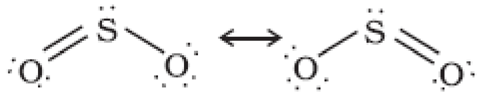
1. $S + O_2 \qquad SO_2$ Suplhur burnt in air or oxygen gives $SO_2$ along with a little (6-8%) $SO_3$.
2. Suplhites with dilute sulphuric acid.
   $SO_3^{2-}(aq) + 2H^+(aq) \qquad H_2O(l) + SO_2(g)$
3. By product of roasting sulphide ores.
   $4FeS_2 + 11O_2(g) \longrightarrow 2Fe_2O_3(s) + 8SO_2(g)$

**Properties**:

1. Colourless gas with pungent smell.
2. Highly soluble in water.
3. Liquifies at room temp. under a pressure of 2atm and boils at 263K.
4. $SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$ (sulphurous acid)
5. $NaOH + SO_2 \longrightarrow Na_2SO_3$ (sodium sulphite) + $H_2O$
   $Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$ (sodium hydrogen sulphite)
6. Reacts with chlorine in the presence of charcoal as catalyst to give sulphuryl chloride.

$SO_2(g) + Cl_2(g) \longrightarrow SO_2Cl_2(l)$

7. Oxidised to sulphur trioxide in the presence of $V_2O_5$
   $2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$
8. Moist $SO_2$ behaves as reducing agent. Converts Iron(III) ions to Iron(II) ions and
   $2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
   decolourizes acidified $KMnO_4$ solution
   $5SO_2 + 2MnO_4^- + 2H_2O \longrightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$
9. $SO_2$ is angular.

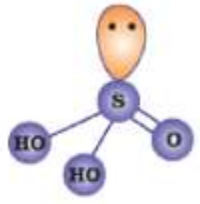


**Uses of $SO_2$:**

1. In refining petroleum.
2. In bleaching wool and silk.
3. As an anti-colour, disinfectant and preservative.
4. Sulphuric acid, $NaHSO_3$ and $Ca(HSO_3)_2$ are manufactured from sulpur dioxide.
5. Liquid $SO_2$ is used as a solvent to dissolve a number of organic and inorganic chemicals.

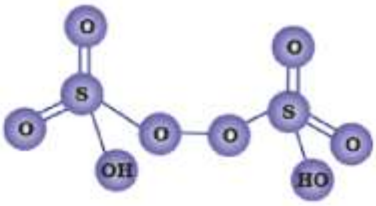
## OXOACIDS OF SULPHUR

Forms oxoacids of the formula $H_2SO_3$, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$ (x=2 to 5), $H_2SO_4$, $H_2S_2O_7$, $H_2SO_5$, $H_2S_2O_8$.

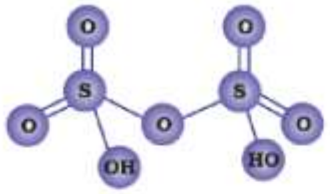


Sulphurous acid ($H_2SO_3$)

Sulphuric acid ($H_2SO_4$)



Peroxodisulphuric acid ($H_2S_2O_8$)



Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

## SULPHURIC ACID

**Manufacture:**

By contact process. The steps are:

1. Burning of sulphur or sulphide ores in air to generate $SO_2$.
   $S + O_2 \longrightarrow SO_2$
   $4FeS_2$ (Iron pyrites) $+ 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$
2. Conversion of $SO_2$ to $SO_3$ by the reaction with oxygen in the presence of catalyst $V_2O_5$.
   $2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \quad \Delta H^o = -196.6 KJmol^{-1}$
   This is the key reaction in the process. High yield of $SO_3$ will lead to more production of $H_2SO_4$.
3. Absorption of $SO_3$ in 98% $H_2SO_4$ to give Oleum ($H_2S_2O_7$).
   $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$
4. Dilution of oleum with water to get desired concentration of sulphuric acid.
   $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$ (Sulphuric acid prepared is 96-98% pure)

## Conditions favouring maximum yield of sulphur trioxide:

Key step in the manufacture of sulphuric acid is catalytic oxidation of $SO_2$ with $O_2$ to give $SO_3$.

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \qquad \Delta H^o = -196.6 KJmol^{-1}$$

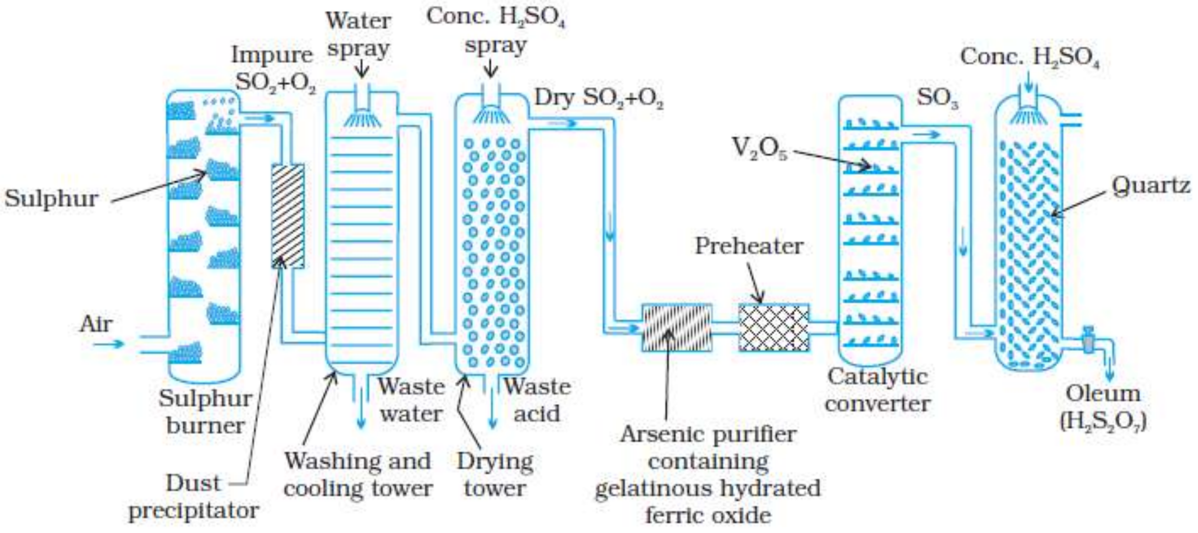
The reaction is exothermic and reversible.

a) **Low temperature**: Favours oxidation of $SO_2$ as reaction is exothermic (according to Le-Chateliar's principle). But it is essential to have a minimum temperature of 720K, to give maximum yield.

b) **High Pressure**: Favours oxidation as volume of gaseous products are less. A pressure of 2 to 3 bar is sufficient. Very high may cause corrosion of the vessel.

c) **Use of catalyst**: $V_2O_5$ increases the speed of reaction.

## Description of the Plant (Manufacture of $H_2SO_4$ by Contact Process):



*Flow diagram for the manufacture of sulphuric acid*

1. **Sulphur burners**: Sulphur or Iron pyrites are burnt.
2. **Purification unit**: The gaseous mixture coming out of sulphur burner is generally impure. Purified as:
   - I. **Dust Chambers**: Steam is introduced to remove dust.
   - II. **Coolers**: The gases are cooled to about 373K by passing them through cooling pipes.
   - III. **Scrubber**: Gases are passed into washing tower which dissolves mist and other soluble impurities.
   - IV. **Drying Tower**: A spray of conc. $H_2SO_4$ used for drying gases.
   - V. **Arsenic purifier**: This chamber contains shelves with gelatinous ferric hydroxide. The impurities of arsenic oxide are absorbed by ferric hydroxide.
3. **Testing Box**: The purifies gases are tested by passing a strong beam of light. Impurities present will scatter the light.
4. **Contact Chamber or Converter**: Pure gases are then heated to about 723-823K in a pre-heater and then introduced into contact chamber. It is a cylindrical chamber fitted with iron pipes packed with catalyst $V_2O_5$. In this $SO_2$ is oxidized to $SO_3$.

   As the forward reaction is exothermic, the pre-heating is stopped once the oxidation has started.

5. **Absorption tower**: It is a cylindrical tower packed with acid proof flint. $SO_3$ escaping out from converter is led from the bottom of the tower and conc. $H_2SO_4$ (98%) is sprayed from top. $SO_3$ gets absorbed by $H_2SO_4$ to form oleum or fuming sulphuric acid.
   $H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$ (oleum)
   Oleum is then diluted with calculated amount of water to get acid of desired concentration.
   $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

**PROPERTIES OF $H_2SO_4$**:

1. Colourless, dense and oily liquid.
2. Conc. $H_2SO_4$ dissolves in water with evolution of large quantity of heat. Hence conc. $H_2SO_4$ must be added slowly in water with constant stirring.
3. Chemical reactions of $H_2SO_4$ are as a result of:
   a) Volatility
   b) Strong acidic character
   c) Strong affinity of water
   d) Ability to act as oxidising agent
4. In aqueous solution, sulphuric acid ionizes as:
   $H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq) \quad K_{a1}$=very large (>10)
   $H_2SO_4^-(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + SO_4^{2-}(aq) \quad K_{a2}=1.2\times10^{-2}$
   Larger $K_{a1}$ means – easily dissociated into $H^+$ and $HSO_4^-$ and is a stronger acid.
5. Forms two types of salt:
   Normal sulphates (e.g. sodium sulphate, copper sulphate)
   Acid sulphates (e.g. hydrogen sulphate)
6. Can be used to form more volatile acids from their corresponding salts.
   $2MX + H_2SO_4 \longrightarrow 2HX + M_2SO_4$ (X=F,Cl, $NO_3$)
7. Acts as dehydrating agent. Can dry gases and also removes water from organic compounds.
   $C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$
8. Hot conc. $H_2SO_4$ is a strong oxidising agent. Both metals and non-metals are oxidized and itself is reduced to $SO_2$.
   $Cu + 2H_2SO_4\,(conc.) \longrightarrow CuSO_4 + SO_2 + 2H_2O$
   $3S + 2H_2SO_4\,(conc.) \longrightarrow 3SO_2 + 2H_2O$
   $C + 2H_2SO_4\,(conc.) \longrightarrow CO_2 + 2SO_2 + 2H_2O$

**USES**:

1. Important industrial chemical.
2. Used in manufacture of fertilizers (e.g. ammonium sulphate, superphosphate)
3. Petroleum refining
4. Paints, pigments and dyestuff
5. Detergent industry
6. Metallurgical applications
7. storage batteries
8. Laboratory reagent
9. In the manufacture of nitrocellulose products

## GROUP 17

F, Cl, Br, I, At (radioactive) are called halogens. Most reactive non-metals and most electronegative.

$F_2$: Pale yellow gas
$Cl_2$: Greenish yellow gas
$Br_2$: Reddish brown liquid, sparingly soluble in $H_2O$
$I_2$: Lustrous, grayish black solid, sublimes on heating sparingly soluble in $H_2O$, soluble in org. solvents.

**Bond Energy**:

$F_2 < Cl_2 > Br_2 > I_2$

Anomalous behavior of $F_2$ is due to the fact that the lone pair of electrons are very close which lead to repulsions.

**Electron Affinity**:

$F < Cl > Br > I$

This is because F being small in size repels the incoming electron.

Occurs as:

F – Fluorides
Cl – NaCl in oceans
Br – Bromides
I – Iodides and iodates ($IO_3^-$)

| **Oxidizing power** | $F_2 > Cl_2 > Br_2 > I_2$ |
|---|---|
| **Radii** | $F < Cl < Br < I$ |
| **I.E** | $F > Cl > Br > I$ |
| **E.N** | $F > Cl > Br > I$ |

**Preparation of Chlorine**:

**$Cl_2$:**

*Electrolysis of natural brine (NaCl)

* Deacon's process: Oxidation of HCl(g) in presence of CuCl2 at 723K

$4HCl(g) + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

By oxidation of HCl by $MnO_2$ or $KMnO_4$ (Lab Method)

$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + Cl_2$

By oxidation of NaCl

$2NaCl + 2H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$

**Trends in Group 17**:

| | |
|---|---|
| **$F_2$**<br>**$Cl_2$**<br>**$Br_2$**<br>**$I_2$** | **F is the most electronegative element i.e. has good acceptance of an electron and is therefore the strongest oxidizing agent.**<br>**Oxidizing character decreases down the group. Thus one halogen oxidises halide ions of higher atomic number halogens.** |

**Oxidizing Action**:

$F_2 > Cl_2 > H_2SO_4 > Br_2 > I_2$

$F_2 + 2X^- \longrightarrow 2F^- + X_2$ (X=Cl, Br, I)
$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$ (X=Br, I)
$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$

Similar reactions as above cannot be used for the preparation of HBr and HI as $H_2SO_4$ is a stronger oxidizing agent and will oxidize the HBr, HI formed to $BR_2$, $I_2$ respectively.

$NaBr + H_2SO_4 \longrightarrow HBr \longrightarrow Br_2 \uparrow$
$NaI + H_2SO_4 \longrightarrow HI \longrightarrow I_2 \uparrow$

The decreasing oxidizing ability of the halogens in aqueous solution is evident from their standard electrode potentials which is dependent on the dissociation enthalpy of $X_2(g)$. electron gain enthalpy of X(g) and hydration enthalpy to form $X^-(aq)$.

The relative oxidizing power of halogens can be further illustrated by their reaction with water:

$2F_2(g) + 2H_2O(l) \longrightarrow 4H+(aq) + 4F- + O_2(g)$
$X_2(g) + H_2O(l) \longrightarrow HX(aq) + HOX(aq)$ ( Where X= Cl or Br)

$I^-$ can be oxidized with $O_2$ in acidic medium:

$4I^-(aq) + 4H^+(aq) + O_2(g) \longrightarrow 2I_2(s) + 2H_2O(l)$

Reverse reaction is true for F.

HX are colourless, irritating gases.

HF has a higher b.p due to H-bonding.

Reactivity of halogens with metals or non-metals decreases down the group. $F_2 > Cl_2 > Br_2 > I_2$

e.g. $Mg + Br_2 \longrightarrow MgBr_2$
$Xe + 3F_2 \longrightarrow XeF_6$

Ionic character of M-X bond decreases down the group. M-F > M-Cl > M-Br > M-I

Low O.S of M $\longrightarrow MCl_2$
High O.S of M $\longrightarrow MCl_4$ more covalent than $MCl_2$

**Acidic Character**:

HF << HCl < HBr < HI

Low acidic character of HF is due to strong H-bonding and higher bond dissociation enthalpy. HF is corrosive and attacks glass.

$NF_3$ is an exothermic compound but $BCl_3$ is endothermic because bond energy of $F_2$ is lower than $Cl_2$ and N-F bond is smaller and stronger than N-Cl bond.

**Stability**:
Decreases down the group due to decreased bond dissociation enthalpy.
HF > HCl > HBr > I

**Reducing Nature**:
HF < HCl < HBr < HI

**Oxides**:
Halogens form many oxides with oxygen. Fluorine forms only $OF_2$ and $O_2F_2$ – oxygen fluorides, they are good fluorinating agents.

$$Pu + 3O_2F_2 \longrightarrow PuF_6 + 3O_2 \quad \text{(removed as } PuF_6\text{)}$$

$O_2F_2$ oxidises Pu to $PuF_6$ and the reaction is used in removing Pu as $PuF_6$ from spent nuclear fuel.

Chlorine, Bromide and iodine form oxides where o.s ranges from +1 to +7. The higher oxides of halogens tend to be more stable than the lower ones.

Chlorine oxides, $Cl_2O$, $ClO_2$, $Cl_2O_6$ and $Cl_2O_7$ are highly reactive oxidizing agents. $ClO_2$ is used as bleaching agent for paper pulp and textiles and in water treatment.

Bromine oxides $Br_2O$, $BrO_2$, $BrO_3$ are least stable halogen oxides. They are powerful oxidizing agents.

The iodine oxides, $I_2O_4$, $I_2O_5$, $I_2O_7$ are insoluble solids and decompose on heating. $I_2O_5$ is a very good oxidizing agent and is used in the estimation of CO.

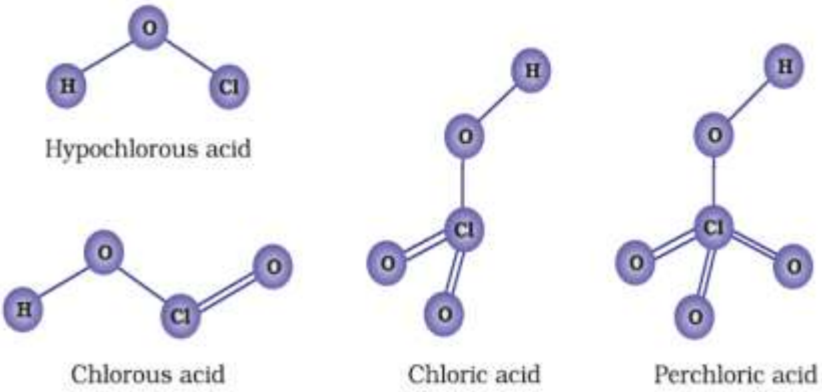
**Reactivity towards Metals**:

Halogens react with metals to form metal halides. $Mg(s) + Br_2(l) \longrightarrow MgBr_2(s)$
Ionic character of the halides decreases in the order: MF > MCl > MBr > MI where M is a monovalent metal.

If metal exhibits more than one O.S, higher O.S halides are more covalent than low O.S halides

**Oxoacids of Halogens**:

| | | | | |
|---|---|---|---|---|
| **Halic (I) acid (Hypohalous acid)** | **HOF (Hypofluorous acid)** | **HOCl (Hypochlorous acid)** | **HOBr (Hypobromous acid)** | **HOI (Hypoiodous acid)** |
| **Halic (III) acid (Halous acid)** | **–<br>–** | **HOClO (chlorous acid)** | **–<br>–** | **–<br>–** |
| **Halic (V) acid (Halic acid)** | **–<br>–** | **$HOClO_2$ (chloric acid)** | **$HOBrO_2$ (bromic acid)** | **$HOIO_2$ (iodic acid)** |
| **Halic (VII) acid (Perhalic acid)** | **–<br>–** | **$HOClO_3$ (perchloric acid)** | **$HOBrO_3$ (perbromic acid)** | **$HOIO_3$ (periodic acid)** |



The structures of oxoacids of chlorine

**Inter Halogen Compounds**:

When two different halogens react with each other, interhalogen compounds are formed. E.g. XX′, $XX'_3$, $XX'_5$ and $XX'_7$ where X is halogen of larger size and X′ of smaller size and X is more electropositive than X′.

**Preparation**:

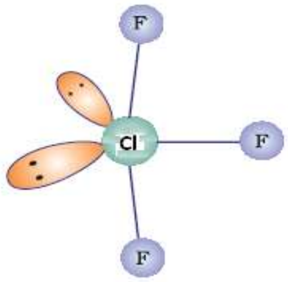
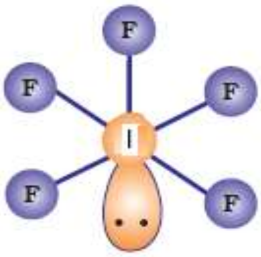
They are prepared by the direct combination or by the action of halogen on lower interhalogen compounds. For e.g.,

$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{437\,K} 2ClF;$ $\qquad I_2 + \underset{\text{(excess)}}{3Cl_2} \rightarrow 2ICl_3$

$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573\,K} 2ClF_3;$ $\qquad \underset{\text{(diluted with water)}}{Br_2 + 3F_2} \rightarrow 2BrF_3$

$\underset{\text{(equimolar)}}{I_2 + Cl_2} \rightarrow 2ICl;$ $\qquad Br_2 + \underset{\text{(excess)}}{5F_2} \rightarrow 2BrF_5$

**Properties**:

| | | |
|---|---|---|
| **XX′** | **ClF, BrF, IF (unstable), BrCl, ICl, IBr** | |
| **$XX'_3$** | **$ClF_3$ (Bent T-Shaped,, because it is sp3d hybridized)**<br>**$BrF_3$ (Bent T-Shaped,, because it is sp3d hybridized)**<br>**$IF_3$ (Bent T-Shaped,, because it is sp3d hybridized)**<br>**$ClF_3$ (Bent T-Shaped,, because it is sp3d hybridized)** |  |
| **$XX'_5$** | **$IF_5$ (Square pyramid)**<br>**$BrF_5$ (Square pyramid)**<br>**$ClF_5$ (Square pyramid)** |  |
| **$XX'_7$** | **$IF_7$ (Pentagonal bipyramidal)** | |

1. They are all covalent and diamagnetic in nature. They are volatile solid or liquid except ClF which is a gas.
2. They are more reactive than halogens because X-X′ bond in inter halogens is weaker than X-X bond in halogens except F-F bond.
3. All these undergo hydrolysis giving halide ion.
   $XX' + H_2O \rightarrow HX' + HOX$ the bigger one forms hypohalous acid.

**Uses**:

The compounds are used as non aqueous solvents. They are useful fluorinating agents. $ClF_3$ and $BrF_3$ are used for the production of $UF_6$ in the enrichment of $^{235}U$.

$$U(s) + 3ClF_3(l) \rightarrow UF_6(g) + 3ClF(g)$$

**Properties of Chlorine**:

1. Greenish yellow gas with pungent and suffocating odour.
2. Reacts with metals and non-metals to form chlorides.
   $2Al + 3Cl_2 \longrightarrow 2AlCl_3$
   $2Na + Cl2 \longrightarrow 2NaCl$
   $2Fe + 3Cl_2 \longrightarrow 2FeCl$
   $P_4 + 6Cl_2 \longrightarrow 4PCl_3$
   $S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$
3. Can react with hydrogen to form HCl.
   $H_2 + Cl_2 \longrightarrow 2HCl$
   $H_2S + Cl_2 \longrightarrow 2HCl + S$
   $C_{10}H_{16} + 8Cl_2 \longrightarrow 16HCl + 10C$
4. With excess of $NH_3$, chlorine gives nitrogen and ammonium chloride while with excess of chlorine, nitrogen trichloride is formed.
   $8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_2$; $NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$
   (excess) (excess)
5. With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.
   $2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$
   (cold and dilute)
   $NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$
   (hot and conc.)
6. With dry slaked lime it gives bleaching powder.
   $2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$
   The composition of bleaching powder is $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$.
7. Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons. For example,
   $CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$
   $C_2H_4 + Cl_2 \xrightarrow{\text{Room temp.}} C_2H_4Cl_2$
8. Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl.

9. It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$

$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$

$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$

$I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$

10. It is a powerful bleaching agent; bleaching action is due to oxidation.

$Cl_2 + H_2O \rightarrow 2HCl + O$

Coloured substance + O → Colourless substance

**Uses**:

1. Used for bleaching woodpulp, bleaching cotton and textiles.
2. In extraction of gold and platinum.
3. In manufacture of dyes, drugs and organic compounds.
4. In sterilizing drinking water.
5. Preparation of poisonous gases such as phosgene ($COCl_2$), tear gas and mustard gas.

## HYDROGEN CHLORIDE:

**Preparation**:

Prepared by heating sodium chloride with concentrated sulphuric acid.

$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$

$NaHSO_4 + NaCl \xrightarrow{823K} Na_2SO_4 + HCl$

HCl gas can be dried by passing through concentrated sulphuric acid.

**Properties**:

1. Colourless and pungent smelling gas. Easily liquefied.
2. Extremely soluble. $HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$

   Its aqueous solution is called hydrochloric acid.
3. Reacts with $NH_3$ and gives white fumes. $NH_3 + HCl \longrightarrow NH_4Cl$
4. 3 parts of conc. HCl and 1 part of con. $HNO_3$ forms aqua regia.

   $Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$

   $3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$
5. It decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.

   $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

   $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

   $Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$

**Uses**:

1. In manufacture of chlorine, $NH_4Cl$ and glucose.
2. In medicine and as laboratory reagent.

**Uses of halogens and its compounds**:

| | |
|---|---|
| **$F_2$** | • Manufacture of $UF_6$ for nuclear power generation and $SF_6$ for dielectrics. |
| **HF** | • Chemicals obtained are chlorofluorocarbons like Freon used as a refrigerant and polytetra-fluorethylene called Teflon used in nonstick pans.<br>• Also used in glass industry as an etching agent and in the manufacture of fluoride salts. |
| **NaF** | • Used for fluoridation of water, (1ppm of fluoride in drinking ware prevents tooth decay) |
| **$SnF_2$** | • Used in fluoride toothpastes. |
| **$Cl_2$** | • Used for bleaching paper, pulp, textiles.<br>• Used as disinfectant for sterilizing drinking water.<br>• Used in production of organic compounds- PVC, chlorinated hydrocarbons, pharmaceuticals.<br>• Used in production of inorganic compounds. E.g. HCL, $PCl_3$, NaOCl |
| **$C_2H_2Br_2$** | • Used as gasoline additive. |
| **$Br_2$** | • Used to make AgBr for photography. |
| **$I_2$** | • Used for preparation of iodoform and KI |
| **NaI, $NaIO_3$ or KI, $KIO_3$** | Added to table salt and is called iodised salt. (Insufficient iodine in the diet leads to Goitre. |

## GROUP 18

Known as Noble gases as their valance shell orbitals are completely filled and react with a few elements under certain conditions.

| | |
|---|---|
| **He $1s^2$**<br>**Ne $2s^2 2p^6$**<br>**Ar $3s^2 3p^6$**<br>**Kr $4s^2 4p^6$**<br>**Xe $5s^2 5p^6$**<br>**Rn $6s^2 6p^6$** | • **Atmospheric abundance of the noble gases in dry air ~1% by volume of which Ar is major constituent.**<br>• **Helium or Neon is also found in radioactive minerals, e.g. pitchblende, monazite, cleveite.**<br>• **Natural gas is commercial source of helium.**<br>• **Radon is obtained as decay product of $^{226}Ra$.**<br>$^{226}_{88}Ra \longrightarrow ^{222}_{86}Rn + ^{4}_{2}He$ |

**Electronic Configuration**:

General electronic configuration is $ns^2np^6$ except He ($1s^2$). Due to fully filled configuration noble gases are inactive in nature

**IonizationEnthalpy**:
Due to stable electronic configuration, they have high I.E. Decreases down the group due to increase in atomic size.

**Atomic Radii**:
Increases down the group due to increase in number of shells.

**Electron Gain Enthalpy**:
Noble gases have stable electronic configuration, so no tendency to accept electron and hence have large positive values of $\Delta_{eg}H$.

**Physical Properties**:
1. Monoatomic, colourless, odourless and tasteless.
2. Sparingly soluble in water.
3. Low m.p and b.p due to weak dispersion forces.
4. Can be liquefied at low temperature due to weak forces.

**Chemical Properties**:
Chemically inert due to:
1. Completely filled electronic config. $ns^2np^6$ in their valance shell.
2. High ionization enthalpy.
3. More positive electron gain enthalpy.

**Uses of Noble Gases**:

**Helium**:
- Non inflammable and light gas. Used in filling balloons for meteorological observations.
- Used in gas cooled nuclear reactors.
- Liquid He (b.p. 4.2K) is used as cryogenic agent for carrying out various experiments at low temperatures.
- Used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems.

**Neon**:
- Used in discharge tubes.
- Used in fluorescent bulbs for advertisement display purpose.

**Argon**:
- Used to provide an inert atmosphere in high temperature metallurgical processes.
- Used for filling electric bulbs.
- Used in lab for handling substances that are air sensitive.

**Kr, Xe**:
- Used in light bulbs used for special purposes.

**Energy of Compounds of Noble Gases**:

In 1962, Neil Bartlett prepared a red compound $O_2^+PtF_6^-$. He realised that the first I.E of $O_2$=1175 kJmol$^{-1}$ was almost identical to I.E of Xe=1170 k Jmol$^{-1}$. He prepared a similar red colour compound by mixing Xe and $PtF_6$.

$$Xe + PtF_6 \longrightarrow Xe^+[PtF_6]^-$$

After this, a number of compounds of Xe with electronegative elements like fluorine and oxygen have been synthesised.

**Xenon-fluorine compounds**

Xenon forms three binary fluorides, $XeF_2$, $XeF_4$ and $XeF_6$ by the direct reaction of elements.

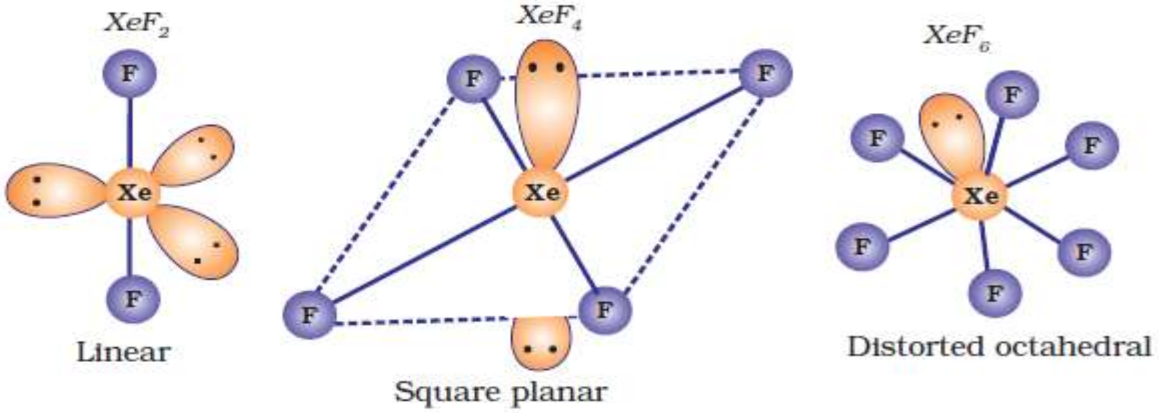
$$Xe\,(g) + F_2\,(g) \xrightarrow{673k,\ 1bar} XeF_2\,(s)$$
(Xe in excess)

$$Xe\,(g) + 2F_2\,(g) \xrightarrow{873k,\ 7bar} XeF_4\,(s)$$
(1:5 ratio)

$$Xe\,(g) + 3F_2\,(g) \xrightarrow{573k,\ 60\text{-}70bar} XeF_6\,(s)$$
(1:20 ratio)

$XeF_6$ is also prepared as $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$ at 143K.

**Structure**:



**Properties**:

1. $XeF_2$, $XeF_4$ and $XeF_6$ are colourless crystalline solids.
2. Sublime readily at 298 K.
3. They are powerful fluorinating agents. They react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

   $XeF_2 + PF_5 \rightarrow [XeF]^+ [PF_6]^-$ ;  $XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$

   $XeF_6 + MF \rightarrow M^+ [XeF_7]^-$  (M = Na, K, Rb or Cs)
4. They are readily hydrolysed even by traces of water.

   $2XeF_2\,(s) + 2H_2O(l) \rightarrow 2Xe\,(g) + 4HF(aq) + O_2(g)$

**Xenon-oxygen compounds**:

Hydrolysis of $XeF_4$ and $XeF_6$ with water gives $XeO_3$.

$$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

Partial hydrolysis of $XeF_6$ gives oxyfluorides

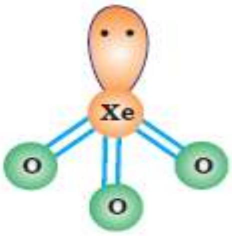
$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$$

Hydrolysis of $XeF_6$ is not a redox reaction as there is no change in oxidation state.

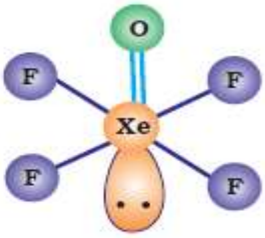
**Structure**:

$XeO_3$ (colourless explosive solid)



Pyramidal

$XeOF_4$ (colourless volatile liquid)



Square pyramidal

**Hands –on / IT Enabled work**:

Whole chapter will be done with the help of presentation.

## Assignment

### Chapter 6: p -Block Elements

1. (a) Give reasons:
   (viii) When $Cl_2$ reacts with excess of $F_2$, $ClF_3$ is formed and not $FCl_3$.
   (ix) Dioxygen is a gas while sulphur is a solid at room temperature.
   (b) Draw the structures of the following:
   (i) $XeF_4$
   (ii) $HClO_3$
   (iii) $H_2S_2O_7$
   (iv) $XeF_6$

2. (a) Arrange the following in the decreasing order of their reducing character:
   HF, HCl, HBr, HI
   (b) Complete the following reaction:
   (i) $XeF_4 + SbF_5 \longrightarrow$
   (ii)$NH_3 + 3Cl_2$(excess) ------>
   (iii) $XeF_6 + 2H_2O$ ------>
3. Give reasons:
   (i) Thermal stability decreases from $H_2O$ to $H_2Te$.
   (ii) Fluoride ion has higher hydration enthalpy than chloride ion.

4. Assign appropriate reason for each of the following observations:
   a) Sulphur in vapour state exhibits some paramagnetic behaviour.
   b) $H_2O$ is a liquid but $H_2S$ is a gas.
   c) Hydrogen bonding in Hydrogen fluoride is much stronger than that in water, yet water has much higher boiling point.
   d) The majority of known noble gas compounds are those of Xenon.
   e) Halogens are strong oxidants.
   f) The value of electron gain enthalpy with negative sign for sulphur is higher than that for oxygen.
   g) $ClF_3$ molecule has a T-shaped structure and not a trigonal planar one.
   h) $O_2$ and $F_2$ both stabilize higher oxidation states of metals but $O_2$ exceeds $F_2$ in doing so.
   i) Structures of xenon fluorides cannot be explained by Valence Bond Approach.
   j) $SF_6$ is kinetically inert.
   k) All the bonds in $SF_4$ are not equivalent..
   l) ICl is more reactive than $I_2$.
   m) Despite lower value of its electron gain enthalpy with negative sign, $F_2$ is a stronger oxidizing agent than $Cl_2$.
   n) Bond dissociation enthalpy of $F_2$ is lower than that of $Cl_2$.
   o) Ozone is thermodynamically unstable.
   p) Fluorine forms only one oxoacid HOF.

5. Write the reaction of preparation of $XeF_4$, $XeF_6$, $XeO_3$

6. Draw the structures of the following:
a) $XeF_2$ b). $XeF_4$ c) $XeOF_4$ d) $BrF_3$ e)$XeO_3$ f) $XeOF_4$ g) $SF_4$ h) $H_2SO_5$ i) $ClF_3$
j) $H_2S_2O_7$ k) $H_2S_2O_8$ l) $BrF_5$

7. Complete the equations:
a. $XeF_2 + PF_5 \rightarrow$
b. $Cl_2$ + NaOH ( cold and dil.) $\rightarrow$
c. $F_2$ (g) + $H_2O$ (l) $\rightarrow$
d. $I^-$(aq.) + $H_2O$(l) + $O_3$(g) $\rightarrow$
e. $XeF_4 + O_2F_2 \rightarrow$
f. NaOH (hot & conc) + $Cl_2 \rightarrow$
g. Xe(g) (excess)+ $F_2$(g) $\xrightarrow{673K,\ 1bar}$

8. (i)Compare the oxidizing action of $F_2$ and $Cl_2$ by considering parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy.
(ii)Write the conditions to maximize the yield of $H_2SO_4$ by contact process.
(iii) How is $SO_2$ an air pollutant?

9. Predict the shape and the asked angle($90^{o}$ or more or less) in each of the following cases:
(a) $SO_3^{2-}$ and the angle O-S-O.
(b) $XeF_2$ and the angle F-Xe-F.

10. Which noble gas is used for filling balloons for meteorological observations?

11. How does supersonic jet aeroplanes responsible for depletion of ozone layers?

## More Practice

## Chapter 6: p -Block Elements

1. Assign appropriate reason for each of the followaing observations:
   1) Hydrogen fluoride is a much weaker acid than HCl in aqueous solution.
   2) $SCl_6$ is not known where as $SF_6$ is known
   3) Halogens are coloured .
   4) Dioxygen is a gas but sulphur is a solid.
   5) Fluorine forms only one oxoacid, HOF .
   6) Sulphur has a greater tendency for catenation than oxygen.
   7) The lower oxidation statebecomes more stable with increasing atomic number in group 18.
   8) Fluorine exhibits only -1 oxidation state whereas halogens exhibit higher positive oxidation states also.
   9) On addition of ozone gas to KI solution, violet vapours are obtained.
   10) Chlorine act as both oxidizing and bleaching properties.
   11) Chlorine loses its yellow colour on standing.
   12) Bond dissociation energy of $F_2$ is less than that of $Cl_2$.
   13) $SF_4$ is easily hydrolysed whereas $SF_6$ is not easily hydrolysed.
   14) $XeF_2$ has a straight linear structure and not a bent angular structure.
   15) Fluorine does not exhibit any positive oxidation state.
   16) Oxygen shows catenation property less than Sulphur.
   17) Helium is used in diving apparatus.

2. Describe the steps involved in the contact process for the manufacture of $H_2SO_4$.

3. Give Chemical reaction in support of each of the following statements:
   a) Bleaching of flowers by $Cl_2$ is permanent while by $SO_2$ is temporary.
   b) Fluorine is a stronger oxidizing agent than chlorine.
   d) Chlorine reacts with a cold and dilute solution of sodium hydroxide.
   e) Orthophosohorous acid is heated.
   f) $PtF_6$ and Xenon are mixed together.

4. Arrange the following in the decreasing order of the property indicated:

| | |
|---|---|
| a. $H_2O$ , $H_2S$, $H_2Se$ , $H_2Te$ | boiling point |
| b. MF, MBr, MCl, MI | Ionic character of the bond |
| d. HF, HCl, HBr, HI | Acid strength |
| e. $H_2S$, $H_2O$, $H_2Se$, $H_2Te$ | Thermal stability |
| f. $HClO_4$, $HClO_3$, $HClO_2$, HClO | Oxidizing power |
| g. $Cl_2$ , $Br_2$ , $F_2$ , $I_2$ | Oxidizing power |
| h. $HClO_4$, $HIO_4$, $HBrO_4$ | Oxidising ability |

5. With what neutral molecule $ClO^-$ is isoelectronic? Also give the formula of a noble gas species isostructrual with $ICl_4^-$ and $IBr^{--}$.

## d-and f-block elements

d-block of the periodic table contains elements of the groups 3-12 in which the orbitals are progressively filled in each of the four long periods. The elements constituting the *f*- block are those in which the 4*f* and 5*f* are progressively in the later two long periods; these elements are formal members of group 3 from which they have been taken outto form separate *f*-block of the periodic table.

The transition metals are those elements which have incompletely filled d-subshells in there ground stateor in any one of their oxidation state.

Cu,Ag and Au are transition metals because in their commonly occuring states, they have partly filled d-sub shells. Zn, Cd and Hg of group 12 do not have partly filled d-sub shell in their elementary state or commonly occuring oxidation state, and hence, are not considered as transition elements. However, being the end members their chemistry is studied with transition elements.

**Electronic Configuration**- $(n-1)d^{1-10}\ ns^{1-2}$

**Transition series**- The d-block elements are called transition elements as they represent change in properties from most electropositive s-block elements to least electropositive (or most electropositive) p-block elements.

Transition elements consist to of 4 rows: These series are called transition series.

First transition series- 3d series

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| $3d^14s^2$ | $3d^24s^2$ | $3d^34s^2$ | $3d^54s^1$ | $3d^54s^2$ | $3d^64s^2$ | $3d^74s^2$ | $3d^84s^2$ | $3d^{10}4s^1$ | $3d^{10}4s^2$ |

Second Transition series – 4d series

| Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
|---|---|---|---|---|---|---|---|---|---|
| 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 |
| $4d^15s^2$ | $4d^25s^2$ | $4d^45s^2$ | $4d^5s^1$ | $4d^65s^1$ | $4d^75s^1$ | $4d^85s^1$ | $4d^{10}5s^0$ | $4d^{10}5s^1$ | $4d^{10}5s^2$ |

Third transition Series – 5d series

| La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg |
|---|---|---|---|---|---|---|---|---|---|
| 57 | 72 | 73 | 74 | 75 | 76 | 777 | 78 | 79 | 80 |

Fourth transition Series- 6d Series

| Ac | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | Uub |
|---|---|---|---|---|---|---|---|---|---|
| 89 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 |

## GENERAL POPERIES OF TRANSITION ELEMENTS

**Atomic radii:** The atomic radii is intermediate between those of s-and p- block elements. The

Following trends are observed:

a) The atomic radii of elements of a particular series decrease with increase in atomic number but this decrease in atomic radii become small after midway.

**Reason**- The atomic radii decreases in the beginning because of increase in atomic no., the nuclear charge goes on increasing progressively, but the electrons enter the penultimate shell and the added d-electrons screen the outermost s-electrons. The shielding effect is small so that net electrostatic attraction between the nuclear charge and outermost electrons increases. Consequently atomic radius decreases. As the no. of d-electrons increase the screening effect increases. This neutralizes the effect of increased nuclear charge due increase in atomic number and consequently atomic radius remains almost unchanged after chromium.

b) At the end of each period, there is slight increase in atomic number

**Reason**- This is because of increased electron-electron repulsions between the added electrons in the same orbital which exceeds the attractive forces due to increased nuclear charge. Therefore, electron cloud expands and size increase.

c) The atomic radii increase while going down the group.

**Reason** – The atomic radii of second transition series is larger than that of first transition series because of increase in no. of outermost shell.

The third transition series have nearly the same radii as metals of second transition series. This is because of lanthanide contraction. This is associated with the interventions of 4f- orbitals which are filled before 5d-series. 4f- orbital have poor screening effect, This results in regular decrease in atomic radii which compensates the expected increase in atomic size with increase in atomic no.

**Ionic Radii-** The ionic radii follows the same trend as atomic radii. Since metals exhibit different oxidation states, radii of ions also differ. The ionic radii decrease with increase in nuclear charge.

**Metallic character-** All transition elements are metals. They have high density, hardness, high m.p.& b.p. & high tensile strengths, ductility, high, thermal and electrical conductivity and lustre.

**Reason** – The metallic character is due to their relatively low ionization enthalpies and number of vacant orbitals in the outermost shell. The hardness of there metals suggests the presence of strong bonding due to overlap of unpaired electrons between different metal atoms. Therefore, they exhibit high enthalpy of atomization. Enthalpy of atomization is maximum in the middle indicates one unpaired electron is particularly favorable for strong atomic interaction. Hence, max enthalpy of atomization.

**Density**- All metals have high density. Within a period, the densities vary inversely with atomic radii, ie., densities increase along a period. Also densities increase upon descending down the group.
**Reason** – The atomic volumes of transition elements are low because electrons are added in (n-1)d sub shell and not in ns subshell . Therefore, increased nuclear charge is partly screened by the d-electrons and outer electrons are strongly attracted by the nucleus. Moveover, electrons are added in inner orbital. Conequently, densities of transition metals are high.

**Melting and boiling points**

The transition metals have high m.p. & b.p. The m.p. and b.p. of metals rise to a maximum value and then decrease with increase in atomic number. However, Mn and Tc have abnormally low m.p. & b.p.

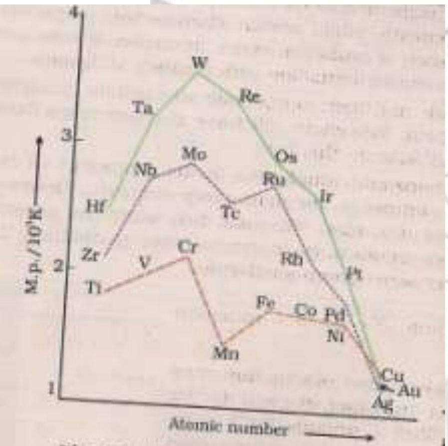


*Fig. 8.1: Trends in melting points of transition elements*

**Reason** – The high m.p. &b.p. is due to strong metallic bonds between the atoms of these elements. The metallic bond is formed due to interaction of electrons in the outermost orbital. The strength of bonding depends on the number of outer most electrons. Greater is the number of valance electrons, stronger is the metallic bonding and consequently, m.p. is high.

Therefore metallic strength increase up to the middle till d$^5$ confignation and then decreases with the decrease in availability of unpaired d- electrons(from Fe onwards) . Therefore, m.p. decrease after the middle because of increase an pairing of electrons.

The dip in the curve in Mn and Tc is due to the fact that Mn has stable electronic configuration (3d$^5$ 45$^2$). As a result 3d electrons are more tightly held by Mn atomic nucleus and this reduces delocalization of electrons resulting in weaker metallic bonding.

**Ionization Enthalpies-** The following trend is observed in the ionization enthalpies of d- block elements.The ionization enthalpies of d-block elements are lower than those of p-block elements. The I.E. increase along a series.
**Reason** - The increase in ionization enthalpy is due to the effect of increasing nuclear charge which would tend to attract outer electron with greater force. Consequently, ionization enthalpy is expected to increase. But the addition of electrons take place in last but one d-sub shell and this increases the screening effect. With the increase in electrons in d-sub shell the outer electrons are

shielded more & more. Thus, effect of increased nuclear charge is opposed by additional screening effect of the nucleus and ionization enthalpy increases but slowly.

The irregular trend in first I.E. of first transition series elements is due to the fact that removal of one electron alters the relatives energies of 4s and 3d orbitals. Therefore, there is reorganization energy which gains in exchange energy due to increase in no. of electrons in $d^n$ configuration and from transference of s-electrons in d- orbital.

***Some exceptions observed in ionization enthalpies are:-***

a) Cr and Cu have high I.E. This is attributed to their half filled ($d^5$) and completely ($d^{10}$) electronic configuration .

b) The value of second I.E. for zinc is low because ionization involves removal of an electron resulting in stable $3d^{10}$ configuration.

c) The trend in third I.E. shows high value for $Mn^{+2}$ and $Zn^{+2}$ because of stable $3d^5$ and $3d^{10}$ electronic configuration.

Similarly, $I.E_3$ for Fe $<I.E_3$ for Mn because of stable $3d^5$ in Fe. In general, third I.E. values are very high because of filled 4*f*-orbitals which have poor shielding effect.

**Oxidation States-**

a) Transition metals exhibit a larger number of oxidation states in their compound.

**Reason** - This is because of participation of inner (n -1)d electrons in addition to outer ns-electrons because the energies of ns and ( n -1)d electrons are almost equal.

The elements which gave the greatest number of oxidations states occur in or near the middle of the series. Eg.Mn ; oxidation states from + 2 & +7

The lesser number of oxidation states at the extreme ends is either due to too few electrons to lose or share or too many d electrons, hence fewer orbital are available in to available to share electrons with others, thus higher valence cannot be attained.

eg. Cu can have oxidation state of +1& +2

Zn can have oxidation state of +2 only

***Oxidation state of first row transition elements***

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| $3d^14s^2$ | $3d\ ^24s^2$ | $3d^34s^2$ | $3d^54s^1$ | $3d^54s^2$ | $3d^64s^2$ | $3d^74s^2$ | $3d^84s^2$ | $3d^{10}4s^1$ | $3d^{10}4s^2$ |
| +3 | +2<br>+3<br>+4 | +2<br>+3<br>+4<br>+5 | +2<br>+3<br>+4<br>+5<br>+6 | +2<br>+3<br>+4<br>+5<br>+6<br>+7 | +2<br>+3<br>+4<br>+6 | +2<br>+3<br>+4 | +2<br>+3<br>+4 | +1<br>+2 | +2 |

b) Except Sc, the most common oxidation state of first rose correlation elements is +2 which arises due to loss of 4s- electrons. This means Sc, 3d–orbitals are more stable and lower in energy than 4s- orbital. As a result electrons are first removed from 4s- orbital.

c) Zinc is +2 in which no d-electrons are involved.

d) Within a group, maximum oxidation state increases with atomic number. For e.g. in group 8 , Fe shows +2 and +3 but Rutheniun and Osmium form compounds in +4 , +6 and + 8 oxidation state .

e) In + 2 and + 3 oxidation state, bonds formed are ionic and in the compounds of higher oxidation state bonds are covalent.

Transition elements show low oxidation states in some compounds or complexes having ligands such as CO, for e.g. in Ni $(CO)_4$ , Ni has zero oxidation state.

**Standard electrode potential**

The magnitude of ionization enthalpy gains the amount energy required to remove electrons from particular oxidation state of metal in compounds. Smaller the I.E. the metal, the stable is its compound.

$Ni \rightarrow Ni^{+2} + 2e^-$ I.E = $2.49 \times 10^3$ kJ/mol

$Pt \rightarrow Pt^{+2} + 2e^-$ I.E = $2.66 \times 10^3$ kJ/mol

Ni(II) compounds are thremodynamically more stable thaPt(II) compounds.

$Ni \rightarrow Ni^{+4} + 4e^-$ I.E = $8.80 \times 10^3$ kJ/mol

$Pt \rightarrow Pt^{+4} + 4e^-$ I.E = $6.70 \times 10^3$ kJ/mol

Pt(IV) compounds are relatively more stable than Ni(IV) compounds. Stability of the compounds depend on electrode.

In addition to ionization enthalpy, $\Delta H_{sub}$ , $\Delta H_{hyd}$ energy, explain the stability of a particular oxidation state.

1) $M(s) \longrightarrow M(g)$ $\Delta_{sub}H^0$

2) $M(g) \longrightarrow M^+(g) + e^-$ 1. E $\Delta H = \Delta_{sub} H + I.E + \Delta_{hyd} H$

3) $M^+(g) + nH_2O \longrightarrow M^+(aq)$ $\Delta_{hyd} H$

Smaller the value of total energy charge for a particular oxidation state in aqueous solution, greater will be the stability of that oxidation state. The electrode potential is a measure of total energy charge.

The lower the electrode potential, ie, more negative the standard reduction potential of the electrode, more stable is the oxidation state of the transition metal in aqueous solution.

More negative values of $E^0$ for Mn and Zn are due to the stability of half filled ($3d^5$ ) in $Mn^{+2}$ and completely filled ($3d^{10}$ ) configuration in $Zn^{+2}$ .

### *Trend in $M^{3+}$ / $M^{2+}$ standard electrode potential*

Except copper and Zinc, all other elements of first transition series show +3 oxidation states to from $M^{+3}$ in aqueous solution.
a) Low value of Sc reflects stability of $Sc^{+3}$ which has a noble gas configuration.
b) High value for Mn shows that $Mn^{+2}$ ($d^5$) is particularly stable.
c) Low value for Fe, shows extra stability for $Fe^{+3}$ configuration.

### *Trends in stability of higher oxidation states*-

The highest oxidation state is generally shown among halides and oxides.

a) Transition metals react with halogens at high temp as they have high activation energies. High temp is required to start the reaction but heat of reaction is sufficient to continue. The reaction.
   Order of reactivity: $F_2 > Cl_2 > Br_2 > I_2$
b) In general elements of I transition series react in low oxidation state.
c) Since fluorine is the most electronegative element, the transition elements show high oxidations states with fluorine.
d) The highest oxidation states are found in $TiX_4$, $VF_5$, $CrF_6$.
e) The +7 oxidation states are not shown by simple halides.
f) V(V)is shown by VFs only . Other halides undergoing hydrolysis form oxo halides $OX_3$.
g) Fluorides are unstable in their low oxidation state. Eg –V forms $VX_2$ (X = C1,Br or I) Cu can form CuX (X=Cl ,I) Cu (II) halides are known except the iodide.
h) The ability of oxygen to stabilize the highest oxidation state is exhibited in their oxides. The highest oxidation states in member of group number. Eg-Sc in $Sc_2O_3$ is +3 and is a member of group 3. Mn in group7 has +7 oxidation state in $Mn_2O_7$.Mangnese forms highest oxidation state fluorides as $MnF_4$ whereas the highest oxide is $Mn_2O_7$.Tthis is due to tendency of oxygen to form multiple bonds. In the covalent oxide $Mn_2O_7$ ,each Mn is tetrahedrally surrounded by oxygen atoms and has Mn-O-Mn bridge. Tetrahedral $MnO_4^{-2}$ ions are also known for V(V),Cr(VI), Mn(VI) and Mn(VII).

### <u>Formation of colored ions</u>-

Most of the compo undo of transition metals are colored in solid or solution form.

**Reason**- The colour is due to the presence of incomplete (n-1)d sub shell. Under the influence of approaching ions towards central metal ion, the d-ordinals of central metal split into different energy levels. This phenomenon is called crystal field splitting. For e.g. When six ions or molecules approach the metal ion (octahedral field) , the d-orbitals split into two sets:- One set consisting of two d-orbital of higher energy ($dx^2$-$y^2$, $dz^2$) end other set consisting of d-orbitals (dxy, dyz & dxz ) of lower energy. The electrons are easily promoted from one to another energy level in the same d-sub shell. There are called d-d transition. The amount of energy required to excite some of the electrons to higher energy states within the same d-sub shell corresponds to energy of certain colours of visible light. Therefore, when white light falls on the compounds, some part of its energy corresponding to certain colour is absorbed and the electron gets raised from lower energy to higher energy & the excess colour is transmited. The observed colour is complementary of colour absorbed. Eg-$Ti^{+3}$ ($d^1$) is purple.

**Magnetic Properties-**

Paramagnetism arises from the presence of unpaired electrons. Diamagnetic substances are repelled by the applied magnetic field while the paramagnetic substances are attracted whereas the ferromagnetic substances are attracted the most.

Each unpaired electron has a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the 1st transition series, the contribution of orbital angular momentum is effectively less and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and can be calculated by 'spin only'

$\mu = \sqrt{n(n+2)}$ BM

N= no. of unpaired e-

$\mu$ = Magnetic moment in Bohr magnetron ($\mu_b$ ) units

($\mu_b = eh/ 4m = 9.27\times10^{-24}$ $Am^2$ or $Jt^{-1}$**)**

$\mu$ increase with the increasing number of unpaired electrons or in other words observed magnetic moment guise a useful indication about the number of unpaired electrons.

Eg- Calculate the magnetic moment of $Mn^{2+}$ if the at no. =25 ,

Z=25 So, $d^5$ has 5 unpaired electrons , n=5

$\mu = 5(5+2) = 5.92\mu_b$

**Formations of complex compounds** :- The transition metals form a large no. of complex compo undo due to

(i) the comparitively smaller sizes of the metal ions,
(ii) their high ionic charges and
(iii) the availability of d-orbital for bond formation

Eg .$[PtCl_4]^{2-}$ , $[Cu(NH_3)_4]$, $[Fe(CN)_6]^{4-}$ etc.

**Catalytic Properties**-

a) Transition metals show catalytic property because of their ability to adopt multiple oxidation states. Catalysts at a solid surface involve the formation of bond between reactant molecules and atoms of the surface of the catalyst. This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules & the activation energy is lowered, moreover transition metals can change their oxidation states.

   Eg- $Fe^{3+}$ catalyses the reaction between $I_2$& persulphate ions.

b) The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of low activation energy and therefore increase the rate of reaction. The reaction intermediates decompose yielding products and regenerating the original substance. The transition metals form reaction intermediates due to the presence of vacant orbitals & tendency to form variable oxidation state.

**Formation of interstitial compounds** :-

Many of the transition metals form interstitial compounds which are formed when small atoms like B,H, N or C are trapped inside the crystal lattices of metals. They are usually non-stoichiomatric and are neither typically ionic nor covalent. There small atoms enter into the void sites, eg In, Ti. If C enters the void going the composition TiC or $TiH_{1.7}$, $VH_{0.56}$ etc.

***Physical & Chemical characteristics of these compounds***

(i) High m.pt, higher than pure metals.
(ii) Very hard , some borides approach diamond in hardness
(iii) Retain metallic conducting
(iv) Chemically inert

**Alloy Formation:**-

Alloys are homogenous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other but the metals should have similar metallic radii within 15% of each other.

The alloys formed have high m.pt & are hard.

Eg. Alloys of Cr, V, W, Mo, Mn etc, stainless steel is or alloys of Fe, Ni, Cr

Alloys of transition metals with non-transition metals, such as Brass (Cu-Zn), Bronze (Cu- Sn).

**Some important compounds of transition elements**

***Oxides & oxo metals ions***

$\text{Metal} + O_2 \xrightarrow{\text{high/ temp}} M_xO_y$

The higher oxidation state in the oxides coincides with the group no. eg, $Sc_2O_3$(Sc is +3), $Mn_2O_7$(Mn is +7).

Beyond group 7- no higher oxides. Eg- $Fe_2O_3$(Fe is +3)

Besides the oxides, oxocations, stabilize V(V) as $VO_2^+$, V(IV) as $VO^{2+}$ and Ti(IV) as $TiO^{2+}$.

As the oxidation number of metal increases, ionic character decreases .

$Mn_2O_7$ is a covalent compound which is green oil.

$Mn_2O_7$ gives $HMnO_4$ Acids in high oxidation state.

$CrO_3$ gives $H_2Cr_2O_7$

$V_2O_5$ is amphoteric, $V_2O_3$ is basic and $V_2O_4$ is less basic.

When dissolved in acidic salts it gives $VO^{2+}$ salts.

CrO is basic and $Cr_2O_3$ is amphoteric. (High oxidation states are more covalent and more acidic).

**Potassium Dichromate , $K_2Cr_2O_7$ –**

***Preparation* - From Chromite ore**

Chromates in turn are formed by fusion of Chromite ore( $FeCr_2O_4$) with $Na_2CO_3$ or $K_2CO_3$.

$4\,FeCr_2O_4 + Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2.$

Excess

$Na_2CrO_4$ is filtered and treated with $H_2SO_4$ to obtain orange crystals of $Na_2CrO_7.2H_2O$

Sodium dichromate is more stable than pot. dichromate

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

Chromates and dichromates are interchangeable in aqueous solution depending upon pH of the solution.

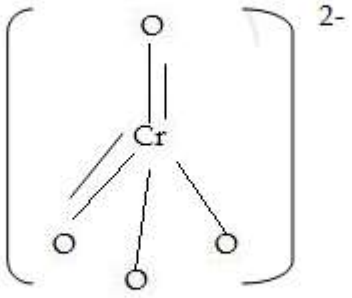
The O.S. of Cr in $CrO_4^{2-}$ and $Cr_2O_7^{2-}$ is same.

$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

(+6) (+6)

$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

**Chromate ion**



**Dichromate ion**

$Na_2Cr_2O_7$& $K_2Cr_2O_7$ : Strong oxidizing agents

Used in Organic Chemistry

Used in volumetric analysis

<u>Chemical properties of $K_2Cr_2O_7$</u> :-

In acidic solution, its oxidizing action can be represented as follows –

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Acidified $K_2Cr_2O_7$ oxidises iodides to iodine, sulphide to S, Sn(II) to Sn(IV), Fe(II) to Fe(II) to Fe(III)

$$6I^- \longrightarrow 3I_2 + 6e^-$$

$$3\,H_2S \longrightarrow 6H^+ + 3S + 6e^-$$

$$3Sn^{2+} \longrightarrow 3Sn^{4+} + 6e^-$$

$$6Fe^{2+} \longrightarrow 6Fe^{3+}\ \ 6e^-$$

The full ionic equation can be obtained by adding half equation for potassium dichromate to half equation for the reducing agent, for eg.,

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^2 \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Uses – In leather industry, preparation of azo dyes.

**Potassium Permanganate ($KMnO_4$)**

**Preparation –**

$$2MnO_2 + 4KOH + O_2 \xrightarrow{KNO_3} 2K_2MnO_4 + 2H_2O$$

Oxidizing agent

$$\underset{(+6}{3MnO_4^{2-}} + 4H^+ \longrightarrow \underset{(+7)}{2MnO_4^-} + \underset{(+4)}{MnO_2} + 2H_2O$$

Commercially prepared by alkaline oxidative fusion of $MnO_2$ followad by the electrolytic oxidation of Manganate (VI)

Fuse with KOH

$$MnO_2 \longrightarrow MnO_4^{2-}$$

Oxidize with air or $KNO_3$

$$MnO_4^{2-} \xrightarrow{\text{Electrolytic oxidation}} MnO_4^-$$

in alkaline solution

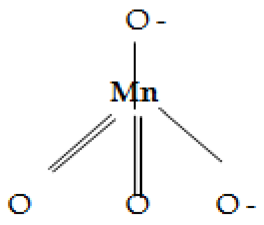
In the laboratory manganese (II) ion salt is oxidized by peroxodisulplate to permanganate

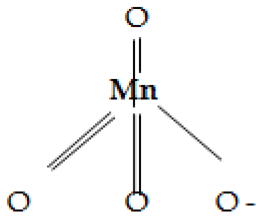
$$2Mn^{+2} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-}\ 16H^+$$

**Properties-**

1. Forms dark purple crystals
2. Not very soluble in water
3. Decomposes when heated at 513K

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$





**Tetrahedral manganese (green)ion** **Tetrahedral Permanganate (purple) ion**

$MnO_4$ is a strong oxidizing agent, both in neutral & acidic medium

Acidified $KMnO_4$ oxidises oxalates to $CO_2$, Iron(II) to iron (III), nitrites to nitrates and iodides to free iodine The half reaction of reductants are-

$$5\begin{array}{l}COO^-\\ |\\ COO^-\end{array} \longrightarrow 10CO_2 + 10e^-$$

$$Fe^{+2} \longrightarrow 5Fe^{+3} + 5e^-$$

$$5NO_2^- + 5H_2O \longrightarrow 5NO_3^- + 10H^+ + 10e^-$$

$$10I^- \longrightarrow 5I_2 + 10e^-$$

Full reactions can be written by adding the half reactions of $KMnO_4$ to half reactions of the reducing agents and balancing them.

Acidic solutions –

$10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{+2} + 8H_2O + 5I_2$ (iodides to KI)

$5C_2O_4^{2-} + 2MnO_4^- + 16H \longrightarrow 2Mn^{+2} + 8H_2O + 10CO_2$ (oxalate ions to $CO_2$)

$5Fe^{2+} + MnO_4^- + 8H \longrightarrow Mn^{+2} + 4H_2O + 5Fe^{2+}$ ($Fe^{2+}$(green) to $Fe^{3+}$ (yellow))

$5S^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{+2} + 8H_2O + 5S$ ($H_2S$ to S)

$5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{+2} + 3H_2O + 5SO_4^{2}$ (sulphites to sulphates)

$5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{+2} + 3H_2O + 5NO_3^-$ (nitrites to nitrates)

Neutral medium -

$2MnO_4^- + H_2O + I^- \longrightarrow MnO_2 + OH^- + IO_3^-$ (iodides to iodates)

$8MnO_4^- + H_2O + 3S_2O_3^{2-} \longrightarrow 8MnO_2 + 2OH^- + 6SO_4^{2}$ (thiosulphates to sulphates)

$MnO_4^- + 2H_2O + 3Mn^{2+} \longrightarrow 4H^+ + 5MnO_2$ (Manganese salt to $Mn^{2+}$)

Uses- Used as uxidant, used for bleaching wool, cotton, silk and decolorization of oils.

## The Inner Transition elements (*f*- Block)

Consists of two series:-

| Lanthanoides (Ln; general Symbol) | Actinoides |
|---|---|
| (14elements following La ) | (14 elements following Ac) |

**Lanthanoides :-**

**Electronic Configuration:-**

| Atomic No. | Name | Symbol | E.C. |
|---|---|---|---|
| 57 | Lanthanum | La | $5d^1 6s^2$ |
| 58 | Cerium | Ce | $4f^1 5d^1 6s^1$ |
| 59 | Praseodymium | Pr | $4f^3 6s^2$ |
| 60 | Neodymium | Nd | $4f^4 6s^2$ |
| 61 | Promethium | Pm | $4f^5 6s^2$ |
| 62 | Samarium | Sm | $4f^6 6s^2$ |
| 63 | Europuim | Eu | $4f^7 6s^2$ |
| 64 | Gadolinium | Gd | $4f^7 5d^1 6s^2$ |
| 65 | Terbium | Tb | $4f^9 6s^2$ |
| 66 | Dysprosium | Dy | $4f^{10} 6s^2$ |
| 67 | Holmium | Ho | $4f^{11} 6s^2$ |
| 68 | Erbium | Er | $4f^{12} 6s^2$ |
| 69 | Thulium | Tm | $4f^{13} 6s^2$ |
| 70 | Ytterbium | Yb | $4f^{14} 6s^2$ |
| 71 | Lutetium | Lu | $4f^{14} 5d^1 6s^2$ |

**Atomic & Ionic Series :-** Decrease from La to Lu is due to Lanthanoid Contraction (The shielding of one $4f$ electron by another less than that by one d electron by another & the increase in nuclear charge along the series.

The almost identical radii of Zr (160pm.) and Hf (159), a consequence of the lanthanoid contraction, account their occurrence together in nature and for the difficulty faced in their separation.

**Colour and Para magnetism**

$Ln^{3+}$ are coloured both in solid and in aqueous solution due to the presence of f electrons.

$La^{3+}$ and $Lu^{3+}$ do not show any colour. However absorption bands are narrow probably because of the excitants with in f level.

$Ln^{3+}$ are paramagnetic except $La^{3+}$& $Ce^{4+}$ ($f^0$ type) &$f^{14}$ type ( $Yb^{2+}$& $Lu^{3+}$ ). Paramagnetism rises to maximum in Neodymium .

**Ionization enthalpies**

I.E. depends on the degree of stability of empty, half filled and completely filled f-level.

This is indicated from the abnormally low values of the third ionization enthalpy of La, Gd, Lu.

**Oxidation states.:-**

$Ln^{3+}$ compounds are predominant species. +2 & +4 ions in solution or in solid compounds are also obtained occasionally.

Ce (IV) formation is favoured due to extra stability of noble gas configuration, but it is a strong oxidant reverting to the common +3 state .

Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, $MO_2$

$Eu^{2+}$ is formed by losing the two s- electrons & its +7 configuration.

**Properties and use :-**

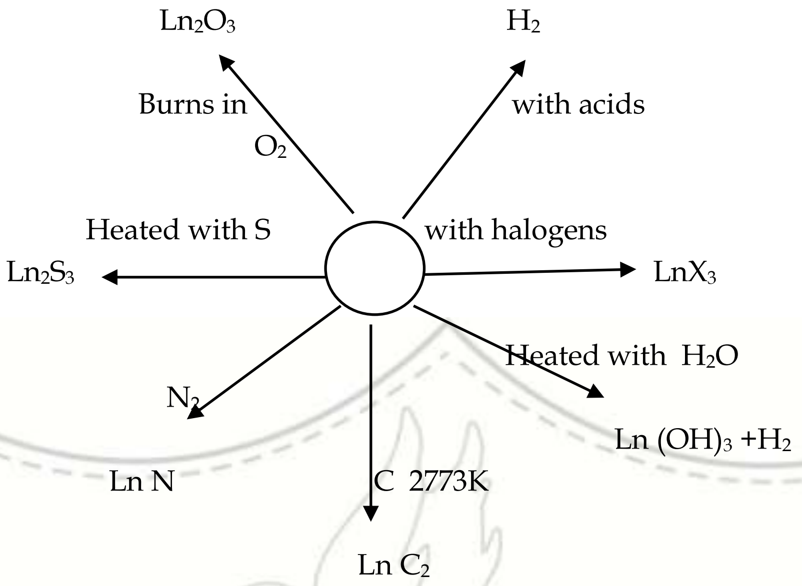
Ln are silvery white soft metals and tarnish rapidly in air. Hardness increases with increasing atomic number. M.pt. ranges from 1000K – 1200K

Sm is steel hard. (m.pt 1623K)

**Chemical behavior**

In general earlier members of the series are quite reactive similar to Ca, with increasing atomic number they behave more like aluminum.

$Ln^{3+}(aq) + 3e^- \longrightarrow Ln(s)$



$$Ln + C \xrightarrow{\Delta} Ln_3C + Ln_2C_3 + LnC_2 \text{ (carbides)}$$

**Use** :- Used in the production of alloy steels for plates & pipes eg. Mischmetal is an alloy which consists of a lanthanoid metal (95%) and iron (5%) and trace of S, C, Ca and Al. A good amount of this allay is used in Mg-based alloy to produce bullets, shell & lighter flint.

- Mixed oxides of Ln are used as catalyst in petroleum cracking .
- Ln oxides are used as phosphors in television screens & similar fluorescing surfaces.

**The Actinoids:-**

| Atomic no. | Name | Symbol | E.C. |
|---|---|---|---|
| 89 | Actinium | Ac | $6d^1 7s^2$ |
| 90 | Thorium | Th | $5f^0 6d^2 7s^2$ |
| 91 | Protactinium | Pa | $5f^2 6d^1 7s^2$ |
| 92 | Uranium | U | $5f^3 6d^1 7s^2$ |
| 93 | Neptunium | Np | $5f^4 6d^1 7s^2$ |
| 94 | Plutonium | Pu | $5f^6 7s^2$ |
| 95 | Americium | Am | $5f^7 7s^2$ |
| 96 | Curium | Cm | $5f^7 6d^1 7s^2$ |
| 97 | Berkelium | Bk | $5f^9 7s^2$ |
| 98 | Californium | Cf | $5f^{10} 7s^2$ |
| 99 | Einsteinium | Es | $5f^{11} 7s^2$ |
| 100 | Fermium | Fm | $5f^{12} 7s^2$ |
| 101 | Mendelevium | Md | $5f^{13} 7s^2$ |
| 102 | Nobelium | No | $5f^{14} 7s^2$ |
| 103 | Lawrencium | Lr | $5f^{14} 6d^1 7s^2$ |

Although the naturally occurring elements & the earlier member have relatively long half lives, the latter members have values ranging from a day to 3 minutes for Lr (Z=103) These facts and high radioactivity renders their study more difficult.

**Electronic Configuration**

The irregularities in the electronic configurations of the actinoids like those of in the lanthanoids are related to the stability of $f^0$ ,$f^7$ and $f^{14}$ occupancies of the 5*f* orloitals.
Eg.Am : [Rn] $5f^7 7s^2$
Cm : [Rn] $5f^7 6d^1 7s^2$

5f orbital can & do participate in bonding.
Common oxidation state is +3
The maximum oxidation state increases from +4 in Th, +5 in Pa, +6 in U and +7 in Np but decreases in succeeding elements.

**Magnetic Properties**:- the variation of magnetic properties with the no. of unpaired 5*f* electrons is similar to that of Ln.

**Ionic Sizes:** Decrease in size due to increase in the effective nuclear charge on the outermost shell and poor shielding by 5f electrons. This is referred to as **actinoid contractions.**

**Ionization Enthalpy** :
The I.E. of early actinoids is lesser than that of early Ln as when 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons, will therefore, be more effectively shielded from the nuclear charge than are the 4f electrons of the corresponding Ln. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

**Physical and Chemical Reactivity**

The actinoids are highly reactive when they are finely divided.

Actinoid $\xrightarrow{\text{Boiling water}}$ $M_xO_y + MH_n$

moderate temp
Actinoid + Non metal $\longrightarrow$ Corresponding compound
Actinoid + HCl $\longrightarrow$ $M_xO_y$ oxide layer
Actinoid + $HNO_3$ $\longrightarrow$ $M_xO_y$
Actinoid + Alkali $\longrightarrow$ No reaction

Metallic radii of actinoids is more as compared to lanthanoids.

**Comparison With Lanthanoids**

1. Structural variability in actinoids is obtained due to irregularities in metallic radii which are greater then lanthanoids.
2. Magnetic properties in actinoids are more complex than lanthanoids.

3. Ionization enthalpies of early actinoids, though not accurately known are lower than early lanthanoids. This is because 5f electrons penetrate less into the inner core and hence the outer electron are less firmly held, they are available for bonding in actinoids.

**Applications of d-and f Block Elements**

1 Iron and steel are important construction materials. Their production is based on reduction of iron oxides, removal of impurities, and addition of carbon and alloying metals such as Cr, Mn, and Ni.
2 TiO is used in pigment industry.
3 $MnO_2$ is used in battery cell. Also Zn and Ni/Cd.
4 Elements of group II are coinage metals.
5 $V_2O_5$ catalyses oxidation of $SO_2$ in contact process,
6 Iron catalyst is used in Haber's process.
7 $TiCl_4$ and $Al(CH_3)_3$ forms Ziegler-Natta Catalyst.
8 Ni complexes are used in polymerization of alkynes.

**Hands –on / IT Enabled work**:

Whole chapter is done with the help of a presentation.

## Assignment

### Chapter 7: d -and f -Block Elements

1. Complete and balance the following equations:

   (i) $Fe^{2+} + MnO_4^- + H^+ \rightarrow$

   (ii) $MnO_4^- + H_2O + I^- \rightarrow$

2. Give reason:

   (i) $E^0$value for the $Mn^{3+}/Mn^{2+}$ couple is highly positive as compared to $Fe^{3+}/Fe^{2+}$ .
   (ii) Iron has high enthalpy of atomization than that of copper.
   (iii) $Sc^{3+}$ is colourless in aqueous solution whereas $Ti^{3+}$ is coloured.
   (iv) Actinoid contration is greater from element to element than lanthanoid contraction.

3. Write the formula of an oxo-anion of Manganese (Mn) in which it shows the oxidation state equal to its group number.
4. Account for the following :
   (i) Transition metals form large number of complex compounds.
   (ii) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.
   (iii) E° value for the $Mn^{3+}/Mn^{2+}$ couple is highly positive (+1.57 V) as compare to $Cr^{3+}/Cr^{2+}$.

5. (i) How is the variability in oxidation states of transition metals different from that of the p-block elements ?
   (ii) Out of $Cu^+$ and $Cu^{2+}$, which ion is unstable in aqueous solution and why ?
   (iii) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali.Why?

6. Describe the general characteristics of transition elements with special reference to the following :
   (i) Variable oxidation states
   (ii) Formations of coloured ions.

7. (i) What are interstitial compounds? Why are such compounds well known for transition elements?
   (ii) What are alloys? Name an alloy which contains a lanthanoid metal.
8. How is it that several transition metals act as catalysts? Give two examples of reactions catalyzed by them?
9. Complete the following reactions:
   (a) $Cr_2O_7^{2-}(aq.) + I^-(aq.) + H^+ \longrightarrow$
   (b) $MnO_4^-(aq.) + Fe^{2+}(aq.) + H^+(aq.) \longrightarrow$
   (c) $MnO_4^-(aq.) + S_2O_3^{2-}(aq.) + H_2O(l) \longrightarrow$
   (d) $5NO_2^-(aq.) + 2MnO_4^-(aq.) + 6H^+(aq.) \longrightarrow$

   (e) $Cr_2O_7^{2-}(aq.) + H_2S(g) + H^+(aq.) \longrightarrow$
   (f) $Cr_2O_7^{2-}(aq.) + Fe^{2+}(aq.) + H^+(aq.) \longrightarrow$
   (g) $MnO_2(s) + KOH(aq.) + O_2 \longrightarrow$

(h) $2CrO_4^{2-} + 2H^+ \longrightarrow$

(i) $Cr_2O_7^{2-}(aq.) + 3Sn^{2+} + 14\,H^+ \longrightarrow$

10. (a)Compare the chemistry of actinoids with that of lanthanoids with reference to
(i) electronic configuration (ii) oxidation state
(iii) atomic sizes (iv) chemical reactivity
(b) Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons.
(c) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.

11. When chromite ore $FeCr_2O_4$ is fused with NaOH in presence of air, a yellow coloured compound (A) is obtained which on acidification with dilute sulphuric acid gives a compound (B). Compound (B) on reaction with KC*l* forms a orange coloured crystalline compound (C).
(i) Write the formulae of the compounds (A), (B) and (C).
(ii) Write one use of compound (C).

12. What may be the possible oxidation states of the transition metals with the following d electronic configurations in the ground state of their atoms:
$3d^34s^2$, $3d^54s^2$ and $3d^64s^2$. Indicate relative stability of oxidation states in each case.

13. Calculate the number of unpaired electrons in following gaseous ions: $Mn^{3+}$, $Cr^{3+}$, $V^{3+}$ and $Ti^{3+}$. Which one of these is the most stable in aqueous solution?

14. How would you account for the following:
(a) The metallic radii of the third(5d) series of transition metals are virtually the same as those of corresponding group members of the second (4d) series.
(b) Among lanthanoids, Ln(III) compounds are predominant. However, occasionally in solutions form solid compounds,+2 and+4 ions are also obtained.
(c) The $E^0_{M2+/M}$ for copper is positive (0.34V), copper is the only metal in the first series of transition elements showing this behavior.
(d) The higher oxidation states are usually exhibited by the members in the middle of the series of transition elements.
(e) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.
(f) Actinoids show irregularities in their electronic configurations.

15. a) Which metal in the first transition series (3d series) exhibits +1 oxidation state most frequently and why?
b) Which of the following cations are coloured in aqueous solution and why?
$Sc^{3+}$, $V^{3+}$, $Ti^{4+}$ , $Mn^{2+}$

## More Practice

## Chapter 7: d- and f -Block Elements

1. What is Lanthanide contraction? What effect does it have on the chemistry of the elements which follow lanthanoids.

2. Why is HCl not used to acidify a permanganate solution in volumetric estimations of $Fe^{2+}$ or $C_2O_4^{2-}$ ?

3. Why are Zn , Cd and Hg normally not regarded as transition metals ?

4. Which of the following ion is paramagnetic: $Sc^{3+}$ (Z=21), $Cu^{+}$ (Z=29).

5. Why is the third ionization energy of Manganese (Z=25) unexpectedly high?

6. Evaluate the magnetic moment of a divalent ion in aqueous solution if its atomic no. is 25.

7. Explain why:
   (1) $Ce^{3+}$ can be easily oxidized to $Ce^{4+}$ ( At. no. of Ce =58).
   (2) Zr (Z=40) and Hf (Z=70) have very close value of atomic radii.
   (3) The lowest oxidation state of manganese is basic while the highest is acidic.
   (4) $CrO_4^{2-}$ is a strong oxidizing agent while $MnO_4^{2-}$ is not.

8. Predict which of the following will be coloured in aqueous solution?
   $Ti^{3+}$,$V^{3+}$,$Cu^{+}$,$Sc^{3+}$,$Mn^{2+}$ ,$Fe^{3+}$,$Co^{2+}$

9. Explain the following observations:
   (i) In general the atomic radii of transition elements decrease with atomic number in a given series.
   (ii) The $E^o$ value for $Mn^{3+}/Mn^{2+}$ couple is much more positive than for $Cr^{3+}/Cr^{2+}$ or $Fe^{3+}/Fe^{2+}$ couple.
   (iii) $Cu^{+}$ ion is unstable in aqueous solutions.
   (iv) Although $Co^{2+}$ ion appears to be stable, it is easily oxidised to $Co^{3+}$ ion in the presence of a strong ligand.
   (v) With the same $d^4$ d-orbital configuration $Cr^{2+}$ ion is reducing while $Mn^{3+}$ ion is oxidising.
   (vi) The enthalpies of atomisation of the transition elements are quite high.
   (vii) Transition metals form compounds which are usuallly coloured.
   (viii) Transition metals exhibit variable oxidation states.
   (ix) The actinoids exhibit a greater range of oxidation states than the lanthanoids.
   (x) There occurs much more frequent metal-metal bonding in compounds of heavy transition elements (3rd series).
   (xi) There is in general an increase in density of element from titanium (Z=22) to copper (Z=29).
   (xii) The gradual decrease in size (actinoid contraction) from element to element is greater among the actinoids than that among the lanthnoids. (lanthanoid contraction).
   (xiii) The greatest numbers of oxidation states are exhibited by the members in the middle of a transition series.

(xiv) With the same d-orbital configuration ($d^4$) $Cr^{2+}$ ion is a reducing agent but $Mn^{3+}$ ion is an oxidising agent.

10. What is meant by 'disproportionation' ? Give two examples.

11. Why $Ce^{4+}$is oxidizing and $Sm^{2+}$, $Eu^{2+}$ are reducing in nature?

12. A mixed oxide of iron and chromium $FeOCr_2O_3$ is fused with sodium carbonate in the presence of air to form an yellow coloured compound (A) On acidification the compound the compound forms an orange coloured compound (B), which is a strong oxidizing agent .
(i) Identify the compounds (A) and (B)
(ii)Write balanced chemical equation for each step.

13. Explain the following facts:
(a) transition metals act as catalysts.
(b)Chromium group elements have the highest melting points in their respective series.
(c) The enthalpies of atomization of transition elements are high.
(d) From element to element the actinoid contraction is greater than the lanthanoid contraction.
(e) The $E^o$ value for the $Mn^{3+}/Mn^{2+}$ couple is much more positive than that for $Cr^{3+}/Cr^{2+}$
(f) Scandium (Z=21) does not exhibit variable oxidation states and yet it is regarded as a transition element.

14. An element 'A' exists as a yellow solid in standard state . It forms a volatile hydride 'B' which is a foul smelling gas and is extensively used in qualitative analysis of salts. When treated with oxygen ,'B' forms an oxide 'C' which is a colourless , pungent smelling gas.This gas when passed through acidified $KMnO_4$ solution , decolorizes it.'C' gets oxidized to another oxide'D' in the presence of a heterogenous catalyst . Identify A,B,C,D, and also give the chemical equation of reaction of 'C' with acidified $KMnO_4$ solution and for conversion of 'C' to 'D'.

15. (a) A blackish brown coloured solid 'A' when fused with alkali metal hydroxides in the presence of air, produces a dark green compound 'B', which on electrolytic oxidation in alkaline medium gives a dark purple coloured compound C. Identify A, B and C and write the reactions involved.
(b) What happens when acidic solution of green compound (B) is allowed to stand for some time? Give the equations involved .What is this type of reaction called?

## Assignment

### Chapter 8: Coordination Compounds

1. Write the coordination number and oxidation state of Platinum in the complex $[Pt(en)_2Cl_2]$
2. (a) Write the formula of the following coordination compound: Iron(III)hexacyanoferrate(II).
   (b) What type of isomerism is exhibited by the complex $[Co(NH_3)Cl]SO_4$?
   (c) Write the hybridization and number of unpaired electrons in the complex $[CoF_6]^{3-}$

3. (i) What type of isomerism is shown by the complex $[Co(NH_3)_6]$ $[Cr(CN)_6]$ ?
   (ii) Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless ? (At. no. of Ni = 28)
   (iii) Write the IUPAC name of the following complex : $[Co(NH_3)_5(CO_3)]Cl$.

4. Write IUPAC name of the following:
   1) $[Pt(NH_3)_2Cl_2]$ 2) $[CoBr_2(en)_2]^+$ 3) $[Ni(NH_3)_6]Cl_2$
   4) $K_4[Fe(CN)_6]^{3+}$ 5) $[NiCl_4]^{2-}$ 6) $[CrCl_2(en)_2]Cl$
5. Write the formulas in the following cases.
   1) Tetrahydroxozincate(II), 2) Hexaamminecobalt(III) sulphate
   3) Hexaammineplatinum(IV), 4) Pentaamminenitrito-N-cobalt(III)

6. Give the formula of each of the following coordination entities:
   (a) $Co^{3+}$ ion is bound to one $Cl^-$, one $NH_3$ molecule and two bidentate ethylene diamine(en) molecules.
   (b) $Ni^{2+}$ ion is bound to two water molecules and two oxalate ions.
   Write the name and magnetic behavior of each of the above coordination entities.

7. When a co-ordination compound $CrCl_3.6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write
   (i) Structural formula of the complex.
   (ii) IUPAC name of the complex.
8. In the ring test for identification of nitrate ion, what is the formula of the compound responsible for the brown ring formed at the interface of two liquids?

9. a) For the complex $[Fe(CN)_6]^{3-}$, write the hybridization type, magnetic character and spin nature of the complex. (At. number : Fe = 26).
   b) Draw one of the geometrical isomers of the complex [Pt(en)2Cl2]2+ which is optically active.
10. Show the possible isomers of the following coordination entities?
    (i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[Co(NH_3)_3Cl_3]$ (iii) $[Co(en)_2Cl_2]Cl$

11. Name the isomerism exhibited by the following pair of coordination compounds:
    $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$
    Give one chemical test to distinguish between these two compounds.
12. Using valence bond theory, predict the geometry and hybridization of $[Cr(NH_3)_6]^{3+}$ ion, $[Fe(CN)_6]^{3-}$ (paramagnetic due to single unpaired electron) and $[FeF_6]^{3-}$ (paramagnetic due to 5 unpaired electron) [ Cr = 24, Fe=26].

13. How many ions are produced from the complex $[Co(NH_3)_6]Cl_2$ in aqueous phase.

14. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

15. (i) Draw a sketch to show the splitting of d- orbitals in an octahedral crystal field. State for a $d^6$ ion how the actual configuration of the split d- orbitals in an octahedral crystal field is decided by the relative values of $\Delta^o$ and P.
    (ii) On the basis of CFT, write the electronic configuration of $d^4$ ion if $\Delta_0 > P$.

16. Give reasons:
    1) $K_3[Fe(CN)_6]$ is weakly paramagnetic whereas $K_3[FeF_6]$ is highly paramagnetic.
    2) Though CO is a weak lewis base yet it forms a number of stable metal carbonyls . Explain.

17. Compare the following complexes with respect to their shape, magnetic behaviour and the hybrid orbitals involved: (i) $[CoF_4]^{2-}$, (ii) $[Cr(H_2O)_2(C_2O_4)_2]^-$
    (Atomic number Co = 27, Cr =24 )

18. Discuss briefly giving an example in each case the role of coordination compounds in:
    (i) biological systems (ii) medicinal chemistry
    (iii) analytical chemistry (iv) metallurgy of metals.

19. (a) What is a ligand? Give an example of a bidentate ligand.
    (b) Explain as to how the two complexes of nickel, $[Ni(CN)_4]^{2-}$ and $Ni(CO)_4$, have different structures but do not differ in their magnetic behaviour. (Ni =28)

20. Explain the following:
    (a) The $\pi$-complexes are known for transition elements only.
    (b) Nickel(II) does not form low spin octahedral complexes.
    (c) $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions.

21. Hard water does not form leathers with soap. Rita uses a washing powdercontaining sodium metapolyphosphate and ethylenediamine tetracetate(EDTA) while Sita is using ordinary washing power.
    (a) Which washing powder is move effective for washing clothes in hard waterand why?
    (b) Name the values associated with the above passage.

22. (i) Name the ligand (compound) used for treatment of Lead poisoning.
    (ii) Write the reaction involved for removal of lead from living organism.
    (iii) Write the name of coordination compound used as a chemotherapeutic agent to curb the growth of tumours.

## More Practice

## Chapter 8: Coordination Compounds

1. Write IUPAC name of the following:
   1) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$
   2) linkage isomer of $[Co(NH_3)_5(ONO)]^{2+}$
   3) $[Co(NH_3)_6]Cl_3$
   4) $[Co(NH_3)_4Cl(NO_2)]Cl$
   5) $[Mn(H_2O)_6]^{2+}$
   6) $[Co)(en)_3]^{3+}$
   7) $[Cr(H_2O)_4Cl_2]Cl$
   8) $[Co(NH_3)_4(H_2O)_2]Cl_3$
   9) $[Pt(NH_3)_4][NiCl_4]$

2. Give the electronic configuration of the
   (a) d-orbitals of Ti in $[Ti(H_2O)_6]^{3+}$ ion in an octahedral crystal field.
   (b) Why is this complex coloured? Explain on the basis of distribution of electrons in the d-orbitals.
   (c) How does the colour change on heating $[Ti(H_2O)_6]^{3+}$ ion?

3. A metal ion $M^{n+}$ having $d^4$ valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $\Delta o > P$
   a. draw the diagram showing d orbital splitting during this complex formation.
   b. Write the electronic configuration of the valence electrons of the metal $M^{n+}$ ion in terms of $t_{2g}$ and $e_g$.
   c. What type of hybridization will $M^{n+}$ ion have?
   d. Name the type of isomerism exhibited by this complex.

4. Write the shape of $Fe(CO)_5$ , $Mn_2(CO)_{10}$ , $Co_2(CO)_8$, $Ni(CO)_4$ molecule

5. For the complex $[Fe(en)_2Cl_2]Cl$, (en = ethylene diamine), identify
   1) The oxidation number of iron.
   1) The hybrid orbitals and the shape of the complex
   2) The magnetic behaviour of the complex
   3) The number of geometrical isomers
   4) Whether there is an optical isomer
   5) Name of the complex. (At. No. of Fe =26)

6. Write the formulas in the following cases.
   1) Tetrabromidocuprate(II)
   2) Diamminedichloridoplatinum(II)
   3) Amminebromidochloridonitrito-N-platinate (II)
   4) Dichlorodobis (ethane-1,2-diamine) platinum (IV) nitrate

## Chapter 9- Haloalkanes and Haloarenes

## POLYHALOGEN COMPOUNDS

1. **<u>$CH_2$ $CL_2$ (Methylene Chloride) / (Dichloromethane)</u>**

Uses: Used as a solvent as a paint remover, propellant in aerosol, as a process solvent in the manufacture of drugs and as a metal cleaning and finishing solvent.

Harmful effects: Harms human central nervous system. Higher level in air causes dizziness, nausea, tingling and numbness in the fingers and toes. Direct contact with skin causes intense burning and can burn cornea of eyes.

2. **$CHCl_3$ (chloroform/trichloromethene)**

Uses: Solvents, fats, alkaloids, iodine and other substances, in production of Freon refrigerant R-22. Inhaling chloroform vapours depresses the central nervous system. Was used as an anesthetic but now has been replaced by less toxic anesthetics.

$$CHCl_3 + O_2 \xrightarrow{\text{Light}} \underset{\text{(Carbonyl chloride)}}{2COCl_2} + 2HCl$$

Chloroform is slowly oxidized by the presence of light to an extremely poisonous gas, phosgene which when inhaled may cause damage to liver, kidneys, and some people develop sores when the skin is immersed in closed dark coloured bottles completely filled so that air is kept out.

3. **$CHI_3$ (lodoform/ Triiodomethane)**

It has strong unpleasant smell .It was used as an antiseptic but the antiseptic properties are due to the liberation of $I_2$ and not due to $CHI_3$. Due to its objectionable smell objectionable smell, other formulations containing $I_2$ are used.

4. **$CCL_4$(carbon tetrachloride/ Tetra chloromethane)**

Uses: Used in synthesis of chlorofluorocarbons, manufacture of refrigerants and propellants or aerosol cans, s a solvent, cleaning fluid, fire extinguishers.

Harmful effects: Exposure to $CCl_4$ may cause liver cancer, dizziness, lightheadedness, nausea and vomiting which can cause permanent damage to nerve cells. When $CCl_4$ is released into the air , it rises to the atmosphere and depletes the ozone layer which increases human exposure to UV rays, leading to increased skin cancer, eye diseases and disorders and possible disruptions to the immune system.

5. **Freon (Chlorofluoro carbon compounds of $CH_4$ and $C_2H_6$)**

Freon is stable, unreactive, non toxic, non corrosive and easily liquefiable gases. Eg. Freon 12 ($CCl_2F_2$)

Preparation- $CCl_4 + 2\ AgF / SbF_2 \longrightarrow CCl_2F_2$ (Swartz reaction)

Uses- Aerosol propellants, refrigeration and air conditioning.

Freons, eventuall diffuse unchanged into the stratosphere here it initiates radical chain reaction that can upset $O_3$ balance.

6. **DDT (p,p′-Dichlorodiphenyltrichloromethane**) - It is the first organic chlorinated nsecticide.

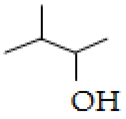
**Uses**- as used against mosquito that spreads malaria and lice that carry typhus. Later, many species of insects developed resistance to DDT, and it as also discovered to have toxicity towards fish. DDT is not metabolized very rapidly by animals; instead it is deposited and stored in fatty tissues.

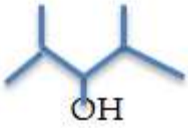
## Assignment

### Chapter 9: Haloalkanes and Haloarenes

1. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why?

2. (a) Identify the chiral molecule in the following pair:





(b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.
(c)Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH.

3. Write the structure of 1-Bromo-4-chlorobut-2-ene.

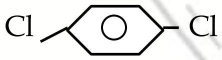
4. Following compounds are given to you :
2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane
(i) Write the compound which is most reactive towards $S_N2$ reaction.
(ii) Write the compound which is optically active.
(iii)Write the compound which is most reactive towards β-elimination reaction.

5. Name the following halides according to IUPAC system:

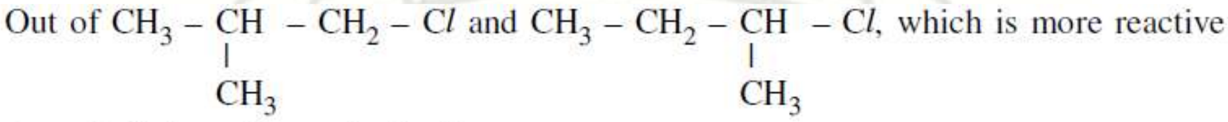
(a) $CH_3CH(Br)CH=C(CH_3)CH_2Cl$ (b)

(c) $CH_3CH(CH_3)CH(Br)CH_3$ (d) $ClCH_2C=CCH_2Br$

(e)



(f) $CH_3CH \equiv C\text{-}I$



6. Out of $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Cl$ and $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-Cl$, which is more reactive towards $S_N1$ reaction and why ?

7. What happens when bromine attacks $CH_2=CH\text{-}CH_2\text{-}C \equiv CH$?

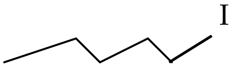
8. Write the structures of the following organic compounds:
   (i) 2-Chloro-3-methylpentane
   (ii) 1-Chloro-4-ethylcyclohexane
   (iii) 2-(2-Chlorophenyl)-1-iodo octane
   (iv) 4-tert-Butyl-3-iodoheptane

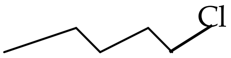
9. Answer the following questions:
   (i) What is meant by chirality of the compound? Give an example.

   (ii) Which of the following compounds is more easily hydrolysed by KOH and why?

$CH_3CH(Cl)CH_2CH_3$ or $CH_3CH_2CH_2Cl$

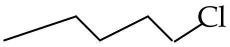
(iii) Which one undergoes $S_N2$ faster and why?



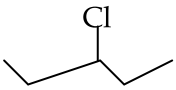


Or

10. Which one of the following reacts faster in an $S_N1$ reaction and why?



or



11. State one use of DDT and iodoform. Why chloroform is kept in dark coloured bottles completely filled?

12. What are ambident nucleophiles? Explain with the help of an example.

13. Write short notes on:
    (a) Fittig reaction (b) Swartz reaction

14. Account for the following:
    a) tert-Butyl chloride reacts with aqueous NaOH by $S_N1$ mechanism while n-butyl chloride reacts by $S_N2$ mechanism.
    b) Among HI, HBr and HCl, HI is most reactive.
    c) Alkyl halides though polar, are immisible with water.
    d) Chlorobenzene is extremely less reactive towards nucleophillic substitutionreaction.
    e) C–C*l* bond length in chlorobenzene is shorter than C–C*l* bond length in CH3–C*l*.
    f) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
    g) $S_N1$ reactions are accompanied by racemization in optically active alkyl halides.

15. Carry out the following conversions:
    i) 1-Chlorobutane to n-octane
    ii) Toluene to benzyl alcohol
    iii) Benzyl chloride to benzyl alcohol

16. What will be the mechanism for the substitution of -Br by –OH in $(CH_3)_2C(Br)CH_2CH_3$?

17. Identify the following compounds from A to N:

(a) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{Acetone}} A$

(b) $(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{Ethanol}} B$

(c) $CH_3CH(Br)CH_2CH_3 + NaOH\ (aq) \longrightarrow C$

(d) $CH_3CH_2Br + KCN \xrightarrow{\text{ethanol}} D$

(e) $(CH_3)_3CBr + H_2O \xrightarrow{\text{heat}} E$

(f) $(CH_3)_2CHCH(Br)CH_2CH_3 \xrightarrow{C_2H_5ONa,\ \text{heat}} F$

(g) $CH_3CH_2Cl + SbF_3 \xrightarrow{\text{heat}} G$

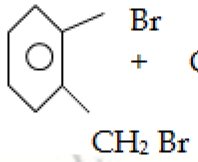
(h) $CH_2{=}CHCH_2Br + H_2O \longrightarrow H$

(i) $C_6H_4CH_2Cl + C_2H_5ONa \longrightarrow I$

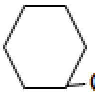
(j) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow J$

(k) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} K$

(l) $CH_3CH{=}C(CH_3)_2 + HBr \longrightarrow L$

(m) 

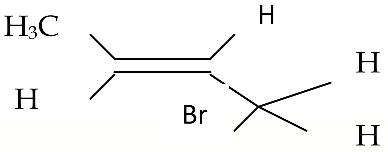
$+ \ CH_3NH_2 \longrightarrow M$

(n) 

$CH_2CH_2OH + HBr \longrightarrow N$

## More Practice
## Chapter 9: Haloalkanes and Haloarenes

1. Name the following halides according to IUPAC system:
   (i) $(CCl_3)_3CCl$
   (ii) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$
   (iii) $(CH_3)_3CCH{=}C(Cl)C_6H_4I\text{-}p$



2. Arrange the following compounds in an increasing order of their acid strengths:
   $(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$

3. Write the structures of the following organic compounds:

4. Arrange the following compounds in increasing order of reactivity towards nucleophillic substitution reaction:
   1,4-Dichlorobenzene , 4-Methoxy chlorobenzene, benzene , 2,4,6- Trinitro chlorobenzene

5. Account for the following:
   a) The dipole moment of chloro benzene is lower than that of cyclohexyl chloride.

   b) Vinyl chloride is unreactive towards nucleophillic substitution reactions.

   c) Grignard reagent should be prepared under anhydrous conditions.

   d) Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions.

6. Carry out the following conversions:
   (i) Propene to propyne
   (ii) Ethanol to but-1-yne

7. Identify the following compounds from A to K:

   (i) $(CH_3)_3CBr + H_2O \xrightarrow{\text{heat}} A$

   (ii) $(CH_3)_2CHCH(Br)CH_2CH_3 \xrightarrow{C_2H_5ONa,\ \text{heat}} B$

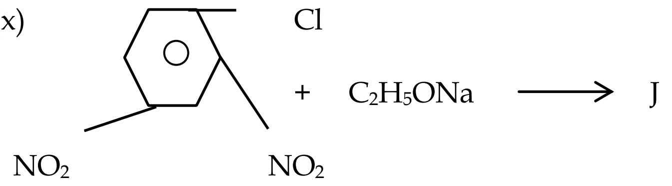
   (iii) $CH_2{=}CHCH_2Br + CH_3C \equiv CNa \xrightarrow{\text{liq } NH_3} C$

   (iv) $C_6H_4CH_2Cl + C_2H_5ONa \longrightarrow D$

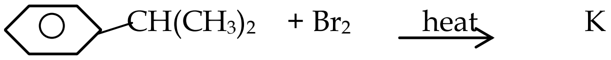
   (v) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow E$

   (vi) $CH_3CH{=}C(CH_3)_2 + HBr \longrightarrow F$

(x)



(xi)

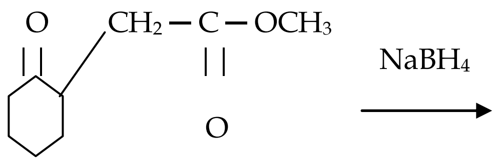


## Assignment

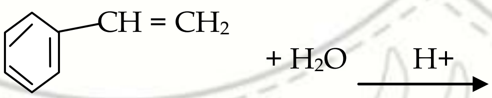
## Chapter 10: Alcohols, Phenols and Ethers

1. Write the structures of the main products in the following reactions:

i.



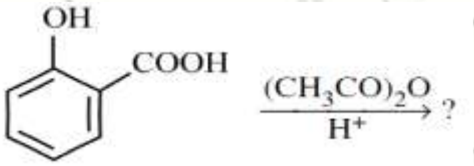
ii.

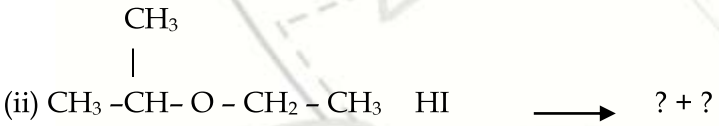


iii.

2. (a) Write the product(s) in the following reactions :

(i)





(ii) $CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-O-CH_2-CH_3 \quad HI \longrightarrow ? + ?$

(iii) $CH_3-CH=CH-CH_2-OH \xrightarrow{PCC} ?$

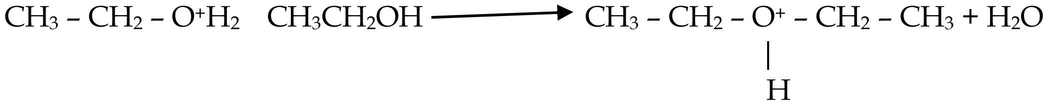
Give simple chemical tests to distinguish between the following pairs of compounds :

(i) Ethanol and Phenol

(ii) Propanol and 2-methylpropan-2-ol

3. (a) Write the formula of reagents used in the following reactions :
(i) Bromination of phenol to 2,4,6-tribromophenol
(ii) Hydroboration of propene and then oxidation to propanol.
(b) Arrange the following compound groups in the increasing order of their property indicated :
(i) p-nitrophenol, ethanol, phenol (acidic character)
(ii) Propanol, Propane, Propanal (boiling point)

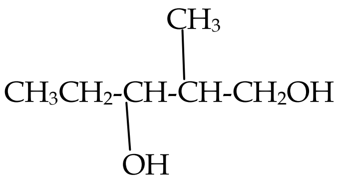
(c) Write the mechanism (using curved arrow notation) of the following reaction :



$CH_3-CH_2-O^+H_2 \quad CH_3CH_2OH \longrightarrow CH_3-CH_2-\underset{\underset{H}{|}}{O^+}-CH_2-CH_3+H_2O$

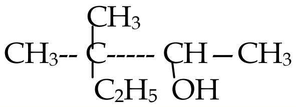
4. Give the I.U.P.A.C. name of the following:

(i)



$CH_3CH_2\text{-}\underset{OH}{\underset{|}{C}H}\text{-}\overset{CH_3}{\overset{|}{C}H}\text{-}CH_2OH$

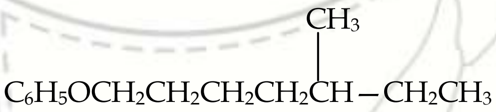
(iii)



$CH_3\text{--}\underset{C_2H_5}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{-----}\underset{OH}{\underset{|}{C}H}-CH_3$

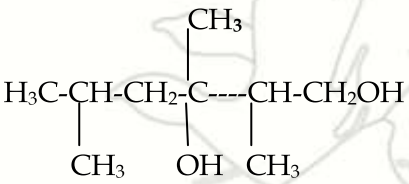
(iii ) $CH_3-CH_2\text{-}CH_2\text{-}OCH_2\text{-}CH\text{-}CH\text{-}CH_2CH_3$

( iv)



$C_6H_5OCH_2CH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}H}-CH_2CH_3$

(v)



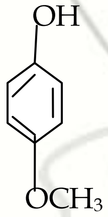
$H_3C\text{-}\underset{CH_3}{\underset{|}{C}H}\text{-}CH_2\text{-}\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{----}\underset{CH_3}{\underset{|}{C}H}\text{-}CH_2OH$

5. **Arrange the following as**

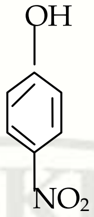
(i) Decreasing order of boiling points:
2-methyl-2-propanol, 1-butanol,2-methyl –1-propanol and 2-butanol.

(ii) Decreasing order of their acidic character:

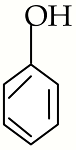
(a)



(b)



(c)



(iii ) Increasing reactivity towards Lucas reagent:
1-butanol , 2-methyl-2- propanol , 2-butanol.

6. Write the chemical equation when 1-propanol react with

(i) excess of HBr (ii) $H_2SO_4$ at 410 K

(iii ) $H_2SO_4$ at 443K (iv) acidified $KMnO_4$

7. How does phenol react with the following?

(i) Acetyl chloride.

(ii) Bromine in water.

(iii) Chloroform in presence of NaOH.

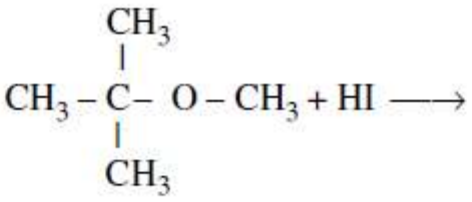
8. Convert
   (1) Phenol to picric acid
   (2) Cumene to phenol.
   (3) Phenol to Salicyaldehyde
   (4) Phenol to anisole
   (5) Propan-2-ol to 2-Methylpropan-2-ol

9. Explain giving reasons:-
   (i) Alcohols are generally soluble in water but alkyl halides are not.
   (ii) Phenols exhibit an acidic character.
   (iii) Phenols has a smaller dipole moment than methanol.
   (iv) 2,3- dimethylbutanol has got lower boiling point than hexanol .
   (v) 2-Nitrophenol is more volatile than 4-Nitrophenol.

10. Write the mechanism of the following reaction :

$$2CH_3CH_2OH \xrightarrow[413\ K]{Conc.\ H_2SO_4} CH_3CH_2-O-CH_2-CH_3$$

11. Write the main product(s) in each of the following reactions :

(i) 

$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O-CH_3+HI\longrightarrow$$

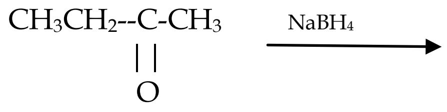
(ii) $$CH_3-CH=CH_2 \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6}$$

(iii) $$C_6H_5-OH \xrightarrow[(ii)\ CO_2,\ H^+]{(i)\ aq.\ NaOH}$$

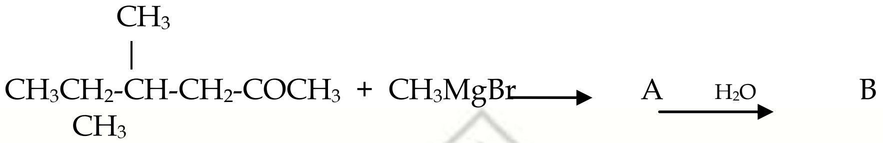
## More Practice

## Chapter 10: Alcohols, Phenols and Ethers

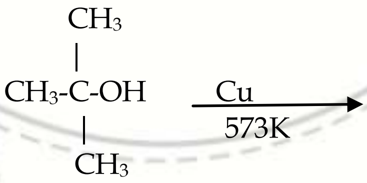
1. Complete the following reactions:

(a) 

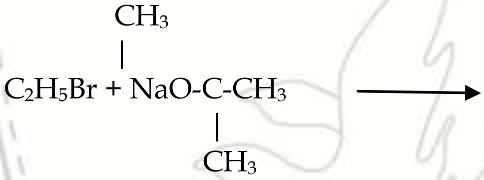
$CH_3CH_2\text{--}\underset{\underset{O}{||}}{C}\text{-}CH_3 \xrightarrow{NaBH_4}$

(b) 

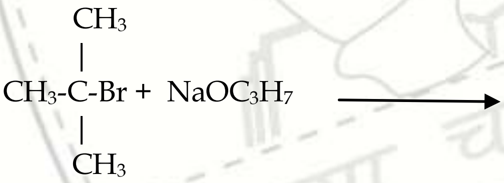
$CH_3CH_2\text{-}\overset{\overset{CH_3}{|}}{CH}\text{-}CH_2\text{-}COCH_3 + CH_3MgBr \longrightarrow A \xrightarrow{H_2O} B$

(c ) 

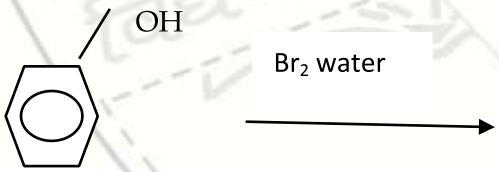
$CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}OH \xrightarrow[573K]{Cu}$

(d) 

$C_2H_5Br + NaO\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}CH_3 \longrightarrow$

(e ) 

$CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}Br + NaOC_3H_7 \longrightarrow$

(f) 

(g) $CO + 2H_2 \xrightarrow[200\text{-}300\ atm,\ 573\text{-}673\ K]{Cu\text{-}ZnO – Cr_2O_3}$

(h) 

2 Convert:

(i) Chlorobenzene to Phenol

(ii) Aniline to phenol

(iii) Propanone to Propene

## Assignment

## Chapter 11: Aldehydes, Ketones and Carboxylic Acids

1 (A), (B) and (C) are three non-cyclic isomers of a carbonyl compound with molecular formula $C_4H_8O$. Isomers (A) and (C) give positive Tollen's test whereas isomer (B) does not give Tollen's test but gives positive Iodoform test. Isomers (A) and (B) on reduction with Zn(Hg)/conc.HCl gives the same product D.

(i) Write the structures of (A), (B), (C) and (D).

(ii) Out of (A), (B) and (C) isomers, which one is most reactive towards addition of $NaHSO_3$ and why?

2 How do you convert the following:
(a) Ethanal to propanone
(b) Toluene to benzoic acid

(c) Benzoic acid to benzaldehyde

(d) Benzoic acid to benzaldehyde

(e) Prapanone to Propene

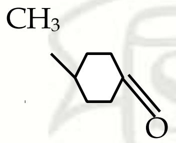
3 Account for the following:
(a) Aromatic carboxylic acids do not undergo Friedal-Crafts reaction.
(b) pKa value of 4-nitrobenzoic acid is lower than that of benzoic acid.

4 Write structures of compounds A, B and C in each of the following reactions :

$C_6H_5Br \xrightarrow{Mg/\text{dry ether}} A \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } CO_2(g)} B \xrightarrow{PCl_5} C \longrightarrow$

) $CH_3CN \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } SnCl_2/HCl} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta} C \longrightarrow$

5 Write IUPAC names for the following :

(a)


(b) $CH_2=CHCH_2CHO$
(c) $(CH_3)_2C=CHCOCH_2CH_3$

6 a) Arrange the following compounds as directed:
b) Acetaldehyde, acetone, Methyl tert-butyl ketone (reactivity towards HCN)
c) Benzoic acid, 3,4-Dinitrobenzoic acid, 4-methoxybenzoic acid
d) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$ (acid strength)
e) a) $CH_3CHO$, $CH_3CH_2OH$, $CH_3OCH_3$, $CH_3CH_2CH_3$(increasing order of their boiling point)
f) b) Ethanal, propanal, propanone, butanone (increasing order of their reactivity towards nucleophilic addition).

7 Give brief description with suitable example:
a) Cannizzaro Reaction

b) Hell-Volhard Zelinsky Reaction.
c) Clemmensen Reduction
d) Wolff-Kishner Reduction.
e) Cross aldol condensation
f) Etard reaction

8 Account for the following:
a) Carboxylic acids have higher boiling points than alcohols of comparable molecular masses.
b) Electrophilic substitution in benzoic acid takes place at meta-position.
c) Monochloroethanoic acid has a higher pKa value than dichloroethanoic acid.
d) Ethanoic acid is a weaker acid than benzoic acid.
e) The boiling points of aldehydes and ketones are lower than of the corresponding acids.

9 How will you convert the following?
a) Acetaldehyde into 2-Butenal
b) Acetic acid to Acetic anhydride
c) Butanol to butanoic acid
d) 4-Methylacetophenone to benzene-1,4-dicarboxylic acid
e) Butan-2-one to butan-2-ol
f) Phenol to 2,4,6- tribromophenol

10 Distinguish between the following
a) $CH_3CHO$ and $C_6H_5CHO$
b) $C_2H_5OH$ and $CH_3CH_2COCH_2CH_3$
c) $C_6H_5COOH$ and $C_6H_5OH$
d) $C_6H_5COCH_3$ and $C_6H_5COC_6H_5$
e) $CH_3COCH_3$ and $C_2H_5OH$
f) $CH_3COCH_3$ and $C_3H_7OH$

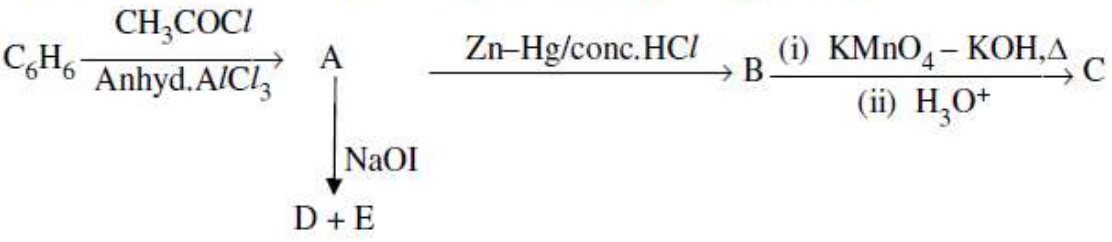
11 Complete the following reactions:

(a) $CH_3CO\ CH_3 + NH_2NH_2 \xrightarrow{KOH/glycol}$

(b) $C_6H_5COCH_3 + C_6H_5OH \xrightarrow{NaOH/\ I2}$

(c) $C_6H_5NH_2 \xrightarrow[\Delta]{NaOH/CaO}$

12 (a) Write the structures of A, B, C, D and E in the following reactions :



13 (a) Write the chemical equation for the reaction involved in Cannizzaro reaction.

(b) Draw the structure of the semicarbazone of ethanal.

(c) Why pKa of F-$CH_2$-COOH is lower than that of $Cl - CH_2 - COOH$ ?

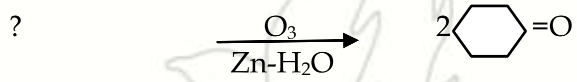
(d) Write the product in the following reaction :

$$CH_3 - CH = CH - CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}}$$

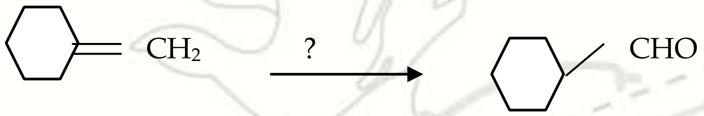
(e) How can you distinguish between propanal and propanone ?

14 Complete the following reaction statements by giving the missing starting material, reagent or product as required:

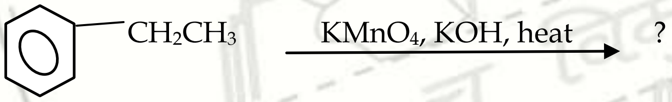
(i)



(ii)



(iii)



## More Practice

## Chapter 11: Aldehydes, Ketones and Carboxylic Acids

1 Account for the following:

a) Formaldehyde gives Cannizzaro's reaction whereas acetaldehyde does not

b) Carboxylic acids do not give the characteristic reactions of carbonyl group.

c) Aldehydes are more reactive than ketones towards nucleophilic addition reactions.

d) Chloroacetic acid has lower pKa value than acetic acid.

e) The aldehydes an ketones undergo a number of addition reactions.

f) Ethanoic acid is a weaker acid than benzoic acid.

2 How will you convert the following?
i) Acetophenone to Ethyl benzene
ii) Acetone to tert-butyl alcohol
iii) Benzyl alcohol to phenyl ethanoic acid
iv) Bromobenzene to benzoic acid
v) p-methyl acetophenone to benzene 1,4 –dicarboxylic acid
vi) Benzoic acid to benzyl amine
vii) p-nitrobenzamide to p-nitroaniline
viii) A primary alcohol to an aldehyde
ix) Ethanol to acetone
x) Benzene to acetophenone
xi ) Benzoic acid to benzaldehyde

3 (a) Although phenoxide ion has more number of resonating structures than Carboxylate ion, Carboxylic acid is a stronger acid than phenol. Give two reasons.

(b) How will you bring about the following conversions ?

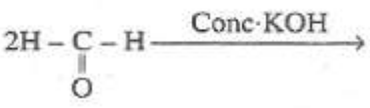
(i) Propanone to propane

(ii) Benzoyl chloride to benzaldehyde

(iii) Ethanal to but-2-enal

4 (a) Complete the following reactions :

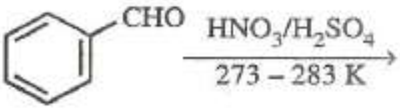
(i)



$2H-\underset{\overset{\|}{O}}{C}-H \xrightarrow{\text{Conc}\cdot\text{KOH}}$

(ii) $CH_3COOH \xrightarrow{Br_2/P}$

(iii)



(b) Give simple chemical tests to distinguish between the following pairs of compounds :

(i) Ethanal and Propanal

(ii) Benzoic acid and Phenol

**5** An organic compound contains 69.77% carbon, 11.63% hydrogen and the rest is oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and gives a positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acids. Deduce the possible structure of the organic compound.

**6** An organic compound with molecular formula C9H10O forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1,2-benzenedicarboxylic acid. Identify the compound.

## Assignment

### Chapter 12: Organic Compounds containing Nitrogen

1. (a) Write the reactions involved in the following:
    - (i) Hofmann bromamide degradation
    - (ii) Diazotization
    - (iii)Gabriel phthalimide synthesis

   (b)Give reasons:
    - (i) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.
    - (ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts.

2. (a)Write the structures of the main products of the following reactions:
    - (i) $C_6H_5NH_2 \xrightarrow{(CH_3CO)_2O,\ Pyridine}$
    - (ii) $C_6H_5SO_2Cl \xrightarrow{(CH_3)_2NH}$
    - (iii) $C_6H_5N_2^+Cl^- \xrightarrow{CH_3CH_2OH}$

   (b)Give a simple chemical test to distinguish between Aniline and N,N-dimethylaniline.

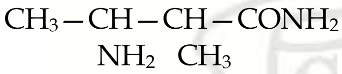
   (c) Arrange the following in the increasing order of their $pK_b$ values:
   $C_6H_5NH_2$ , $C_2H_5NH_2$, $C_6H_5NHCH_3$

3. Write IUPAC name of the following compound :
   $(CH_3CH_2)_2NCH_3$

4. Give reasons :
    - (i) Acetylation of aniline reduces its activation effect.
    - (ii) $CH_3NH_2$ is more basic than $C_6H_5NH_2$.
    - (iii)Although $-NH_2$ is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline.

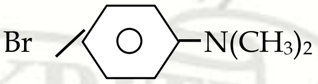
5. Write IUPAC names of the following:

a)



$$CH_3-\underset{NH_2}{CH}-\underset{CH_3}{CH}-CONH_2$$

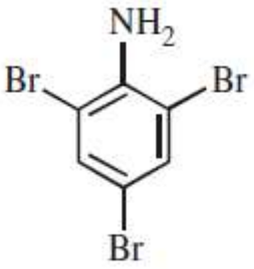
b)



c) $O_2N-CH_2-CH_2-CH=CH-CHO$

d) $(CH_3)_3CCN$

e)



6. For an amine $RNH_2$, write the expression for $K_b$ to indicate its basic strength

7. Describe the following processes giving suitable examples of each:

- i) Diazotization
- ii) Coupling reaction
- iii) Carbyl amine reaction
- iv) Hofmann's bromamide reaction

8. How will you carry out the following conversions:
   - i) Nitrobenzene to acetanilide
   - ii) Methyl amine to ethyl amine
   - iii) Nitrobenzene to phenol
   - iv) Toluene to m-nitro benzoic acid
   - v) Acetic acid to ethyl amine

9. Write structures of the following:
   - i) P- Toluidine
   - ii) Picric acid
   - iii) Sulphanilic acid

10. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.

11. Write reactions for what happens when:
    a) Phenol is treated with benzene diazonium chloride in presence of NaOH
    b) Aniline is treated with benzaldehyde
    c) Ethyl amine is treated with excess of methyl iodide.

12. Arrange in increasing order of boiling point: $C_2H_5NH_2$, $C2H_5OH$, $(CH_3)_3N$

13. Complete the following reaction equations:
    - i) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$
    - ii) $C_6H_5NH_2 + Br_2(aq) \longrightarrow$

14. Write the structures of A, B and C in the following :

(i) $C_6H_5-CONH_2 \xrightarrow{Br_2/\text{aq. KOH}} A \xrightarrow[0\text{-}5\ ^\circ C]{NaNO_2 + HCl} B \xrightarrow{KI} C$

(ii) $CH_3-Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[\Delta]{CHCl_3 + \text{alc. KOH}} C$

## More Practice

## Chapter 12: Organic Compounds containing Nitrogen

1. Account for the following:
   a) Ammonolysis of alkyl halide does not give a corresponding pure amine
   b) $pK_b$ for aniline is more than that for methylamine
   c) Boiling point of methylamine is less than that of methanoic acid
   d) Aniline cannot be prepared by Gabriel Pthalimide synthesis
   e) Nitration of toluene is easier compared to nitrobenzene
   f) Before nitration aniline is converted to acetanilide.
   g) Aniline does not undergo Friedel-Crafts reaction.
   h) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.

2. A compound X having molecular formula $C_3H_7NO$, reacts with $Br_2$ in presence of NaOH to give another compound Y. The compound Y reacts with $HNO_2$ to form ethanol and $N_2$ gas. Identify the compounds X and Y and write the reactions involved.

3. A compound A of the molecular formula $C_3H_7O_2N$ on reaction with Fe and conc. HCl gives a compound B of the molecular formula $C_3H_9N$. Compound B on treatment with $NaNO_2$ and HCl gives another compound C of the molecular formula $C_3H_8O$. The compound C gives effervescence with Na. On oxidation with $CrO_3$, the compound C gives a saturated aldehyde having 3 carbon atoms. Deduce the structures of A, B and C and write the reactions involved.

4. Describe a test to distinguish between each of the following pairs
   a) Ethyl amine and aniline
   b) N-methyl aniline and N,N-dimethyl aniline

5. How will you carry out the following conversions:
   i) Aniline to N-phenyl ethanamide
   ii) Aniline to benzoic acid
   iii) Benzene to m-dichlorobenzene
   iv) 2-nitropropane to acetone
   v) Benzonitrile to acetophenone

## Assignment

### Chapter 13: Biomolecules

1. Define the following with an example of each;
   (i) Polysaccharides
   (ii) Denatured proteins
   (iii) Essential aminoacids

2. (i) Write the product when D- Glucose reacts with bromine water.
   (ii) Amino acids show amphoteric behaviour. Why?
   (iii) Write one difference between α-helix and β-pleated structures of proteins.

3. State two main differences between globular proteins and fibrous proteins. Give one example of each.

4. a) Write the full forms of DNA and RNA. Write the names of the bases in them.
   b) What are three types of RNA molecules which perform different functions?

5. Write chemical equations for the reactions of glucose with
   (i)Acetic Anhydride (ii) $NH_2OH$ (iii) $HNO_3$ (iv) HI

6. Define and classify vitamins. Name the main disease caused due to lack of vitamins and its sources in each of the following ;A , $B_6$, E ,D, $B_{12}$ and K .

7. (a) Write any two reactions of glucose which cannot be explained by the open chain structure of glucose molecule.
   (b) Write the structure of the product obtained when glucose is oxidized with nitric acid.

8. Define enzymes .State the activity of enzyme. How do enzymes differ from ordinary chemical catalysis? Comment on the specificity of enzyme action.

9. In what way is a nucleotide different from a nucleoside? Illustrate with examples?

10. What is essentially the difference between alpha-glucose and beta-glucose? What is meant by pyranose structure of glucose?

11. (a) Name some biological functions of nucleic acids.
    (b) What is the name given to the linkage which holds together two nucleotides

12. Exlain what is meant by
    (i) a peptide linkage
    (ii) a glycosidic linkage

13. a) Write the name of two monosaccharides obtained on hydrolysis of lactose sugar.
    b) Why Vitamin C cannot be stored in our body ?
    c) What is the difference between a nucleoside and nucleotide ?
14. What is glycogen? How is it different from starch? How is starch structurally different from cellulose?

15. How do you explain amphoteric behaviour of amino acids?

16. Define denaturation in proteins.

17. Which of the following is a disaccharide: Starch, Maltose, Fructose, Glucose?

**Hands-on/ IT Enabled work:**

- **The entire chapter is done with the help of a presentation.**
- **A hand–out is given on proteins, vitamins and nucleic acids.**

## Assignment

### Chapter 14: Polymers

1. Write a difference between LDPE and HDPE.

2. What are biodegradable polymers? Give an example.

3. Write the structures of the monomers used for getting the following polymers :
   (i) Dacron
   (ii) Melamine – formaldehyde polymer
   (iii)Buna-N
4. Write the names and molecular structures of the monomers of the following and classify them as addition or condensation polymers :
   (i) Natural rubber (ii) Glyptal (iii) ) Buna-S (iv) Bakelite
   (v) PVC (vi) Nylon-6 (vii) Neoprene (viii) Polypropene

5. (i)What is the role of t-butyl peroxide in the polymerization of ethene? Write its mechanism.
   (ii)Identify the monomers in the following polymer :
   $[NH – (CH_2)_6 – NH – CO – (CH2)_4 – CO– ]n$
   (iii)Arrange the following polymers in the increasing order of their intermolecular forces : Polystyrene, Terylene, Buna-S
   (iv)What are elastomers? Give an example of it.

6. (a) Describe chain growth and step growth polymerization with the help of an example.
   (b) Classify the following as addition or condensation polymers:
   Nylon-66, Neoprene, Polythene
7. (a)What is the difference between nylon-6 and nylon-66?
   (b)What does the part ‘6,6 mean in the name nylon-6,6 ?

8. What is Teflon? What are its uses?
9. Differentiate the following pair of polymers based on the property mentioned against each.
   (i)Novolac and Bakelite (structure)
   (ii)Buna-S and Terylene ( intermolecular forces of attraction)

10. What is the repeating unit in the condensation polymer obtained by combining $HO_2CCH_2CH_2CO_2H$ (succinic acid) and $H_2NCH_2CH_2NH_2$(ethylene diamine).
11. How is melamine polymer prepared? Give its two uses. What type of polymer is it?
12. Name the monomers of Nylon2-nylon6 polymer.
13. PHBV (Poly-β-Hydroxybutyrate-co-β-hydroxy valerate) is a biodegradablepolymer. It is a copolymer of 3-hydroxy valerate acid and 3-hydroxy pentanicacid.
    (a) How PHBV has found utility in medicines as Capsule?
    (b) Write the name of polymer used in artificial limb popularly known as Jaipurfoot.

**Hands-on/ IT Enabled work:**

- **Different samples of polymers will be shown in the class.**
- **A hand out will be given.**

# CHEMISTRY IN EVERYDAY LIFE

## DRUGS

Drugs are chemicals of low molecular masses which interact with macromolecular targets and produce as biological response. When biological response is therapeutic and useful, these chemicals, are called medicines and if taken in higher doses, they behave as poisons. Use of chemicals for therapeutic effect is called Chemotherapy.

Classification of Drugs:

a) On the basis of pharmacological effect: It is useful for doctors because it provides them the whole range of drugs available for treatment of a particular problem. For e.g.: analgesics for pain killing effect, antiseptics kill or arrest growth of microorganisms.

b) On the basis of drug action: It is based on the action of a drug on a particular biochemical process. Eg- antihistamines which inhibit the action of histamines which causes inflammation in the body.

c) On the basis of Chemical structure: Some drugs share a common feature and often have similar Pharmacological activity. Eg; Sulphonamides have $H_2N\text{-}C_6H_4\text{-}SO_2\text{-}NHR$ structural feature in common.

d) On the basis of molecular targets: Drugs usually interact with biomolecules such as carbohydrates, lipids, proteins & nucleic acid. These are called target molecules. Drugs possessing some common structural feature have the same mechanism of action on targets.

## DRUG –TARGET INTERACTION

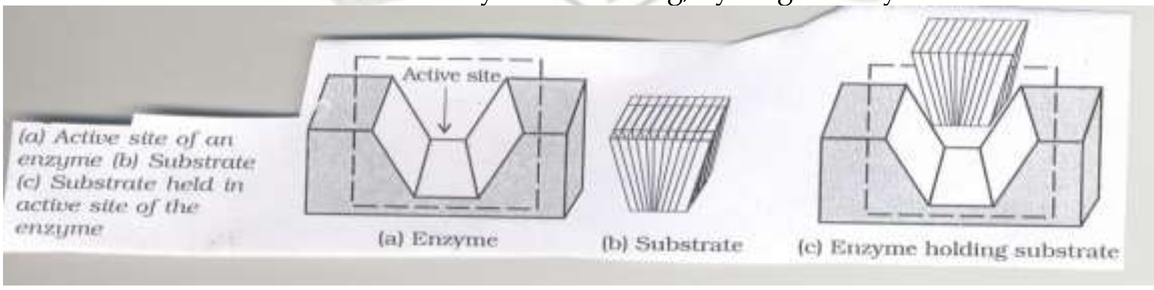
Macromolecules of biological origin perform various functions in the body. For eg- Proteins which perform role of biological catalyst in the body are called ENZYMES & those which are crucial to communication system are called RECEPTORS.

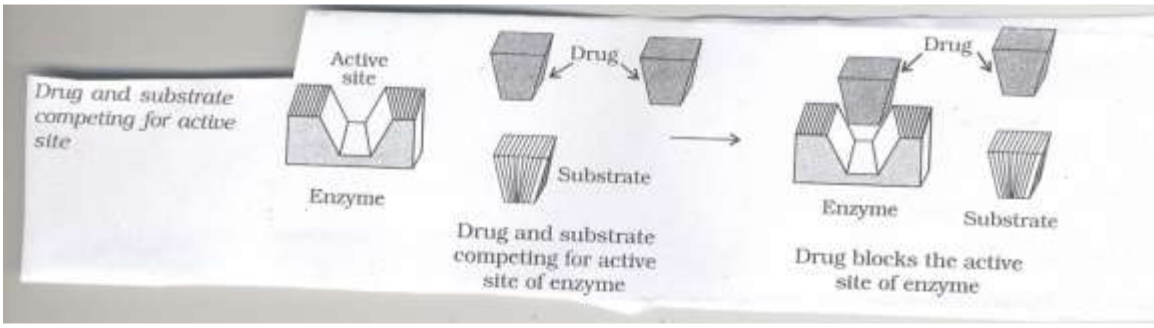
Hormones are biological chemical messengers secreted by endocrine glands. Example- Insulin, noradrenalin.

## ENZYMES AS DRUG TARGETS:

a) Catalytic action of enzymes : For understanding interaction between drug and enzyme we first study the function of enzymes.

Enzymes hold the substrate for a chemical reaction. Active sites of enzymes hold substrate molecule in a suitable position, so that it can be attacked by the reagent effectively. Substrate binds themselves to the active sites by ionic bonding, hydrogen or by vanderwaals interaction.


(a) Active site of an enzyme (b) Substrate (c) Substrate held in active site of the enzyme



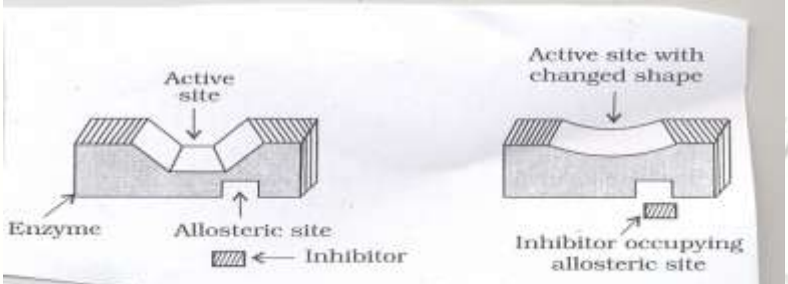
*Drug and substrate competing for active site*

It provides functional groups that will attack the substrate and carry out chemical reaction.

b) <u>Drug-enzyme interaction:</u> Drugs inhibit any of the above mentioned activities of enzymes. These can block the binding site of enzyme and prevent the binding of substrate or can inhibit catalytic activity of enzyme. These are called <u>enzyme inhibitor</u>.
These can occur in two different ways---
(i) Drugs compete with the natural substrate for their attachment on active sites of enzymes. These are called competitive inhibitors.

(ii) Some drugs do not bind to the enzyme's active site. These bind to some different enzyme site called allosteric site. This binding of inhibitor at allosteric site changes the shape of the active site in such a way that substrate cannot recognize it.

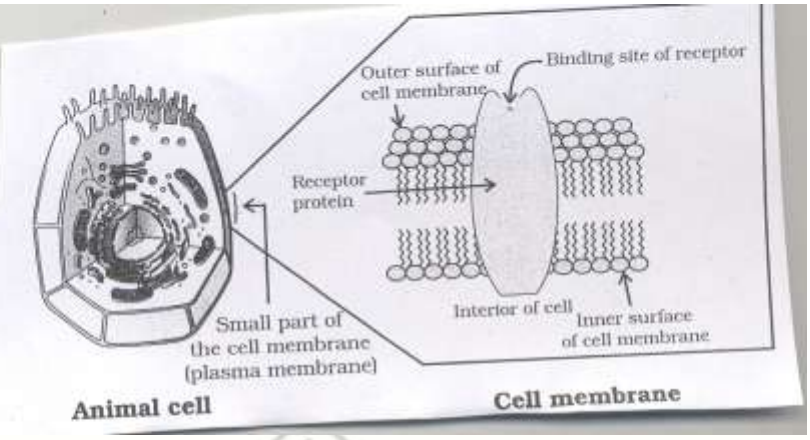
If the bond between an enzyme and inhibitor is a strong covalent bond and it cannot be easily broken, then the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesizes the new enzyme.



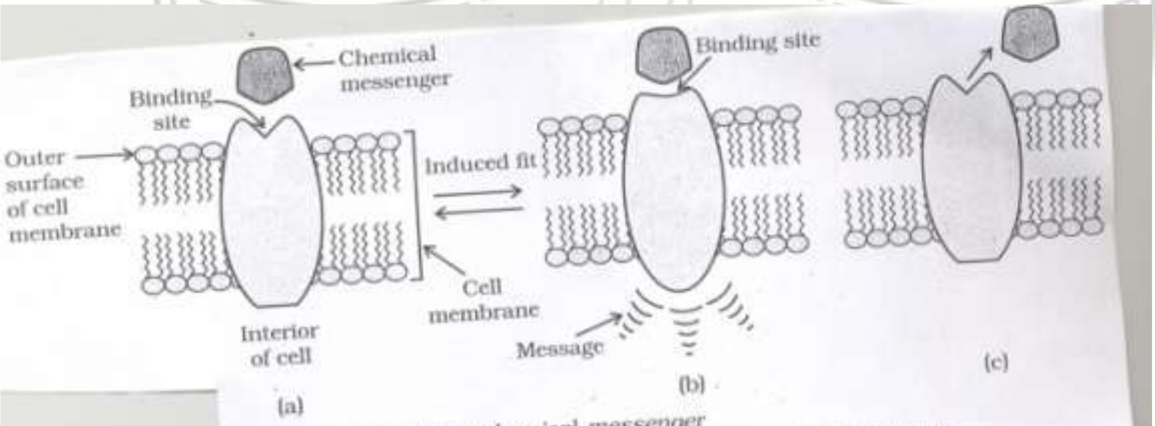
*: Non-competitive inhibitor changes the active site of enzyme after binding at allosteric site.*

## RECEPTORS AS DRUG TARGETS

Receptors are proteins that are crucial to body's communication process. Receptor proteins are embedded in cell membranes in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane.



*Receptor protein embedded in the cell membrane, the active site of the receptor opens on the outside region of the cell.*



*(a) Receptor receiving chemical messenger*
*(b) Shape of the receptor changed after attachment of messenger*
(c) Receptor regains structure after removal of chemical messenger

There are a large no. of different receptors in the body that interact with different chemical messengers. These receptors show selectivity for one chemical messenger over the other because their binding sites have different shape, structure and aminoacid composition.
Drugs that bind to the receptor site and inhibit its natural function are called antagonists. Drugs that mimic the natural messenger by switching on the receptors are called agonists. These are useful when there is lack of natural chemical messenger.

## CHEMICALS IN MEDICINE

The chemical substances used for treatment of diseases and for reducing suffering from pain are called medincines or drugs.
Chemotherapy- is a science in which suitable chemicals are used for treatment of diseases.

1) **Antipyretics**- The chemicals use to lower body temperature in high fever are called antipyretics. Eg- Aspirin, paracetamol and phenacetin

2) **Analgesics**- The chemical substances used to relieve pains without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system are called analgesics. These are of two types.
   a) Non-narcotic drugs or non-addictive drugs- Eg- aspirin, analgin, novalgin, naproxen, ibuprofen & diclofenac sodium or potassium.

Aspirin: Finds use as antipyretic, prevention of heart attack because of its anti-blood clotting action. Aspirin is supposed to be toxic to liver which gets hydrolysed in stomach giving salicylic acid which sometimes cause bleeding in stomach. Therefore, overdosage and its use in empty stomach should be avoided.

b) Narcotic drugs or Addictive drugs- Which produce sleep and unconsciousness. These can also be used as analgesics. Eg- morphine, codeine, heroin, marijuana. When used in medicinal doses, they relieve pain and produce sleep. In excessive doses, they produce stupar coma, convulsions and ultimately leading to death. These narcotics are called opiates because they are obtained from opium poppy.

3) **Antiseptics and disinfectants**:

Antiseptics are chemical substances used either to kill or prevent the growth of micro-organisms. These are not harmful to living tissues and can be applied on wounds, ulcers, diseased skin surfaces. They are also used to reduce odours resulting from bacterial decomposition of the body or in the mouth. Eg- Soframycin, Bithional is added to medicated soaps, tincture of Iodine ( 2-3% soln of iodine in alcohol-water mixture), Iodoform, Boric acid in dilute aqueous solution is antiseptic for eyes etc.

Disinfectants are chemical substances which are used to kill micro-organisms but they cannot be applied on living tissues. They play a major role in water treatment and public health sanitation. These are commonly applied on inanimate objects like floors, drainage system etc. Eg- $Cl_2$ at a conc. of 0.2 to 0.4 ppm makes water fit for drinking, Phenol derivative, thymol.

Some substances act both as antiseptics and disinfectants. Eg- Dettol (a mixture of chloroxylenol and terpineol ), 0.2% soln. of phenol acts as antiseptic & 1% soln acts as disinfectant.

4) **Tranquilizers**: The chemical substances used for treatment of stress, mild and severe mental diseases are called tranquilizers. They release mental tension and reduce anxiety. These are essential component of sleeping pills. These are also called psychotherapeutic drugs. Noradrenaline, a hormone which induces feeling of well being and helps in changing mood. If the level of nordrenaline is low for some reason, then signal sending activity becomes low, and the person suffers from depression. In such situations, antidepressant drugs are required.

Eg: iproniazid and phenalzine are antidepressant drugs. They inhibit the enzyme which catalyse the degradation of noradrenaline.

Chlordiazepoxide and meprobamate are used to relieve tension.

Equanil, diazepam,veronal and serotonin are used in controlling depression and hypertension

Barbiturates like veronal, amytal, membutal, seconal and luminal are hypotonic ie: sleep producing agents.

5) **Antimalarials**: These are chemical substances used for treatment of malaria. Eg- Chloroquine, paraquine etc.

6) **Antimicrobials**: are chemical substances used to cure infections due to micro-organisms. The disease in human beings may be caused due to variety of micro-organisms like virus, bacteria etc. which are called microbes. They can be seen only by microscope. The disease causing microbes are called pathogens. Our body possesses natural defense mechanism against the pathogenic microbes. Skin is impervious to microbes. Our body secretions kill the microbes or inhibit their growth. Some common examples are lysozyme in tears, nasal secretions, saliva, lactic acid in sweat etc. The pathogens reach the tissues due to breach in defence mechanism and cause infections.

The control of microbial diseases can be achieved by:
(i) Drugs which kill organisms in the body (bactericidal)
(ii) Drugs which inhibit or arrest the growth of organisms (bacteriostatic)
(iii) Increasing immunity and resistance to infections of the body (immunity)

Antimicrobial substances may be synthetic chemicals like sulphonamides or antibiotics-like tetracycline, penicillin, chloramphenicol etc. The common example of antimicrobial drug is sulphanilamides which are effective in wide range of micro-organisms.

7) **Antifertility Drugs**: These chemical substances control pregnancy. Their basic aim is to prevent conception or fertilization. The birth control pills are essentially a mixture of esterogen and progesterone derivative. Both of these compounds are hormones. Progesterone suppresses ovulation. Synthetic progesterone are more potent than progesterone.
The common pills used for a combination of progesterone, norethindrone and estrogen (ethynylestradiaol) is novestrol.

8) **Antacids**: The chemical substances which neutralize excess acid in the gastric juices and give relief from acid indigestion, acidity, heart burns, and gastric ulcers are called antacids. Baking soda in water is a common antacid. Other example are magnesium hydroxide, calcium carbonate, sodium bicarbonate, potassium bicarbonate, magnesium carbonate, potassium bicarbonate, aluminium phosphate. Magnesium oxide is also used as an antacid ingredient since it reacts with water to form $Mg(OH)_2$. The antacids are available in the form of liquids, gels or tablets. Generally, liquid antacids are more effective than tablets because of great surface area available for interaction and neutralization of acid. An advancement in treatment of hyperacidity came through the discovery that histamines stimulates the secretion of pepsin and hydrochloric acid. To prevent interaction of histamines with the receptors present in the stomach wall, the drug cimetidine has been designed. This resulted in release of lesser amount of acid. The drug is now replaced by ranitidine. A more effective new class of drugs is omeprazole and lansoprazole which prevents formation of acid in stomach.

9) **Antihistamines**: are chemical substances which diminish or abolish the main actions of histamines release in the body and hence prevent the allergic reactions caused by antigens. Histamines are responsible for nasal congestion associated with common colds, cough, allergic response to pollens etc. Synthetic drugs such as bromopheniramine (Dimetapp) and terfenadine (seldane) are used as antihistamines. Antihistamines are also called anti-allergic drugs. These are used to treat allergy, eg, skin rashes, conjunctivitis etc. These drugs relieve sneezing , nasal discharge, mild asthama, itching of eyes, nose and throat. The common antihistamine drugs are Benadryl, avil, zeet, bromethazine, actidil, anistine, foristal etc.

10) **Anaesthetics**: are chemical sunstances which produce general or local insensibility to pains and other sensations. Cocaine, novocaine are local anaesthetic chloroform, diethyl & vinyl ethers are general anaesthetics.

11) **Antibiotics**: are chemical substances which are produced by micro-organisms (bacteria, fungi and moulds) and can inhibit the growth or even destroy micro-organisms. Antibiotic refers to a substance ( produced wholly or partly by chemical synthesis) which in low concentration inhibits growth or destroys micro-organisms by intervening in their metabolic processes.
First antibiotic produced was penicillin by Alexander Fleming in 1929. Antibiotic can be either bactericidal or bacteriostatic.
Bactericidal: Pencillin, Aminoglycosiders, Ofloxacin.

Bacteriostatic: Erythromcin, Tetracycline, Chloramphenicol.
Pencillin is narrow spectrum. These can be used for curing sore throat, reheumatic fever, local infections etc. Streptomycin, neomycin is used for treatment of tuberculosis, meningitis, pneumonia etc.
Broad spectrum antibiotics are effective against several micr-organisms. Thereforem these are for curing a variety of diseases. Eg- thetracycline, chloromycetin and chloramphenicol. Eg- Chloramphenicol is a broad spectrum antibiotic which is used for curing typhoid, acute fever, dysentery, whooping cough, pneumonia, eye infections, certain urine infections etc. Sulphadrugs are used against pneumonia, tuberculosis, diphtheria etc. Some examples are sulphadiazine, sulphathiazole, sulphaacetamide etc.

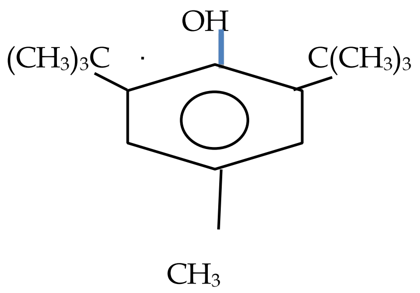
| S.No. | Type of Medicine | Used as | Examples |
|---|---|---|---|
| 1 | Analgesics | Relieve Pain | Aspirin, Ibuprofen |
| 2 | Antipyretics | Lowers body temperature | Paracetamol, Phenacetin |
| 3 | Antiseptics & Disinfectants | Kill or prevent growth of microorganism | Phenol, Chlorine, dettol |
| 4 | Tranquilizers | Treatment of stress & mental diseases | Barbituric acid & its derivatives (Seconal, Luminal, Veronal etc) |
| 5 | Antimicrobials | Cure infections due to microorganisms | Sulphonamides |
| 6 | Antifertility drugs | Birth control | Novestrol (ethynylestradiol) & Progestrone (norethindrone), mifepristone |
| 7 | Antacids | Removes excess acid in stomach | Magnesium hydroxide, Magnesium trisilicate, aluminium hydroxide gel Ranitidine |
| 8 | Antihistamines | Treatment of hyperacidity, stimulates secretion of pepsin & HCl in the stomach. Also responsible for nasal congestion associated with common cold | Brompheniramine & terfenadine |
| 9 | Antibiotics | Produced by microorganisms & can inhibit the growth of other microbes | Pencillin, Tetracycline, Chloramphenicol |

## Chemicals in Food

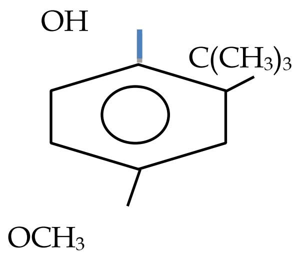
Many chemicals are added to food for their preservation and enhancing their appeal. These include flavourings, sweetness, antioxidants, fortifiers, emulsifiers and antifoaming agents.

1. **Antioxidants**:
   Antioxidants are the important class of compounds which prevent oxidation of food materials. These compounds retard the action of oxygen on the food and thereby help in preservation. These act as sacrificial materials. i.e. they are more reactive towards oxygen than the materials they are protecting. They also reduce the rate of involvement of free radicals in the aging

process. Most important antioxidants used are butylated hydroxy anisole (BHA) and butylated hydroxy toluene (BHT). The addition of BHA to butter increases its storage life.



**BHT**



**BHA**

Sometimes BHT and BHA are added in combination with citric or ascorbic acid to produce a more active synergistic effect. $SO_2$ and sulphate are useful antioxidants for wine and beers, sugar syrups and cut peeled on dried fruits and vegetables.

2. **Preservatives:**
   These are the chemical substances which are added to the food materials to prevent their spoilage and to retain their nutritive value for long periods. These preservatives prevent rancidity of food & inhibit the growth of microorganisms during storage. Example: Common salt, sugar, oils, Sodium benzoate, salts of propanoic acid and ascorbic acid.
3. **Artificial Sweetening agents:**
   The artificial sweetners are another type of food additives. Eg; Saccharin which is marketed as soluble of calcium salt. It is 300 times sweet than cane sugar. It is life saver for diabetic patients and is of great value to people who need to control intake of calories.
   Aspartame: Unstable at cooking temperature, therefore it is used as a sugar substitute to cold foods and soft drinks.
   Alitame: more stable during cooking than aspartame
   Sucralose: good artificial sweetener.

4. **Edible colors**:
   Edible colour that are used for food are dyes; ex- dyes are used to dye orange peels so hat oranges retain their colour. Colour is also added to fruit juices. Food colours do not have any nutritional value. The use of some of the azodyes are dangerous for young children and asthma patients.
   Terazime, a widely used dye is harmful
   Natural dyes like carotene are safe food edible colours.
   PFA {Prevention of food Adulteration Act}- govt. has passed it for the protection of consumer interests.

## SOAPS AND DETERGENT

**Soaps** are sodium or potassium salts of long chain fattyacids. Soaps containing sodium salts are formed by heating fat (ie glyceryl ester of fatty acid) with aqueous sodium hydroxide solution and potassium salts are prepared by using potassium hydroxide. This reaction is known as saponification. Soap obtained remains in colloidal form and is precipitated from the solution by adding NaCl.

$$\begin{array}{l}CH_2\text{-}O\text{-}C\text{-}C_{17}H_{35}\\ |\\ CH_2\text{-}O\text{-}C\text{-}C_{17}H_{35}\\ |\\ CH_2\text{-}O\text{-}C\text{-}C_{17}H_{35}\end{array} \quad + \quad 3NaOH \quad \longrightarrow 3C_{17}H_{35}COONa \; + \quad \begin{array}{l}CH_2OH\\ |\\ CH_2OH\\ |\\ CH_2OH\end{array}$$

Soaps cannot be used in hard water as hard water contains certain metal ions such as $Ca^{2+}$ and $Mg^{2+}$ which form a curdy white precipitate of calcium and magnesium salt. This is called scum and is hinderance to good washing because this insoluble ppt. adheres onto the fibre of the cloth as gummy mass.

**Synthetic detergents**: They are sodium or potassium salts of sulphonic acid. Eg: sodium alkylbenzene sulphonate which have a general formula: $CH_3(CH_2)xC_6H_4SO_3Na^+$

**Advantages of detergents**:

Detergents can be work in hard water. The anions of synthetic detergent do not precipitate in the presence of $Ca^{2+}$ and $Mg^{2+}$. They can work will even in acidic water.

Types of detergents;

There are three types of detergents;

(a) Anionic detergents are synthesized from long chain alcohol. The long chain alcohols are treated with conc. $H_2SO_4$to form alkyl hydrogen sulphate of high molecular mass and finally alkyl sulphate are neutralized with alkali to form salts. It is called anionic detergent because large part of the molecule is anion. The anionic detergent is largest in use as household detergents. E.g.- Alkylbenzenesulphonate . They are effective in acidic solutions to form an alkyl hydrogen sulphate which is soluble where as soap are not effective due to formation of insoluble fatty acids.
$CH_3(CH_2)_{11}OSO_3^-Na^+$, $CH_3(CH_2)_{11}C_6H_4SO_3^-Na^+$

(b) Cationic detergent: These are mostly acetates or chlorides of quaternary ammonium salt. They are more expensive therefore are used to limited extent. Such detergent possess germicidal properties and are extensively used as germicides. e.g $[CH_3(CH_2)_{11}N^+(CH_3)_3]Br^-$

(c) Non-Ionic detergent: Some of the detergent are non- ionic , like the esters of high molecular mass formed by reactions between polyethylene glycol and stearic acid. They do not possess any ion.

$$CH_3(CH_2)_{16}COOH+HO(CH_2CH_2O)_nCH_2CH_2OH \longrightarrow CH_3(CH_2)_{16}COO(CH_2CH_2O)nCH_2CH_2OH$$

Some liquid dishwashing detergents are of non-ionic type branched hydrocarbon chain detergents are non-biodegradable and cause water pollution. The hydrocarbon side chain stops bacteria from attacking and breaking the chain. These molecules degrade slowly leading to water pollution. Unbranched or linear alkyl chain detergents do not create pollution as they are more prone to attack by bacteria, thus can be biodegraded.

**Hands-on/ IT Enabled work:**

**Whole chapter is done with the help of a presenation with animations.**

## Assignment

### Chapter 15: Chemistry in Everyday Life

1. (i) Why is bithional added to soap?
   (ii) What is tincture of iodine? Write its one use.
   (iii) Among the following, which one acts as a food preservative?
   Aspartame, Aspirin, Sodium Benzoate, Paracetamol

2. Define the following and give one example :
   (i) Anionic detergents
   (ii) Antimicrobials
   (iii)Antioxidants
   (iv)Broad spectrum antibiotics
   (v) Artificial sweetening agents
   (vi) Foodpreservatives

3 What type of medicines are omeprazole and lansoprazole?

4 Give an example of drug used in case of mental depression.

5 For which disease chloramphenicol is used?

6 (a)Name the sweetening agent used in preparation of a sweet for a diabetic patient.
(b) What problem arises in using alitame as artificial sweeteners?
(c) Why is use of aspartame limited to cold foods?

7 Name a broad spectrum antibiotic and diseases for which it is prescribed.

8 (a)How are antiseptics distinguished from disinfectants? Give 2 examples of each.
(b) Name a substance that can be used as an antiseptic as well as disinfectant.

9 Name the action of the following on the human body:
(i) Equanil (ii) Morphine (iii) Norethindrone (iv)Aspirin (v) Penicillin
(vi) Luminal (vii) Seconal

10 What are the essential components of dettol?

11 What are detergents? Give their scheme of classification. Why are detergents preferred over soaps?

12 Why is ethanol added to soaps?

13 What are biodegradable and non-biodegradable detergents? What are the consequences of using the latter kind? Give one example of each kind.
14 Why soaps do not act on hard water?
15 Explain the term 'chemotherapy'.

16 Describe the function of the following with one example for each :
a. Tranquilizers b. Antifertility drugs c. Antihistamines
d. Analgesics e. Antioxidants f. Antacids

17 Explain the cleansing action of soaps.

18 Account for the following:

a) Aspirin drug helps in the prevention of heart attack.
b) Diabetic patients are advised to take artificial sweetener instead of natural sweeteners.
c) Detergents are non-biodegradable while soaps are biodegradable.

19 Except for vitamin $B_{12}$, all other vitamins of group B, should be supplied regularly in diet. Why?

20 In order to wash clothes with water containing dissolved calcium hydrogen carbonate which cleaning agent will you prefer and why, soaps or synthetic detergents? Give one advantage of soap over detergents

## Practice paper (Summer Vacation)

## (Electrochemistry, Chemical Kinetics, Solutions, p-block elements, Salt Analysis)

*Time: 1 hr 45 min* *Max. Marks –50*

No. of printed pages: 2

General Instructions:

(i) All questions are compulsory.
(ii) This paper has two parts.
(iii) Part A is theory from question nos. 1 to 14 carrying 35 marks.
(iv) Part B is practical related questions numbering 15 to 19 carrying 15 marks.
(v) Use log tables if necessary, use of calculators is not permitted.

## PART A

1 For a reaction, $A + B \rightarrow P$, the reaction is of first order in reactant A and second order in reactant B. 1

i) How is the rate of this reaction affected when the concentration of B doubled.
(ii) What is the overall order of rection if A is present in large excess.

2 Write the anode and cathode reactions occurring in a mercury cell. 1

3 Why ZnO turns yellow and shows enhanced conductivity on heating? 1

4 Draw the structural formulae of molecules of following compounds: 1

a) $ClF_5$ b)$XeF_4$

5 Complete the following chemical equations: 2

a) $NaOH(aq)$ (Hot and Conc) + $Cl_2(g) \longrightarrow$
b) $XeF_6(s) + H_2O\ (l) \longrightarrow$

6 How many grams of chlorine can be produced by the electrolysis of molten NaCl with a current of 1A for 15 minutes? 2
(given atomic mass of Cl=35.5u, 1F=96500 C/mol)

7 State Kohlrausch law of independent migration of ions. Write and expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch law. 2

8 Non ideal solutions exhibit either positive or negative deviations from Raoult's law. What are these deviations and why are they caused? Explain with one example for each type. 2

9 (i) Why is the freezing point depression of 0.1M sodium chloride solution nearly twice that of 0.1M glucose solution? 2

(ii) A solution containing 8g of a substance in 100g of diethyl ether boils at $36.86^{0}C$ , whereas pure ether boils at $35.6^{0}C$. Determine molecular mass of solute. [For ether, $K_b = 2.02\ K\ Kg\ mol^{-1}$]

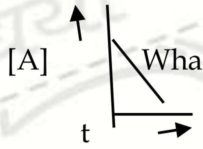
10 The decomposition of phosphine, $PH_3$, proceeds according to the following equation: 2
$4PH_3\ (g) \rightarrow 3P_4\ (g) + 6H_2(g)$
It is found that the reaction follows the following rate equation: Rate = $k[PH_3]$
The half-life of $PH_3$ is 37.9s at $120^0C$. How much time is required for 3/4th of $PH_3$ to decompose? [log2=0.3010]

11 a) What is meant by the 'rate constant, k' of a reaction? If the concentration be expressed in mol $L^{-1}$ units and time in seconds, what would be the units for k (i) for a zero order reaction and (ii) for a first order reaction? 2
b) What type of collisions is known to be effective?

12 A well known mineral fluorite is chemically calcium fluoride. It is known that in one unit cell of this mineral there are $4Ca^{2+}$ ions and $8F^-$ ions and that $Ca^{2+}$ ions are arranged in a fcc lattice. The $F^-$ ions fill all the tetrahedral holes in the face centered cubic lattice of $Ca^{2+}$ ions. The edge of the unit cell is $5.46 \times 10^{-8}$ cm in length. The density of the solid is 3.18 g/$cm^3$. Use this information to calculate Avogadro's number. 3
(Molar mass of $CaF_2$ = 78.08 $gmol^{-1}$)

13 Write the Nernst equation and calculate the e.m.f of the following cell at 298K 3
$Zn(s)|Zn^{2+}(0.1\ M)\ ||\ Cd^{+2}(0.01M)|Cd(s)$
($E^0_{Zn^{2+}/Zn}$= -0.761V, $E^0_{Cd^{2+}/Cd}$ = 0.40V ) . Furthur show:
(i) The carriers of current within the cell.
(ii) $E^0$ values for the electrode 2 $Zn^{+2}$/2Zn .
(iii) Which electrode is negatively charged?
(iv) Individual reactions at each electrode.

14 a) From the graph: 3



What is the order of the reaction?

b) A first order decomposition reaction takes 40 min for 30% decomposition. Calculate its $t_{1/2}$ value. (log10=1, log7=0.8451)

15 a) 2g each of two solutes A and B (molar mass of A > B) are dissolved separately in 200g each of the same solvent. Which will show greater elevation in boiling point? 3

b) The molal elevation constant for $H_2O$ is 0.52 K/m. Calculate the boiling point of solution made by dissolving 6 g of urea ($NH_2CONH_2$) in 200 g of $H_2O$.

16 a) Complete the following chemical reaction equations: 5
i. $XeF_4\ (s) + H_2O\ (l) \longrightarrow$
ii. $ClF + H_2O \longrightarrow$
b) Explain the following observations giving appropriate reasons:
i. Halogens are strong oxidizing agents.
ii. Bleaching action of chlorine is permanent where as that of $SO_2$ is temporary.

## PART B

17 Why is it that tests for Barium, Strontium and Calcium to be done in order? 2

18 Explain one confirmatory test for $Ni^{2+}$. 2

19 (a) Give the formula of reddish yellow vapours evolved during chromyl chloride test? 1,2
(b) Explain the $Cl_2$ water test for iodide with equation.

20 Explain the indicatory and confirmatory tests for sulphide. 3

21 (a) How can one distinguish between sulphite and sulphate using $BaCl_2$ test. 5
(b) What is the colour seen in flame for strontium salt.
(c) What is the yellow ppt. in $K_2CrO_4$ test for lead due to?
(d) What is the canary yellow ppt. in Ammonium Molybdate test for Phosphate due to?
(e) What is the formula for brown ring?

**Academic Session: 2018-19**
**First Term Examination**
**Subject: Chemistry**
**M/1/1**

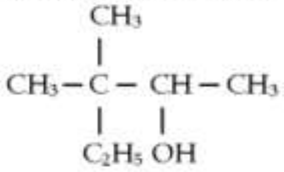
**Time: 3 hrs** **Max marks: 70**

General Instructions:

- All questions are compulsory.
- Question nos. 1- 5 are very short answer questions and carry 1 mark each.
- Question nos. 6 – 12 are short answer questions and carry 2 mark each.
- Question nos. 13 – 24 are also short answer questions and carry 3 mark each.
- Question no. 25, 26 and 27 are long answer question and carries 5 mark.
- Use of calculators is not permitted.
- This paper has 4 printed sides.

Q1. Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of the solid. Would it show cleavage property? (1)

Q2. Write the IUPAC name of the following: (1)



$$CH_3-\underset{C_2H_5}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{CH}}-CH_3$$

Q3. State Raoult's law. (1)

Q4. Write the cathodic and anodic reaction for corrosion of iron. (1)

Q5. Give an example of pseudo first order reaction. (1)

Q6. A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids? (2)

Q7. The vapur pressure of water is 12.3 kPa at 300K. Calculate the vapour pressure of 1 molal solution of a non-volatile solute in it.
(Atomic mass of O=16u and H=1u) (2)

Q8. For the reaction: (2)

$$2N_2O_5\,(g) \rightarrow 4NO_2(g) + O_2\,(g)$$

The rate of formation of $NO_2$ (g) is $2.8 \times 10^{-3}\ Ms^{-1}$. Calculate the rate of disappearance of $N_2O_5$ (g).

Q9. Draw the structures of the following: (2)

a) $XeF_4$
b) $HClO_3$

Q10. a) Arrange the following in the decreasing order of their reducing character: (2)
HF, HCl, HBr, HI
b) Complete the following reaction:
$XeF_4 + SbF_5 \rightarrow$

Q11. a) Out of Chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why? (2)
b) Convert aniline to chlorobenzene.

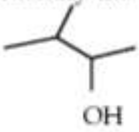
Q12. a) Write the equation involved in Reimer-Tiemann reaction. (2)
b) Ortho-nitrophenol is more acidic than ortho-methoxyphenol. Why?

Q13. An element 'X' (At mass = 40 g/mol) having f.c.c. structure, has unit cell edge length of 400 pm. Calculate the density of 'X' and the number of unit cells in 4g of 'X' ($Na = 6.023 \times 10^{23}\ mol^{-1}$) (3)

Q14. a) Analysis shows that FeO has a non-stoichiometric composition with formula $Fe_{0.95}O$. Give reason. (3)
b) What is Schottky defect?
c) What is meant by the term 'forbidden zone' in reference to band theory of solids?

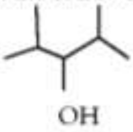
Q15. a) Calculate the freezing point of a solution containing 60g of glucose in 250g of water. (3)
(Molar mass of glucose = 180 g/mol, $k_f$ of water = 1.8k $KKgmol^{-1}$)
b) What are hypertonic solutions?

Q16. a) Identify the chiral molecule in the following pair: (3)



(i)

and



(ii)

Give reasons for your answer
b) Write the structure of the product formed when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.
c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH.

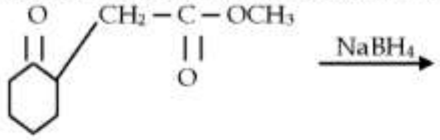
Q17. Give reasons for the following: (3)
a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macro molecules such as proteins and polymers.
b) Aquatic animals are more comfortable in cold water than in warm water.
c) Elevation of boiling point of 1M KCl solution is nearly double than that of 1M sugar solution.

Q18. A first order reaction is 50% completed in 40 minutes at 300K and in 20 minutes at 320K. Calculate the activation energy of the reaction. (3)
[Given log 2 = 0.3010, log 4 = 0.6020, R = 8.314 $JK^{-1}mol^{-1}$]

Q19. For the reaction: (3)
$2AgCl(s) + H_2(g)\,(1atm) \rightarrow 2Ag(s) + 2H^+(0.1M) + 2Cl^-(0.1M)$
Calculate the e.m.f of the cell.
[Given $\Delta G^\circ = -43600$ J at 25°C , $\log 10^{-n} = -n$]

Q20. Give reasons: (3)
a) $H_3PO_3$ undergoes disproportionation reaction but $H_3PO_4$ does not.
b) When $Cl_2$ reacts with excess $F_2$, $ClF_3$ is formed and not $FCl_3$.
c) Dioxygen is a gas while sulphur is a solid at room temperature.

Q21. Write the structures of the main products in the following reactions: (3)

i.


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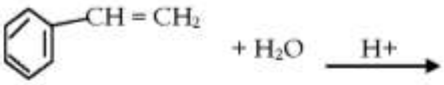
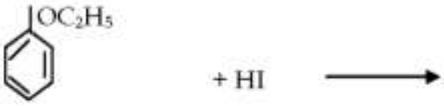


iii.


Q22. a) Compound 'A' with molecular formula $C_3H_8O$ gives positive Lucas reagent test in 5 minutes. Write the reaction for the test with the structure of 'A'. (3)
b) Convert methyl magnesium bromide to 2- Methylpropan-2-ol

Q23. a) What is denatured alcohol? (3)
b) State a test to distinguish between phenol and ethanol.
c) Arrange the following in increasing order of their boiling points: Pentan-1-ol, butan-1-ol, ethanol, propan-1-ol, methanol.

Q24. The following rate data were obtained at 303 K for the following reaction: (3)
$2A + B \rightarrow C + D$

| Experiment | [A]/mol $L^{-1}$ | [A]/mol $L^{-1}$ | Initial rate of formation of D/ mol $L^{-1}$ $min^{-1}$ |
|---|---|---|---|
| I | 0.1 | 0.1 | $6.0 \times 10^{-3}$ |
| II | 0.3 | 0.2 | $7.2 \times 10^{-2}$ |
| III | 0.3 | 0.4 | $2.88 \times 10^{-1}$ |
| IV | 0.4 | 0.1 | $2.40 \times 10^{-2}$ |

What is the rate law? What is the order with respect to each reactant and the overall order? Also calculate the rate constant and write its unit.

Q25. a) Write the cell reaction and calculate the e.m.f of the following cell at 298 K.

$Sn(s) \mid Sn^{2+}(0.004M) \parallel H^{+}(0.20M) \mid H_2(g)(1bar) \mid Pt(s)$ (5)

[Given: $E^{\circ}_{Sn^{2+}|Sn} = -0.14$ V]

b) Give reasons:

i. On the basis of E° values, $O_2$ gas should be liberated at anode but it is $Cl_2$ gas which is liberated in the electrolysis of aqueous NaCl.

ii. Conductivity of $CH_3COOH$ decreases on dilution.

Q26. a) Give mechanism for the following reaction: (5)

$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

b) Write short note on Swartz reaction.

c) Account for the following:

Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the major product.

d) What are freons? Why are they harmful?

Q27. a) When concentrated sulphuric acid was added to an unknown salt present in a tube, a brown gas (A) was evolved. This gas intensified when copper turnings were added to this test tube. On cooling, this gas (A) changed into a colourless solid (B). (5)

i. Identify (A) and (B).

ii. Write the structures of (A) and (B).

iii. Why does gas (A) change to solid on cooling?

b) Among the hydrides of group 15 elements, which have the:

i. Highest boiling point?

ii. Maximum basic character?

iii. Highest bond angle?

iv. Maximum reducing character?

**Academic Session: 2017-18**
**First Term Examination**
**Subject: Chemistry**
**M/1/1**

**Time: 3 Hours** **Max marks: 70**

General Instructions:

- All questions are compulsory.
- Question nos. 1and 5 are very short answer questions and carry 1 mark each.
- Question nos. 6 – 10 are short answer questions and carry 2 mark each.
- Question nos. 11 – 22 are also short answer questions and carry 3 mark each.
- Question no. 23 is Value based question and carry 4 marks.
- Question nos. 24 -26 are long answer question and carry 5 mark.
- Use of calculators is not permitted.
- This paper has 4 printed sides.

Q1. Define molality. (1)

Q2. Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution :- (1)

$Ag^+(aq) + e^- \rightarrow Ag(s) \quad E^\circ = 0.80\ V$

$H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g) \quad E^\circ = 0.00\ V$

On the basis of their standard reduction electrode potential ($E^\circ$) values, which reaction is feasible at the cathode and why?

Q3. According to Arrhenius, rate of reaction increases with increase in temperature. Give reasons? (1)

Q4. Write one similarity between physical adsorption and chemical adsorption. (1)

Q5. Write the structure of 1-Bromo-4-Chlorobut-2-ene. (1)

Q6. A compound forms hexagonal close packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids? (2)

**OR**

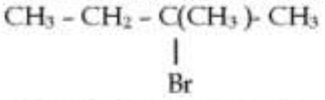
Explain the following with suitable examples:

a) 13 – 15 group compounds
b) Paramagnetism

Q7. Calculate the mass of non volatile solute (molar mass 40 g mol$^{-1}$) which should be dissolved in 114g octane ($C_8H_{18}$) to reduce its vapour pressure to 80%. (Given Atomic mass of C=12u and H=1u) (2)

Q8. The rate constant for a first order reaction is 60s$^{-1}$. How much time will it take to reduce the concentration of the reactant to 1/10th of its initial value? (2)

Q9. a) Which alkyl halide from the following pairs would you expect to react more rapidly by an $S_N1$ mechanism and why? (2)



$CH_3 - CH_2 - \underset{\displaystyle Br}{\underset{|}{C}}(CH_3) - CH_3$ ; $CH_3 - CH_2 - CH_2 - CH_2 - Br$

b) Racemisation occurs in $S_N1$ reactions. Why?

Q10. If the rate of reaction doubles up with a 10° rise in temperature from 295K to 305K, what would be the value of activation energy for this reaction? (2)
[Given $R=8.31 JK^{-1}mol^{-1}$, log2=0.3010)

Q11. a) In terms of band theory, what is the difference between a conductor and a semiconductor? (3)
b) Analysis shows that iron oxide has the formula $Fe_{0.95}O_{1.00}$. What fractions of iron exist as $Fe^{2+}$ and $Fe^{3+}$ ions?

Q12. a) Consider the cell :- (3)
$Mg(s) | Mg^{2+} (0.01\ M) || Ag^{+} (1.0 \times 10^{-4}\ M) | Ag(s)$
Its emf is 2.96 V. Calculate $E^{\circ}_{cell}$
b) Write the products of electrolysis of aq $CuSO_4$ using Cu electrodes.

Q13. a) Why is osmotic pressure considered as a colligative property? (3)
b) Determine the amount of $CaCl_2$ (i=2.47) dissolved in water to give 2.5 litre of solution such that its osmotic pressure is 0.75 atm at 27°C.
(Given: R= 0.0821 Latm/K/mol, Atomic mass of Ca=40u, Cl=35.5u)

Q14. a) Calculate the amount of sodium chloride which must be added to one kilogram of water so that the freezing point of water is depressed by 3K [Given $K_f = 1.86 K\ Kg\ mol^{-1}$, Atomic mass of Na=23u and Cl=35.5u] (3)
b) Why scuba divers carry air cylinders diluted with Helium?

Q15. How will you bring about the following conversions: (3)
a) Benzene to biphenyl
b) Toluene to benzyl alcohol
c) Propene to 1-nitropropane

Q16. The measured resistance of conductivity cell was 100 ohms. If 7.45g of KCl is dissolved per litre of solution. Calculate :- (3)
i. Conductivity
ii. Molar Conductivity
[Given Cell Constant = $1.25\ cm^{-1}$, Molar mass of KCl is 74.5 $gmol^{-1}$]

Q17. a) Give reasons for the following :- (3)
i. Out of $AlCl_3$ and NaCl, which one is more effective in causing coagulation of a negatively charged sol?
ii. What happens when a freshly precipitated $Fe(OH)_3$ is shaken with water containing a small quantity of $FeCl_3$?
b) What do you mean by activity and selectivity of catalyst?

M/1 Page **2** of Set 1

Q18. a) What happens when :- (3)
 i. $(NH_4)_2Cr_2O_7$ is heated?
 ii. $H_3PO_3$ is heated?
 b) Draw the structure of $H_2S_2O_7$.

Q19. Complete the following reactions :- (3)
 i. 2NaOH ( cold and dilute) + $Cl_2$ (excess) →
 ii. $XeF_6 + 3H_2O$ →
 iii. $2I^- + H_2O + O_3$ →

Q20. Account for the following :- (3)
 i. Bi is a strong oxidizing agent in the +5 state.
 ii. $SnCl_4$ is more covalent than $SnCl_2$.
 iii. Iron dissolves in HCl to form $FeCl_2$ and not $FeCl_3$.

Q21. a) Limiting molar conductivities of $NH_4Cl$, NaOH and NaCl are respectively 129.8, 217.4 and 108.9 S cm$^2$ mol$^{-1}$. (3)
 i. Find the limiting molar conductivity of $NH_4OH$.
 ii. Calculate degree of dissociation of $NH_4OH$ if molar conductivity of $10^{-2}$ M solution of $NH_4OH$ is 9.33 S cm$^2$ mol$^{-1}$.
 b) How much charge in terms of Faraday is required for the reduction of 1 mol of $Cu^{2+}$ to Cu?

Q22. a) Explain why Grignard reagent should be prepared under anhydrous conditions? (3)
 b) Primary alkyl halide $C_4H_9Br$ (A) reacted with alcoholic KOH to give compound (B). Compound (B) is reacted with HBr to give (C) which is an isomer of (A). When (A) is reacted with Na metal, it gives compound (D), $C_8H_{18}$ which is different from the compound formed when n-butyl is reacted with sodium. Give the structural formula of (A) and write the equations for all the reactions.

**OR**

 a) Write a short note on Sandmeyer reaction.
 b) Write the mechanism of the following reaction:

$$\text{nBuBr} + \text{KCN} \xrightarrow{\text{EtOH-H}_2\text{O}} \text{n BuCN}$$

Q23. Rama a medical practitioner, gave information to a nearby slum about Kala-azar, a disease caused by mosquito (protozoa) that results in irregular fever, enlargement of spleen and hemorrhages that are generally fatal. She asked the residents to use mosquito repellent and do not allow stagnant water in coolers, overhead tanks etc. (4)
 a) What are the values shown by Rama?
 b) Which metal colloid is used in the treatment of Kala-azar?
 c) Why colloidal medicines are more effective?
 d) Write one point of difference between lyophilic and lyophobic colloids.

Q24. a) Calculate the efficiency of packing in case of a metal crystal for face centred cubic structure. (5)

b) A compound is formed by two elements X and Y. Atoms of element Y (as anions) make ccp and those of element X (as cations) occupy half of the octahedral voids. What is the formula of the compound?

c) An element with density 10 g $cm^{-3}$ forms a cubic unit cell with edge length $3 \times 10^{-8}$ cm. What is the nature of cubic unit cell of the atomic mass of the element is 81 g $mol^{-1}$?

Q25. Consider the reaction $2A + B \rightarrow C + D$ (5)

Following results were obtained in experiments designed to study the rate of reaction :-

| Experiment | Initial conc (mol $L^{-1}$) | | Initial rate formation |
|---|---|---|---|
| | [A] | [B] | [D] (M/min) |
| 1 | 0.10 | 0.10 | $1.5 \times 10^{-3}$ |
| 2 | 0.20 | 0.20 | $3 \times 10^{-3}$ |
| 3 | 0.20 | 0.40 | $6 \times 10^{-3}$ |

a) Find order with respect to [A] and [B] and write the rate law for the reaction.

b) Calculate the value of rate constant for the reaction.

c) Which of the following possible reaction mechanism is in agreement with the rate law found above in part (a)

I. $A + B \rightarrow C + D$ (slow)
$A + E \rightarrow D$ (fast)

II. $B \rightarrow C + E$ (slow)
$A + E \rightarrow F$ (fast)
$A + F \rightarrow D$ (fast)

Q26. a) Arrange the following in the order of the property mentioned :- (5)

i. $H_2O$, $H_2S$, $H_2Se$, $H_2Te$ (increasing acid strength)
ii. HCl, HBr, HI, HF (increasing bond dissociation enthalpy)
iii. $HClO_4$, HClO, $HClO_2$ (increasing oxidizing power)

b) On heating lead(II) nitrate gives a brown gas (A). The gas (A) on cooling changes to colourless solid (B). Solid (B) on heating with NO changes to a blue solid (C). Identify (A), (B), (C) and also write the reactions involved. Also draw the structure of (B).

**Academic session- 2018-19**
**Second Term Examination**
**Subject – Chemistry**
**M/1/1**

***Time: 3 hrs*** ***Max. Marks – 70***

No. of printed pages: **5**

**General Instructions:**

(i) All questions are compulsory.
(ii) Questions nos. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Questions nos. 6 to 12 are short answer questions and carry 2 marks each.
(iv) Questions nos. 13 to 24 are also short answer questions and carry 3 marks each.
(v) Question nos. 25 to 27 are long answer questions and carry 5 marks each.
(vi) Use log tables if necessary, use of calculators is not permitted.

1 Name the linkage connecting the monosaccharide units in polysaccharides. 1

2 Write the coordination number and oxidation state of Platinum in the complex $[Pt(en)_2Cl_2]$ 1

OR

Draw the possible optical isomers of $[CrCl_2(en)(NH_3)_2]^+$

3 What are thermoplastic and thermosetting polymers? 1

4 Complete the reaction: 1

$$C_6H_5N_2^+Cl \xrightarrow{CH_3CH_2OH}$$

5 Which forces are involved in holding the drug to the active site of the enzymes? 1

6 (i) CO(g) and $H_2$(g) react to give different products in the presence of different catalysts. Which ability of catalyst is shown in these reactions? 2
(ii) Draw and write the expression of Freundlich adsorption isotherm.

7 Complete and balance the following equations: 2

(i) $Fe^{2+} + MnO_4^- + H^+ \rightarrow$

(ii) $MnO_4^- + H_2O + I^- \rightarrow$

8 $CoSO_4Cl.5NH_3$ exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer 'B' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$. Answer the following questions: 2

(i) Identify 'A' and 'B' and write their structural formulae.
(ii) Name the type of isomerism involved.

OR

$FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives a test of $Fe^{2+}$ but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give a test of $Cu^{2+}$ ion. Explain why?

9. (i) Write the IUPAC name of the following complex: $[Co(NH_3)_5(CO_3)]NO_3$. 2
(ii) Write the formula of the following coordination compound:
Iron(III)hexacyanoferrate(II).

10. Describe the role of 2
(i) Cryolite in extraction of Aluminum from its ore.
(ii) Flux in metallurgy of iron.

11. How will you prepare 2
(i) $K_2MnO_4$ from $MnO_2$
(ii) $Na_2Cr_2O_7$ from $Na_2CrO_4$?
Write balanced chemical equations.

12. Describe how the following changes are brought about: 2
(i) Zinc oxide into metallic Zinc.
(ii) Impure Ti into pure Ti.
(i) Separate two sulphide ores by froth floatation process
(ii) Pig iron into steel.

13. (A), (B) and (C) are three non-cyclic isomers of a carbonyl compound with molecular formula $C_4H_8O$. Isomers (A) and (C) give positive Tollen's test whereas isomer (B) does not give Tollen's test but gives positive Iodoform test. Isomers (A) and (B) on reduction with Zn(Hg)/conc.HCl gives the same product D. 3
(i) Write the structures of (A), (B), (C) and (D).
(ii) Out of (A), (B) and (C) isomers, which one is most reactive towards addition of $NaHSO_3$ and why?

14. Write the chemical reactions involved in the process of extraction of gold. Explain the role of dilute NaCN and Zn in this process. 3

15. (i) Write one structural difference between low density polythene and high density polythene. 3
(ii) What is a biodegradable polymer? Give an example.
(iii) Arrange the following in increasing order of intermolecular forces:
Nylon6 , Neoprene, Polyvinyl chloride

16. (i) Why is bithional added to soap? 3
(ii) What is tincture of iodine? Write its one use.
(iii) Among the following, which one acts as a food preservative?
Aspartame, Aspirin, Sodium Benzoate, Paracetamol

17. Define the following and give one example : 3
(i) Anionic detergents
(ii) Antimicrobials
(iii) Antioxidants

18. (i) Write the structures of the monomer and one use of the following polymers: 3
Nylon 6 and Polypropene
(ii) Write the structures of the monomers used for getting the polymers:
Melamine – formaldehyde polymer

19. Define the following with an example of each; 3
(i) Polysaccharides
(ii) Denatured proteins
(iii) Essential aminoacids

OR

(i) Write the product when D- Glucose reacts with bromine water.
(ii) Amino acids show amphoteric behaviour. Why?
(iii) Write one difference between α-helix and β-pleated structures of proteins.

20. What happens when 3
(i) a freshly prepared precipitate of $Fe(OH)_3$ is shaken with a small amount of $FeCl_3$ solution?
(ii) persistent dialysis of a colloidal solution is carried out?
(iii) size of dispersed phase changes in gold sol.

21. (i) What is the difference between a nucleotide and nucleoside? Mention two important functions of nucleic acids. 3
(ii) What is the deficiency disease caused by Vitamin A. Mention important sources of this vitamin.

22. (i) Why does acetylation of aniline reduce its activating effect? 3
(ii) Although amino group is o, p- directing in aromatic substitution reactions, aniline on nitration gives substantial amount of m- nitro aniline. Why?
(iii) Account for: $(CH_3)_2NH$ is more basic than $(CH_3)_3N$.

23. (i) Arrange in increasing order of boiling point: $C_2H_5OH$, $(CH_3)_2NH$, $C_2H_5NH_2$. 3
(ii) Draw structures of any two different isomers corresponding to the molecular formula $C_3H_9N$. Write the IUPAC names of the isomers. Will any of these isomers liberate nitrogen gas on treatment with nitrous acid?

M/1 Page 3 of set 1

24. (i) Why is adsorption process always exothermic? 3
(ii) What are shape selective catalysts? Give example.
(iii) What are the physical states of dispersed phase and dispersion medium in froth?

25. Give reason: 5
(i) $E^0$value for the $Mn^{3+}/Mn^{2+}$ couple is highly positive as compared to $Fe^{3+}/Fe^{2+}$.
(ii) Iron has high enthalpy of atomization than that of copper.
(iii)$Sc^{3+}$ is colourless in aqueous solution whereas $Ti^{3+}$ is coloured.
(iv) Actinoid contration is greater from element to element than lanthanoid contraction.
(v) $Cu^+$ ion is not stable in aqueous solution.

OR

Suggest reasons for the following:
(i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.
(iii) Transition metal forms interstitial compounds.
(iv) Of the $d^4$ species, $Cr^{2+}$ is strongly reducing while manganese(III) is strongly oxidising.
(v) Transition metals act as good catalysts.

26. (i) The hexaaquomangnese(II) ion contains 5 unpaired electrons while the hexacyanoion contains only one unpaired electron. Explain using crystal field theory in terms of $t_{2g}$ and $e_g$ configuration. 5
(ii) $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Explain using Valence bond theory.

OR

(i) A metal ion $M^{n+}$ having $d^4$ valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $\Delta o > P$
a) Write the electronic configuration of the valence electrons of the metal $M^{n+}$ ion in terms of $t_{2g}$ and $e_g$.
b) What type of hybridization will $M^{n+}$ ion have? Name the type of isomerism exhibited by this complex.
(ii) Write the hybridization and number of unpaired electrons in the complex $[CoF_6]^{3-}$

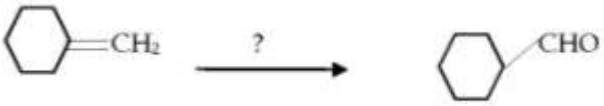
27. (i) Draw the structure of semicarbazone of cyclobutanone. 5
(ii) Two moles of organic compound 'A' on treatment with a strong base gives two compounds 'B' and 'C'. Compound B on hydrogenation with Cu at 573K gives back 'A' while acidification of 'C' yields carboxylic acid 'D' having the formula of $CH_2O_2$. Identify the compound 'A', 'B','C' and 'D'.
(iii) Give chemical test to distinguish between : Ethanal and Propanone.
(iv) Convert : Ethanal to But-2-enoic acid .

OR

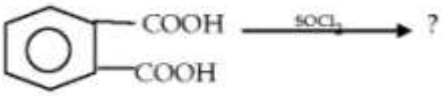
Complete each synthesis by giving missing reagents or products:

(i)

(ii)



(iii)



(iv) $C_6H_5CHO + CH_3CH_2CH_2CHO \xrightarrow{\text{Dil. NaOH}}$

(v) $CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4}$

## Academic session- 2017-18
## Second Term Examination
## Subject – Chemistry
## M/1/2

*Time: 3 hrs* *Max. Marks – 70*

No. of printed pages: **4**

**General Instructions:**

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

1 A coordination compound with molecular formula $CrCl_3.4H_2O$ forms a precipitate of 1 mole of AgCl with $AgNO_3$ solution. Its molar conductivity is found to be equivalent to two ions. What is the structural formula of the compound? 1

2 Write IUPAC name of the following compound : $(CH_3CH_2)_2NCH_3$ 1

3 Out of C and CO, which is a better reducing agent for ZnO? 1

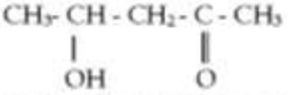
4 Concentrated nitric acid forms an oxide of nitrogen on reaction with $P_4$. Write the formula of the stable molecule formed when the oxide undergoes dimerization. 1

5 Arrange the following in increasing order of intermolecular forces. 1
Nylon 6 , Neoprene, Polyvinyl chloride.

6 (a) Describe the role of depressants in froth floatation process. 2
(b) Out of PbS and $PbCO_3$ (ores of lead), which one is concentrated by froth floatation process preferably and why?

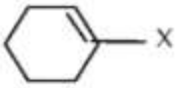
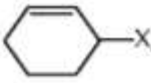
7 (i) How will you prepare $KMnO_4$ from pyrolusite ore? Write equation. 2
(ii) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali. Why?

8 (i) Write the IUPAC name of 2



$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$$

(ii) Write chemical equations to illustrate: Clemmensen reduction.

9 (i) Out of  and , which is an example of allylic halide? 2

(ii) Which of these two compounds would react with NaOH easily and give a positive test with $AgNO_3$ ? Comment.

10 Distinguish between homopolymer and copolymer? Write the name of the monomer/monomers of the polymer $(\text{-NH-}(CH_2)_6\text{-NH-CO-}(CH_2)_4\text{-CO-})_n$? 2

11. (i) A metal ion $M^{n+}$ having $d^4$ valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $\Delta o < P$ 3

a) Write the electronic configuration of the valence electrons of the metal $M^{n+}$ ion in terms of $t_{2g}$ and $e_g$ .

b) Name the type of isomerism exhibited by this complex.

(ii) Find the number of unpaired electrons in $[FeF_6]^{2-}$ which is a paramagnetic complex ion. Also predict the hybridization and shape of the ion. (At. no. of Fe = 26)

12. (i) Write the name and principle of method used for the refining of germanium. 3

(ii) Describe the role of Silica in metallurgy of copper from copper matte?

(iii) What is the significance of leaching in the extraction of aluminium ?

13. (i) Write IUPAC name of the product formed when 3

a) 2-Methyl-1-bromopropane is treated with sodium in the presence of dry ether.

b) 1-Methylcyclohexene is treated with HI.

(ii) Of the following compounds given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane:

a) Which compound is more reactive towards $S_N2$ reaction?

b) Which compound is optically active?

14. (i) What type of isomerism is shown by the complex $[Co(NH_3)_6]\,[Cr(CN)_6]$ ? Write the structure of the isomer. 3

(ii) Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless? (At. no. of Ni = 28)

(iii) Write the IUPAC name of the following complex: $[Co(NH_3)_5(CO_3)]Cl$.

15. (i) What is the difference between a nucleotide and nucleoside? Mention two important functions of nucleic acids. 3

(ii) What happens when D-glucose is treated with bromine water?

16. Define the following and give one example : 3

(i) Anionic detergents

(ii) Broad spectrum antibiotics

(iii)Antiseptics

17. (i) Explain the role of allosteric site in drug-enzyme interaction? 3

(ii) What problem arises in using alitame as artificial sweetener?

(iii) Low level of noradrenaline is the cause of depression. What type of drugs is needed to cure this problem? Give an example.

18. Write the structures of the monomers used for getting the following polymers : 3

(i) Dacron

(ii) Melamine – formaldehyde polymer

(iii) Buna-S

19. (i) Convert: 3

(a) Aniline to p-Bromoaniline.

(b) 4-Nitrotoluene to 2-Bromobenzoic acid.

(ii) Arrange in decreasing order of pKb values:

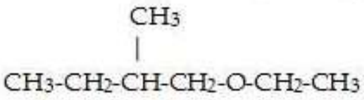
$CH_3NH_2$, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$

20. (i) Why phenol has lower dipole moment than methanol? 3

(ii) Arrange in increasing order of their boiling point:

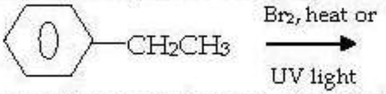
Pentan-1-ol, n-Butane, Pentanal, Ethoxyethane, Pentan-2-ol

(iii) Give major products that are formed by heating the following ether with HI:



$CH_3\text{-}CH_2\text{-}\underset{}{\overset{CH_3}{\overset{|}{C}H}}\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$

21. (i) Predict the major monobromo product of the reaction: 3



(ii) How will you synthesise 1-Phenylethanol from a suitable alkene in one step?

(iii) Write the mechanism (using curved arrow notation) of the following reaction:

$$CH_2 = CH_2 \xrightarrow{H_3O^+} CH_3CH_2^+$$

22. (i) Give one chemical test to distinguish between Benzylamine and Aniline. 3

(ii) Complete the reaction: $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(iii) An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with $Br_2$ and KOH forms a compound 'C' of molecular formula $C_6H_7N$. Write the structures and IUPAC names of the compounds A, B and C.

23. After watching a programme on TV about the presence of carcinogens(cancer causing agents) Potassium bromate and Potassium iodate in bread and other bakery products, Ritu a class XII student decided to aware others about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct canteen contractor to stop selling sandwiches, pizza, burgers and other bakery products to the students. Principal took an immediate action and instructed the canteen contractor to replace the bakery products with some proteins and vitamins rich food like fruits, salads, sprouts etc. The decision was welcomed by the parents 4

and students.

After reading the above passage, answer the following questions :

(i) What are the values (at least two) displayed by Ritu ?

(ii) Which polysaccharide is commonly present in bread? Why sucrose is also called invert sugar?

(iii) Name the two types of secondary structure of proteins.

(iv) Give two examples of water soluble vitamins.

24. (i) Account for the following : 5

(a) Transition metals form large number of coloured compounds.

(b) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.

(c) $E^0$value for the $Mn^{3+}/Mn^{2+}$ couple is highly positive (+1.57 V) as compared to $Fe^{3+}/Fe^{2+}$ .

(ii) Chemistry of Actinoids is complicated as compared to Lanthanoids. Explain.

(iii) Out of $Cu^+$ and $Cu^{2+}$, which is unstable in solution and why?

25. (i) Give reason: 5

(a) Fluorine never acts as a central atom in polyatomic interhalogen compounds.

(b) Chlorine water has both oxidising and bleaching properties.

(c) $SF_4$ is easily hydrolysed whereas $SF_6$ is not easily hydrolysed.

(ii) Complete the reaction:

(a) $XeF_4 + H_2O \rightarrow$

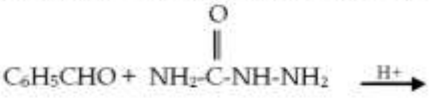
(b) $Cu^{2+} + NH_3 \rightarrow$

26. (i) Arrange in increasing order of their reactivity in nucleophilic addition reactions: 5
Acetaldehyde, Acetone, Di-*tert*-butyl ketone, Methyl *tert*-butyl ketone.

(ii) An organic compound with the formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound. Draw the structure and write the IUPAC name of the compound.

(iii)Write chemical test to distinguish between: Ethanal and Propanone.

(iv) Complete the reaction:



$$C_6H_5CHO + NH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}NH_2 \xrightarrow{H^+}$$

# Academic Session- 2018-19
# Preboard Examination
# Subject – Chemistry
# M/1/1

*Time: 3 hrs* *Max. Marks – 70*

No. of printed pages: **7**

## General Instructions:

(a) All questions are compulsory.
(b) Section A: Q. nos. 1 to 5 are very short answer questions and carry 1 mark each.
(c) Section B: Q. nos. 6 to 12 are short answer questions and carry 2 marks each.
(d) Section C: Q. nos. 13 to 24 are also short answer questions and carry 3 marks each.
(e) Section D: Q. nos. 25 to 27 are long answer questions and carry 5 marks each.
(f) There is no overall choice. However an internal choice has been provided in two questions of one mark, two questions of two marks, four questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.
(g) Use log tables if necessary, use of calculators is not allowed.

## Section- A

1 Analysis shows that FeO has a non-stoichiometric composition with formula $Fe_{0.95}O$. Give reason. 1

OR

The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have coordination number of eight. What is the type of crystal lattice?

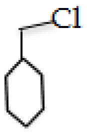
2 What is the reason for stability of lyophilic sols? 1

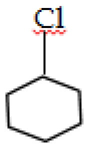
3 What type of isomers are $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$. 1

OR

Write the structures of geometrical isomers of complex ion $[Co(en)_2Cl_2]^+$.

4 In the following pairs of halogen compounds, which would undergo $S_N2$ reaction faster? Explain. 1





5 Identify the monomers in the following polymer: 1

$-[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO-]_n$

## Section – B

6 The rate constant for a first order reaction is 60 $s^{-1}$. How much time will it take to reduce 1 g of the reactant to 0.625 g? (log 1.6 = 0.204) 2

7 Draw the molecular structures of the following : 2

(a) Noble gas species which is isostructural with $BrO_3^{-}$.

(b) Dibasic oxoacid of phosphorus.

8 Calculate the freezing point of a solution containing 8.1 g of HBr in 100 g of water, assuming the acid to be 90% ionized. [ Given : Molar mass HBr = 81 g/mol, $K_f$ water = 1.86 K Kg/mol] 2

OR

Calculate the molality of ethanol solution in which the mole fraction of water is 0.88.

9. (a) Arrange the following in increasing order of Acidic character: 2

$MnO_2$, $Mn_2O_3$, MnO

(b) What happens when $KMnO_4$ is heated? Give chemical equation.

10. Explain the mechanism of the following reaction: 2

$$2C_2H_5OH \xrightarrow[413\ K]{conc\ H_2SO_4} C_2H_5OC_2H_5$$

11. How will you bring about the following conversions? 2

(a) Propanone to propane

(b) Ethanal to but-2-enal

OR

Give simple chemical tests to distinguish between the following pairs of compounds:

(a) Ethanal and Propanal

(b) Benzoic acid and Phenol

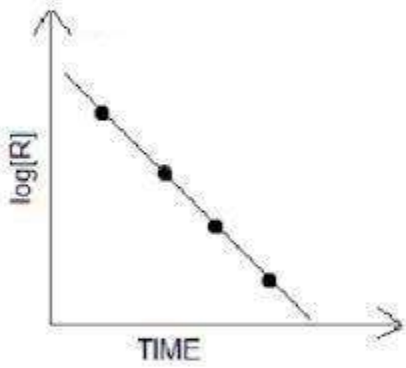
12. Name the type of polymerization involved in the formation of the following polymers from their respective monomers. Draw the structure of the polymer. 2

(i)PVC

(ii) Nylon 6

Section- C

13. Observe the graph in diagram and answer the following questions 3



(a) What is the order of the reaction?
(b) If slope is equal to $-2.0 \times 10^{-6}$ sec $^{-1}$, what will be the value of rate constant?
(c) Give the relationship between half life and its rate constant?

OR

For a certain chemical reaction

$A + 2B \longrightarrow 2C + D$

The experimentally obtained information is tabulated below.

| Experiment | $[A]_o$ Moles/ L | $[B]_o$ Moles/L | Initial Rate of reaction Moles/L/s |
|---|---|---|---|
| 1 | 0.30 | 0.30 | 0.096 |
| 2 | 0.60 | 0.30 | 0.384 |
| 3 | 0.30 | 0.60 | 0.192 |
| 4 | 0.60 | 0.60 | 0.768 |

For this reaction
(a) Derive the order of reaction w.r.t both the reactants A and B.
(b) Write the rate law.

14. Give a reason for the following: 3
(a) Rough surface of catalyst is more effective than smooth surface.
(b) Smoke passed through charged plates before allowing it to come out of chimneys in factories.
(c) Ne gets easily adsorbed over charcoal than He.

15. Niobium crystallises in body-centred cubic structure. If the atomic radius is 143.1 pm, calculate the density of Niobium. (Atomic mass of Niobium = 93 u). 3

16 (a) What process takes place when fruits are preserved by adding concentrated sugar solution to protect against bacterial action. 3
(b) Give Reasons:
(i) When 2 g of benzoic acid is dissolved in 25 g of benzene , the experimentally determined molar mass is always greater than the true value.
(ii) Mixture of chloroform and acetone shows negative deviation from Raoult's Law.

17. Account for the following facts: 3
(a) The reduction of a metal oxide is easier if the metal formed is in the liquid state at the temperature of reduction.
(b) Limestone is used in the manufacture of pig iron from haematite.
(c) Pine oil is used in the froth floatation process used to concentrate sulphide ores.

OR

Describe how the following steps can be carried out?
(a) Recovery of Gold from leached gold metal complex.

(b) Conversion of Zirconium iodide to pure Zirconium,
(c) Formation of slag in the extraction of copper.
(Write the chemical equations also for the reactions involved)

18. (a) $Mn^{2+}$ compounds are more stable than $Fe^{2+}$ towards oxidation to +3 state. 3
(b) In 5d-transition series, which element is not regarded as transition metal and why?
(c) Which bivalent cation in 3d-transition series is most paramagnetic and why?

19. (a) Write IUPAC name of $[Co(en)_3][Cr(C_2O_4)_3]$. 3
(b) Discuss the hybridization, shape and magnetic behaviour of $[Mn(CN)_6]^{4-}$.
( Atomic number of Mn = 25)

20. Give reasons: 3
(a) C-Cl bond length in chlorobenzene is shorter than C-Cl bond length in $CH_3$-Cl.
(b) Grignard reagent is kept under anhydrous conditions.
(c) $S_N1$ reactions are accompanied by racemisation in optically active alkyl halide.

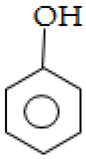
OR

Give reasons:
(a) n-Butyl bromide has higher boiling point than t- butyl bromide.
(b) Racemic mixture is optically inactive.
(c) The presence of nitro group ($-NO_2$) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

21. Complete the following equations: 3

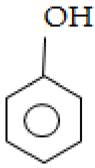
(a) $(CH_3)_3C\text{-}O\text{-}C_2H_5 + HI \longrightarrow$

(b)



$+ \ Br_2(aq) \longrightarrow$

(c)



$+ \ CH_3COCl \xrightarrow{NaOH}$

22. Complete the following reactions: 3

(a) $HC{\equiv}CH + H_2O \xrightarrow[333\ K]{Hg^{2+},\ H_2SO_4}$

(b) $C_6H_5\text{-}CO\text{-}Cl + H_2 \xrightarrow[S]{Pd\text{-}BaSO4}$

(c) $CH_3\text{-}CO\text{-}CH_3 + C_6H_5NHNH_2 \longrightarrow$

23. (a) Give one example of reducing sugar and one example of non-reducing sugar. 3
(b) Give two differences between RNA and DNA.

OR

(a) Which of the following biomolecule is insoluble in water? Justify.
Insulin, Haemoglobin , Keratin
(b) Draw the Haworth structure for α-D-Glucopyranose.
(c) Write chemical reaction to show that glucose contains aldehyde as carbonyl group.

24. Explain the following terms with one suitable example for each: 3
(a) A sweetening agent for diabetic patients
(b) Enzymes
(c) Analgesics

## Section- D

25. (a) Given are the conductivities and molar conductivities of NaCl solutions at 298 K at different concentrations: 5

| Concentration, M | Conductivity, $Scm^{-1}$ | Molar Conductivity $S\ cm^2\ mol^{-1}$ |
|---|---|---|
| 0.100 | $106.74 \times 10^{-4}$ | 106.7 |
| 0.05 | $55.53 \times 10^{-4}$ | 111.1 |
| 0.02 | $23.15 \times 10^{-4}$ | 115.8 |

Compare the variation of conductivity and molar conductivity of NaCl on dilution. Give reason.

(b) Silver is electrodeposited on a metallic vessel of total surface area 900 $cm^2$ by passing a current of 0.5 A for two hours. Calculate the thickness of silver deposited. [Given: density of Ag = 10.5 $gcm^{-3}$, Atomic mass of Ag = 108 u, 1F= 96500 C/mol]

OR

(a) On the basis of the standard reduction potential values for following solution, predict whether $Ti^{4+}$ species may be used to oxidise $Fe^{2+}$ to $Fe^{3+}$.

$Ti^{4+} + e^- \longrightarrow Ti^{3+};\ E^o = +0.01\ V$

$Fe^{3+} + e^- \longrightarrow Fe^{2+};\ E^o = +0.77\ V$

(b) Why is rusting of iron quicker in saline water than in ordinary water?
(c) A copper-silver cell is set up. The copper ion concentration in it is 0.10 M. The conc. of $Ag^+$ is not known. The cell potential measured is 0.422 V. Determine log $[Ag^+]$. [$E^o_{Ag^+/Ag}$ = +0.80 V, $E^o_{Cu^{2+}/Cu}$ = +0.34 V]

26. (a) Write down the equations for hydrolysis of $XeF_4$ and $XeF_6$. Which of these two reactions is a Redox reaction? 5
(b) Account for the following:
    (i) $F_2$ is strongest oxidising agent among halogens.

(ii) Fluorine exhibits only -1 oxidation state whereas other halogens exhibit higher +ve oxidation state.
(iii) Acidity of oxoacid of chlorine is $HOCl < HOClO < HOClO_2 < HOClO_3$

OR

(a) Why does chlorine water lose its yellow colour on standing? How chlorine water has both oxidising and bleaching properties. Give reason
(b) What happens when $Cl_2$ reacts with cold dilute solution of sodium hydroxide? Write equations only.
(c) Account for the following:
    (i) $H_3PO_2$ and $H_3PO_3$ act as good reducing agents while $H_3PO_4$ does not.
    (ii) ICl is more reactive than $I_2$

27 An aromatic compound 'A' of molecular formula $C_7H_7ON$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions:

$$\begin{tikzcd}
\underset{(C_7H_7ON)}{A} \arrow[r, "Br_2 + KOH"] & C_6H_5NH_2 \arrow[r, "NaNO_2 + HCl"] \arrow[d, "CHCl_3 + KOH"] & B \arrow[r, "CH_3CH_2OH"] \arrow[d, "KI"] & C \\
& D & E &
\end{tikzcd}$$

OR

(a) Write the structures of main products when aniline reacts with the following reagents:
    (i) $Br_2$ Water
    (ii) HCl
    (iii) $(CH_3CO)_2O$/pyridine
(b) Arrange the following in the increasing order of their boiling point:
    $C_2H_5NH_2$, $C_2H_5OH$, $(CH_3)_3N$
(c) Give a simple chemical test to distinguish between the following pair of compounds:
    $(CH_3)_2NH$ and $(CH_3)_3N$

**Academic Session: 2017-18**
**Pre Board Examination**
**Subject: Chemistry**
**M/1/1**

**Time : 3 Hrs** **Max marks : 70**

General Instructions:

- **All** questions are compulsory.
- Question nos. 1 – 5 are very short answer questions and carry 1 mark each.
- Question nos. 6 – 10 are short answer questions and carry 2 mark each.
- Question nos.11 – 22 are also short answer questions and carry 3 mark each.
- Question no. 23 is a value based question and carry 4 marks.
- Question nos.24 – 26 are long answer questions and carry 5 mark each.
- Use log tables, if necessary. Use of calculators is not allowed.
- This paper has 5 printed sides.

Q1. In the Arrhenius equation, what does the factor $e^{-Ea/RT}$ corresponds to ? (1)

Q2. Write Reimer -Tiemann reaction. (1)

Q3. What happens when Phenol is treated with $Br_2$ in carbon disulphide as medium. (1)

Q4. Give the structure and IUPAC names of the product expected from the catalytic reduction of butanal. (1)

Q5. Name the reagent used in dehydrogenation of benzyl alcohol to benzaldehyde. (1)

Q6. Complete the following reactions: (2)

(a) $Ca_3P_2 + H_2O \longrightarrow$
(b) $P_4 + KOH + H_2O \longrightarrow$

Q7. Which of the following solutions has higher freezing point? (2)

0.05 M $Al_2(SO_4)_3$ , 0.1 M $K_3[Fe(CN)_6]$. Justify.

Q8. Calculate the emf of the following cell at 298 K: (2)

$Cr(s) \mid Cr^{3+}(0.1M) \parallel Fe^{2+}(0.01\ M) \mid Fe(s)$

[given: $E^0_{cell} = +0.30V$]

**OR**

The conductivity of $10^{-3}$mol/L acetic acid at $25^0$C is 4.1 x $10^{-5}$ S $cm^{-1}$. Calculate its degree of dissociation, if $\Lambda^0_m$ for acetic acid at $25^0$C is390.5 S $cm^2mol^{-1}$.

Q9. Give reason: (2)
(i) $(CH_3)_3N$ is less basic than $(CH_3)_2NH$.
(ii) $C_2H_5NH_2$ has lower boiling point than $C_2H_5OH$.

Q10. (i) Give the Haworth projection of α- D(+)glucopyranose. (2)
(ii) Glucose is oxidized and a dicarboxylic acid is obtained. Write the relevant equation and name the acid formed.

Q11. The freezing point of benzene decreases by 2.12 K when 2.5 g of benzoic acid ($C_6H_5COOH$) is dissolved in 25 g of benzene. If benzoic acid forms a dimer in benzene, calculate the van't Hoff factor and the percentage association of benzoic acid ($K_f$ for benzene = 5.12 K kg $mol^{-1}$) (3)

Q12. (i) What are the linkages present in polynucleotide chain. (3)
(ii) Name a heterocyclic base present in RNA but not in DNA.
(iii) What are essential amino acids? Give one example.

Q13. Starting from elemental sulphur , how would you prepare $H_2SO_4$? Draw the structure of Sulphuric acid and predict its basicity. (3)

**OR**

Write equations for the preparation of Nitric acid by Ostwald process? Draw the structure of Nitric acid and predict its basicity.

Q14. The rate constant for a first order reaction is 60 $s^{-1}$. How much time will it take to reduce 1 g of the reactant to 0.0625 g? [ log 16 = 1.204] (3)

Q15. (i) Name and draw the monomer of Nylon-6. (3)
(ii) What are biodegradable polymers? Give one example of polyamide which is biodegradable.
(iii) Give one use of ethylene glycol in the manufacture of polymers.

Q16. (i)Solutions of two electrolytes 'A' and 'B' are diluted. The limiting molar conductivity of ' B' increases 1.5 times while that of 'A' increases 25 times. Which of the two is a strong electrolyte? Justify your answer. (3)
(ii) The products of electrolysis of aqueous NaCl at the respective electrolytes are: Cathode : $H_2$; Anode : $Cl_2$ and not $O_2$. Explain ca

Q17. (i) What type of detergents create water pollution. (3)
(ii) What is antifertility drug. Give one example.
(i) What is the cause of feeling of depression in human beings. Name the class of drugs used for treating depression.

Q18. (i) Which type of isomerism is shown by [ $Cr(H_2O)_6]Cl_3$, $[CrCl(H_2O)_5]Cl_2.H_2O$, $[CrCl_2(H_2O)_4]Cl.2H_2O$? (3)

(ii) Why is $[Co(en)_3]^{3+}$ more stable than $[Co(NH_3)_6]^{3+}$?
(iii) How many unpaired electrons are present in $[CoF_6]^{3-}$.
(Atomic number of Co is 27).

Q19. (i) Write the principle for the refining of Germanium. (3)
(ii) What happens when silver ore is treated with sodium cyanide? Write the chemical reaction involved.
(iii) Can Magnesium be used as a reducing agent for extracting Aluminium from Alumina at all temperatures. Why/ Why not?

Q20. Give reasons for the following: (3)
(i) Acidic character increases from $H_2O$ to $H_2Te$
(ii) Oxygen does not form $OF_6$ whereas sulphur forms $SF_6$.
(iii) Fluorine does not show higher positive oxidation state.

Q21. Write the structures of compounds A, B, C in the following reaction: (3)

(i) $C_6H_5COOH \xrightarrow{\text{NH3 , }\Delta} A \xrightarrow{\text{Br2/KOH(aq)}} B \xrightarrow[\text{0-5C}]{\text{NaNO2/HCl}} C$

(ii) $C_6H_5N_2^+BF_4^- \xrightarrow{\text{Cu/NaNO2}} A \xrightarrow{\text{Sn/HCl}} B \xrightarrow{\text{Br2(aq)}} C$

Q22. (i) Write the reaction between $3^0$ haloalkanes containing assymetric carbon with methyl amine. Will it form optically active or inactive product. (3)
(ii) Give a chemical reaction to illustrate Williamson Synthesis to prepare aromatic ether.

Q23. It was observed that due to rising air pollution in Delhi , when the AQI levels reached the level of 1000, every individual got concerned to protect themselves. Through the day smog could be seen all over. Air was also filled with poisonous gases. People adopted to various means to breath in pure air. Sujata, who is a class 12 science student , advised the family to plant various forms of plants , use nasal masks, and put air purifiers. Curious brother asked his sister Sujata, what is contained in air purifier? Sujata said it contains filters and adsorbents, that helps to clean the air. (4)
(i) What kind of colloid is smog? Name the dispersed phase and dispersion medium.
(ii) Majority of the particulate matter is filtered at the initial stage of filters in the air purifier , what is then the role of adsorbents. Name one adsorbent.
(iii)What values are discharged by Sujata.

Q24. (i) Following is the schematic alignment of magnetic moments : (5)

⇧ ⇧ ⇩ ⇧ ⇩ ⇧

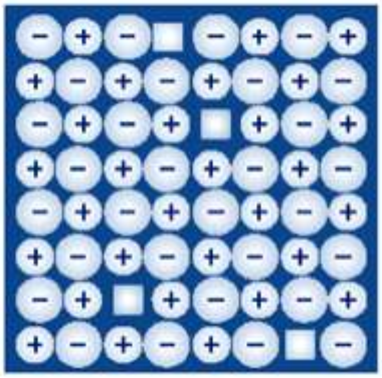
Identify the type of magnetism. What happens when these substances are heated?

(ii) If the radius of the octahedral void is 'r' and radius of the atoms in close packing is' R'. What is the relation between 'r' and ' R'?

(iii) Tungsten crystallizes in body centred cubic unit cell. If the edge of the unit cell is 316.5 pm. What is the radius of tungsten atom?

**OR**

(i) Identify the type of defect shown in the following figure:



What type of substances show this defect?

(ii) A metal crystallizes in a body centred cubic structure . If 'a' is the edge length of its unit cell, 'r' is the radius of the sphere. What is the relationship between 'r' and 'a'?

(iii) An element with molar mass 63 g/mol forms a cubic unit cell with edge length of 360.8 pm. If its density is 8.92 g/cm$^3$. What is the nature of the cubic unit cell?

Q25. (i) Identify the Oxoanion of chromium which is stable in acidic medium. (5)

(ii) What happens when potassium permanganate is heated. Write the equation for the same.

(iii) The magnetic moments of few transition metal ions are given below:

| | Metal ion | Magnetic moment (BM) |
|---|---|---|
| a) | $Sc^{3+}$ | 0.00 |
| b) | $Cr^{3+}$ | 4.90 |
| c) | $Ni^{2+}$ | 2.84 |
| d) | $Ti^{3+}$ | 1.73 |

(at.no. Sc=21, Ti =22, Cr =24, Ni =28)

Which of the given metal ions:

a. has the maximum number of unpaired electrons?
b. forms colourless aqueous solution?
c. exhibits the most stable +3 oxidation state?

**OR**

(i) Write the reaction between dichromate ion and iodide ion in acidic medium.

(ii) The lanthanoid element that exhibits +4 oxidation state.

(iii) Consider the standard electrode potential values ($M^{2+}/M$) of the elements of the first transition series.

| Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|
| -1.63 | -1.18 | -0.90 | -1.18 | -0.44 | -0.28 | -0.25 | +0.34 | -0.76 |

Explain:

(a) $E^0$ value for copper is positive.
(b) $E^0$ value of Mn is more negative as expected from the trend.
(c) $Cr^{2+}$ is a stronger reducing agent than $Fe^{2+}$.

Q26. (i) Complete the following reactions: (5)

(a) $CH_3COOH \xrightarrow{P2O5,\ heat}$
(b) $C_6H_5COOH + Br_2 \xrightarrow{FeBr3}$

(ii) Write the structural formulae and names of all four possible aldol condensation products from ethanal and propanal.

(iii) What is the use of formalin?

**OR**

(i) Distinguish between following pairs of compound by suitable chemical test:

(a) Benzoic acid and Propanol
(b) Formaldehyde and Acetaldehyde

(ii) Convert :

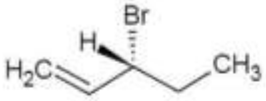
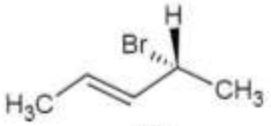
(a) Benzene to m-nitrobenzoic acid
(b) Benzaldehyde to Phenyl acetic acid
(c) Toluene and Methylbenzoate

**Class XII**
**Chemistry (Code – 043)**
**Sample Question Paper 2018-19**

**Time allowed: 3 Hours** **Max. Marks: 70**

**General Instructions:**

*(a) All questions are compulsory.*
*(b) Section A: Q.no. 1 to 5 are very short answer questions and carry 1 mark each.*
*(c) Section B: Q.no. 6 to 12 are short answer questions and carry 2 marks each.*
*(d) Section C: Q.no. 13 to 24 are also short answer questions and carry 3 marks each.*
*(e) Section D: Q.no. 25 to 27 are long answer questions and carry 5 marks each.*
*(f) There is no overall choice. However an internal choice has been provided in two questions of one mark, two questions of two marks, four questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.*
*(g) Use of log tables if necessary, use of calculators is not allowed.*

| | **Section-A** | |
|---|---|---|
| **1.** | ZnO crystal on heating acquires the formula Zn$_{1+x}$O. Give reason. | **1** |
| | OR | |
| | There is an increase in conductivity when Silicon is doped with Phosphorous. Give reason | |
| **2.** | Based on the type of dispersed phase, what type of colloids are micelles? | **1** |
| **3.** | On the basis of crystal field theory, write the electronic configuration of d$^6$ in terms of $t_{2g}$ and $e_g$ in an octahedral field when $\Delta_o < P$. | **1** |
| | OR | |
| | Low spin configuration are rarely observed in tetrahedral coordination entity formation. Explain | |
| **4.** | Identify the compound that on hydrogenation produces an optically active compound from the following compounds:<br><br> <br>(A)<br><br> <br>(B) | **1** |
| **5.** | Write the name of the biodegradable polymer used in orthopaedic devices. | **1** |

## Section-B

**6.** Calculate the freezing point of a solution containing 8.1 g of HBr in 100 g of water, assuming the acid to be 90 % ionized.
[Given: Molar mass Br = 80 g/mol, $K_f$ water = 1.86 K kg / mol] **2**

OR

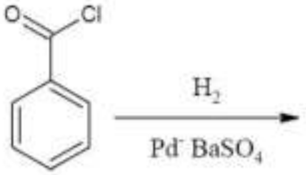
Calculate the molality of ethanol solution in which the mole fraction of water is 0.88.

**7.** Identify the reaction and write the IUPAC name of the product formed: **2**

(a)

$$CH_3\text{-}CH_2\text{-}COOH \xrightarrow{\text{(i) } Br_2 \text{ / Red phosphorous}}$$

(b)

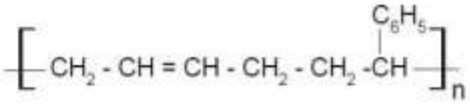


OR

Write the structures and IUPAC names of the cross aldol condensation products only of ethanal and propanal.

**8.** (a) Justify the role of tert-butyl peroxide in the polymerization of ethene. **2**

(b) Write the structures of the monomers of the following polymer:



$$\left[ CH_2 - CH = CH - CH_2 - CH_2 - \underset{|}{\overset{C_6H_5}{CH}} \right]_n$$

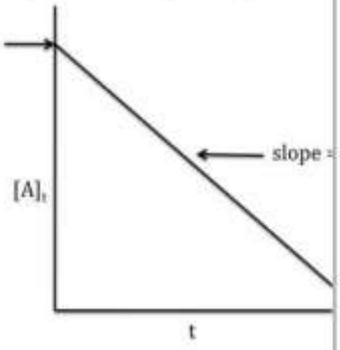
**9.** Write the mechanism of acid dehydration of ethanol to yield ethane **2**

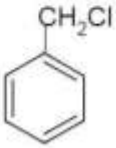
**10.** For a certain chemical reaction variation in concentration [A] vs. time (s) plot is given below:

(i) Predict the order of the given reaction?

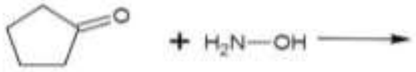
(ii) What does the slope of the line and intercept indicate?

(iii) What is the unit of rate constant k?

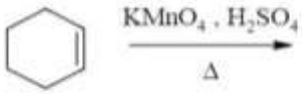


| | | |
|---|---|---|
| **11.** | Draw the molecular structures of the following:<br>(a) Noble gas species which is isostructural with $BrO_3^-$<br>(b) Dibasic oxoacid of phosphorus | **2** |
| **12.** | (i) On the basis of the standard electrode potential values stated for acid solutions, predict whether $Ti^{4+}$ species may be used to oxidise Fe(II) to Fe(III)<br>$Ti^{4+} + e^- \rightarrow Ti^{3+} \quad E^\circ = +0.01V$<br>$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^\circ = +0.77V$<br>(ii) Based on the data arrange $Fe^{2+}$, $Mn^{2+}$ and $Cr^{2+}$ in the increasing order of stability of +2 oxidation state.(Give a brief reason)<br>$E^\circ_{Cr^{3+}/Cr^{2+}} = -0.4V$<br>$E^\circ_{Mn^{3+}/Mn^{2+}} = +1.5V$<br>$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.8V$ | **2** |
| | **Section-C** | |
| **13.** | Niobium crystallises in body-centred cubic structure. If the atomic radius is 143.1 pm, calculate the density of Niobium. (Atomic mass = 93u). | **3** |
| **14.** | Give reasons for the following:<br>a. When 2g of benzoic acid is dissolved in 25 g of benzene, the experimentally determined molar mass is always greater than the true value.<br>b. Mixture of ethanol and acetone shows positive deviation from Raoult's Law.<br>c. The preservation of fruits by adding concentrated sugar solution protects against bacterial action. | **3** |
| **15.** | An alcohol A ($C_4H_{10}O$) on oxidation with acidified potassium dichromate gives acid B ($C_4H_8O_2$). Compound A when dehydrated with conc. $H_2SO_4$ at 443 K gives compound C. Treatment of C with aqueous $H_2SO_4$ gives compound D ($C_4H_{10}O$) which is an isomer of A. Compound D is resistant to oxidation but compound A can be easily oxidised. Identify A, B, C and D. Name the type of isomerism exhibited by A and D | **3** |
| **16.** | Which one of the following compounds will undergo faster hydrolysis reaction by $S_N1$ mechanism? Justify your answer.<br> or $CH_3CH_2CH_2Cl$<br>OR<br>A compound is formed by the substitution of two chlorine atoms for two hydrogen atoms in propane. Write the structures of the isomers possible. Give the IUPAC name of the isomer which can exhibit enantiomerism. | **3** |

**17.** Complete the following reactions : **3**



(a)
(b)



(c)

**18.** Give reasons for the following: **3**

(i) Use of aspartame as an artificial sweetener is limited to cold foods.
(ii) Metal hydroxides are better alternatives than sodium hydrogen carbonate for treatment of acidity.
(iii) Aspirin is used in prevention of heart attacks.

**19.** (a) Name the branched chain component of starch. **3**
(b) Ribose in RNA and deoxyribose in DNA differ in the structure around which carbon atom?
(c) How many peptide linkages are present in a tripeptide?

**OR**

Give three reactions of glucose which cannot be explained by its chain structure

**20.** The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at a constant volume: **3**

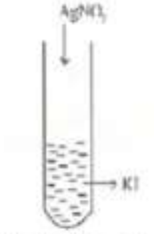
$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

| S.No. | Time (sec.) | Total pressure(atm) |
|---|---|---|
| 1. | 0 | 0.5 |
| 2. | 100 | 0.512 |

Calculate the rate constant

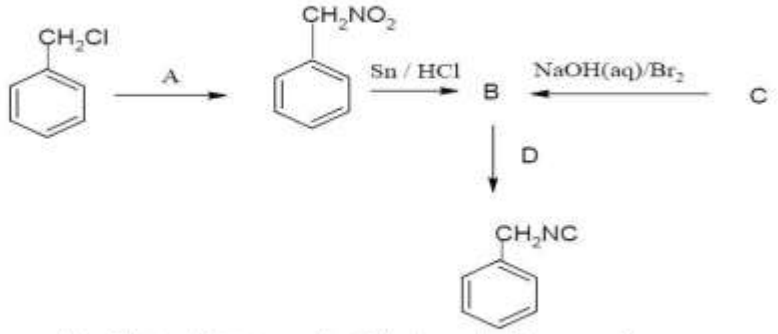
**OR**

Two reactions of the same order have equal pre exponential factors but their activation energies differ by 24.9 kJ $mol^{-1}$. Calculate the ratio between the rate constants of these reactions at 27°C. (Gas constant R = 8.314 J $K^{-1}$ $mol^{-1}$)

| | | |
|---|---|---|
| **21.** | (a) A colloidal sol is prepared by the given method in figure. What is the charge of AgI colloidal particles in the test tube? How is the sol formed, represented?<br><br> <br>(b) Explain how the phenomenon of adsorption finds application in Heterogeneous catalysis.<br>(c) Which of the following electrolytes is the most effective for the coagulation of $Fe(OH)_3$ sol which is a positively charged sol ?<br>NaCl, $Na_2SO_4$, $Na_3PO_4$ | **3** |
| **22.** | Describe how the following steps can be carried out?<br>(a) Recovery of Gold from leached gold metal complex..<br>(b) Conversion of Zirconium iodide to pure Zirconium.<br>(c) Formation of slag in the extraction of copper.<br>(Write the chemical equations also for the reactions involved)<br>**OR**<br>Explain the use of the following:<br>a) NaCN in Froth Floatation Method.<br>b) Carbon monoxide in Mond process.<br>c) Coke in the extraction of Zinc from Zinc Oxide | **3** |
| **23.** | Explain the following:<br>(a) Out of $Sc^{3+}$, $Co^{2+}$ and $Cr^{3+}$ions, only $Sc^{3+}$ is colourless in aqueous solutions. (Atomic no.: Co = 27; Sc = 21 and Cr = 24)<br>(b) The $E^{\circ}_{Cu^{2+}/Cu}$ for copper metal is positive (+0.34), unlike the remaining members of the first transition series<br>(c) $La(OH)_3$ is more basic than $Lu(OH)_3$. | **3** |
| **24.** | A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms **A** and **B**. The form **A** reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia whereas B gives a pale yellow precipitate soluble in concentrated ammonia.<br>(i) Write the formulae of isomers **A** and **B**.<br>(ii) State the hybridisation of chromium in each of them.<br>(iii) Calculate the magnetic moment (spin only value) of the isomer A | **3** |

## Section-D

**25.** (a) Identify A-D **5**



(b) Distinguish between the following pair of compounds:

(i) Aniline and Benzylamine.

(ii) Methylamine and Dimethylamine.

(c) Complete the following:

$$CH_3CH_2CN \xrightarrow{LiAlH_4} A \xrightarrow{0^0 C / HNO_2} B$$

**OR**

(a) Account for the following:

(i) Direct nitration of aniline yields significant amount of meta derivative.

(ii) Primary aromatic amines cannot be prepared by Gabriel phthalimide synthesis.

(b) Carry out the following conversions:

(i) Ethanoic acid into methanamine.

(ii) Aniline to p-Bromoaniline.

(c) Arrange the following in increasing order of basic strength:
Aniline, p-nitroaniline and p-toludine.

**26.** (a) A cell is prepared by dipping a zinc rod in 1M zinc sulphate solution and a silver electrode in 1M silver nitrate solution. The standard electrode potential given: **5**

$E^0_{Zn2+/Zn} = -0.76$ V, $E^0_{Ag+/Ag} = +\ 0.80$ V

What is the effect of increase in concentration of $Zn^{2+}$ on the $E_{cell}$?

(b) Write the products of electrolysis of aqueous solution of NaCl with platinum electrodes.

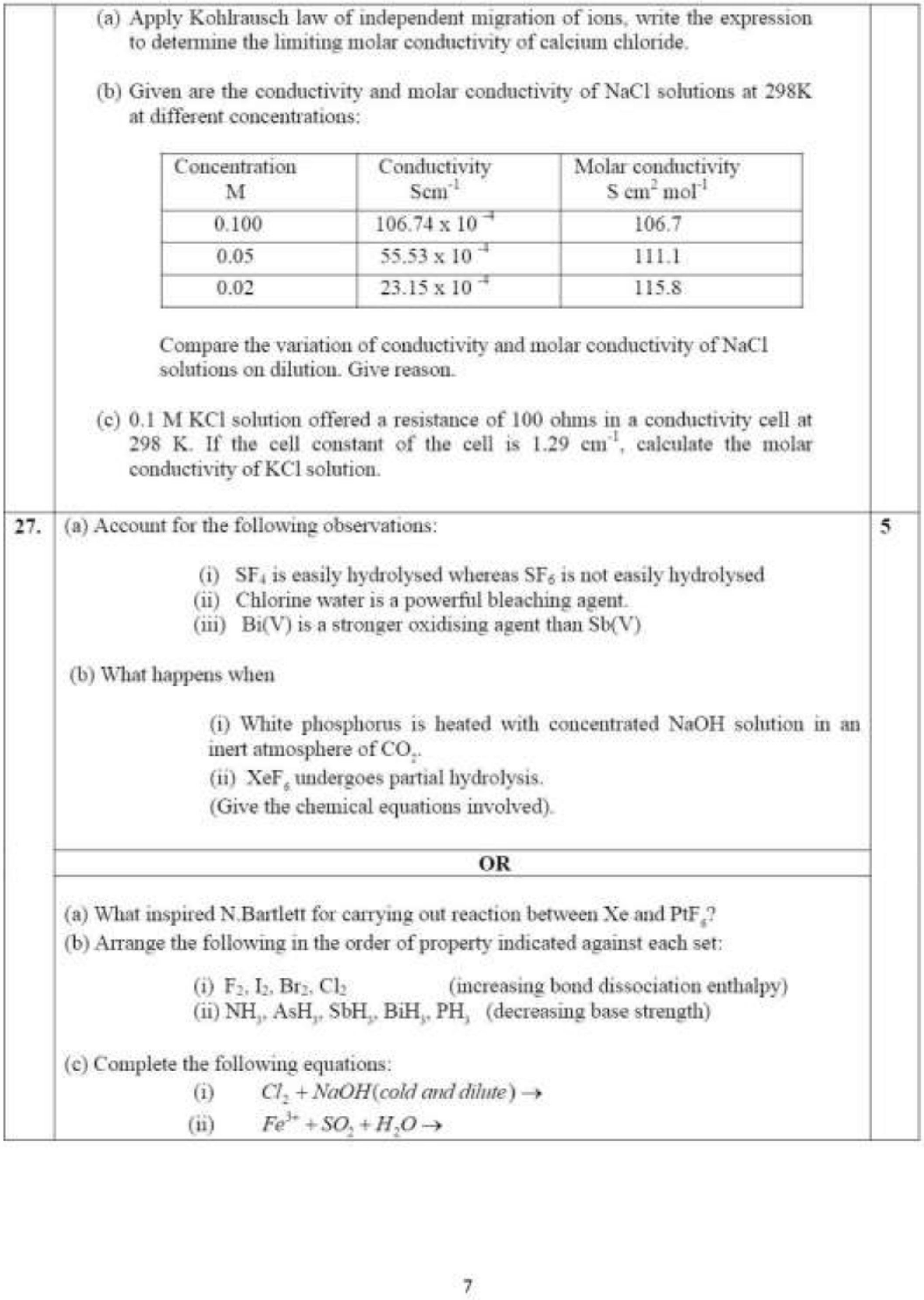
(c) Calculate e.m.f. of the following cell at 298 K:

$Ni(s) / Ni^{2+}$ (0.01 M) // $Cu^{2+}$ (0.1M) / Cu (s)

[ Given $E^0_{Ni2+/Ni} = -0.25$ V , $E^0_{Cu2+/Cu} = +0.34$ V )

Write the overall cell reaction.

**OR**



(a) Apply Kohlrausch law of independent migration of ions, write the expression to determine the limiting molar conductivity of calcium chloride.

(b) Given are the conductivity and molar conductivity of NaCl solutions at 298K at different concentrations:

| Concentration M | Conductivity $Scm^{-1}$ | Molar conductivity $S\ cm^2\ mol^{-1}$ |
|---|---|---|
| 0.100 | $106.74 \times 10^{-4}$ | 106.7 |
| 0.05 | $55.53 \times 10^{-4}$ | 111.1 |
| 0.02 | $23.15 \times 10^{-4}$ | 115.8 |

Compare the variation of conductivity and molar conductivity of NaCl solutions on dilution. Give reason.

(c) 0.1 M KCl solution offered a resistance of 100 ohms in a conductivity cell at 298 K. If the cell constant of the cell is 1.29 $cm^{-1}$, calculate the molar conductivity of KCl solution.

**27.** (a) Account for the following observations: **5**

(i) $SF_4$ is easily hydrolysed whereas $SF_6$ is not easily hydrolysed
(ii) Chlorine water is a powerful bleaching agent.
(iii) Bi(V) is a stronger oxidising agent than Sb(V)

(b) What happens when

(i) White phosphorus is heated with concentrated NaOH solution in an inert atmosphere of $CO_2$.
(ii) $XeF_6$ undergoes partial hydrolysis.
(Give the chemical equations involved).

**OR**

(a) What inspired N.Bartlett for carrying out reaction between Xe and $PtF_6$?
(b) Arrange the following in the order of property indicated against each set:

(i) $F_2$, $I_2$, $Br_2$, $Cl_2$ (increasing bond dissociation enthalpy)
(ii) $NH_3$, $AsH_3$, $SbH_3$, $BiH_3$, $PH_3$ (decreasing base strength)

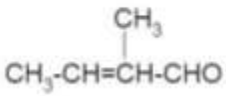
(c) Complete the following equations:

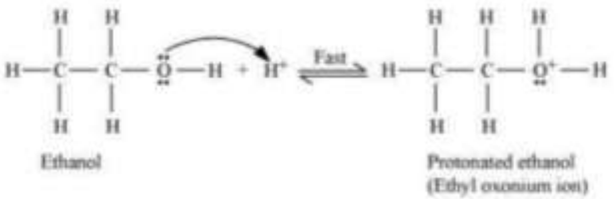
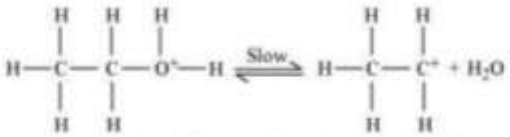
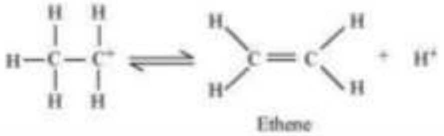
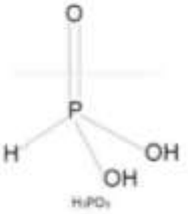
(i) $Cl_2 + NaOH(\text{cold and dilute}) \rightarrow$
(ii) $Fe^{3+} + SO_2 + H_2O \rightarrow$

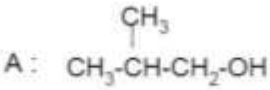
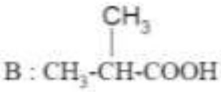
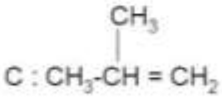
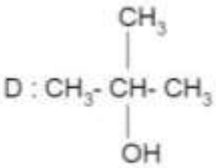
**Class: XII**
**Chemistry**
**Marking Scheme 2018-19**

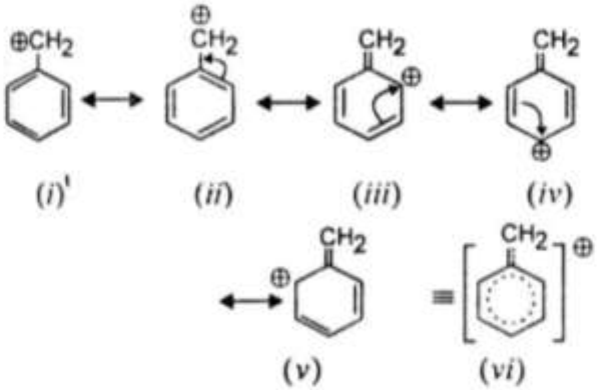
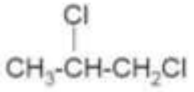
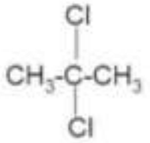
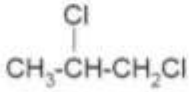
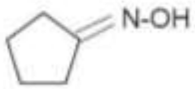
**Time allowed: 3 Hours** **Maximum Marks: 70**

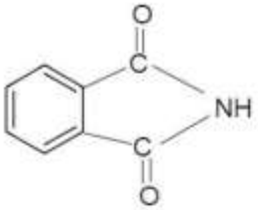
| Q No | SECTION A | Marks |
|---|---|---|
| 1. | On heating ZnO, it loses oxygen and there is excess of $Zn^{2+}$ ions in the crystal. | 1 |
| | **OR** | |
| | When silicon is doped with phosphorous (group 15 element), the increase in conductivity is due to the delocalised negatively charged electrons. | 1 |
| 2. | Associated colloids | 1 |
| 3. | $t_{2g}^{3} e_{g}^{3}$ | 1 |
| | **OR** | |
| | The orbital splitting energies, $\Delta_t$ are not sufficiently large for forcing pairing of electrons in the tetrahedral coordination entity formation. | 1 |
| 4. | B | 1 |
| 5. | *Poly $\beta$ – hydroxybutyrate – co – $\beta$ – hydroxy valerate* | 1 |
| | **SECTION B** | |
| 6. | $HBr \rightarrow H^{+} + Br^{-}$<br>$i = 1 - \alpha + n\alpha$<br>$n = 2$<br>$i = 1 + \alpha$<br>$\Delta T_f = iK_f m$<br>$\Delta T_f = (1+\alpha)1.86 \mathbf{x} \frac{\mathbf{8.1}}{\mathbf{81}} \mathbf{x} \frac{\mathbf{1000}}{\mathbf{100}}$<br>$\Delta T_f = \mathbf{3.53}$<br>$T_f^0 = 0^0 C$<br>$\Delta T_f = T_f^0 - T_f'$<br>$T_f' = -3.534^0 C$ | ½<br>½<br>½<br>½<br>½<br>½ |
| | **OR** | |
| | *Mole fraction of water*, $\chi_{H_2O} = 0.88$<br>*Mole fraction of ethanol*, $\chi_{C_2H_5OH} = 1 - 0.88 = 0.12$<br>$\chi_{C_2H_5OH} = \frac{n_2}{n_1 + n_2}$ ……………..(1) | ½ |

| | | |
|---|---|---|
| | $n_2$= number of moles of ethanol.<br>$n_1$ = number of moles of water.Molality of ethanol means the number of moles of ethanol present in 1000 g of water.<br>$n_1 = \frac{1000}{18} = 55.5\, moles$<br>Substituting the value of $n_1$ in equation (1)<br>$\frac{n_2}{55.5 + n_2} = 0.12$<br>$n_2 = 7.57\, moles$<br>Molality of ethanol ( $C_2H_5OH$) = 7.57 m<br>**Alternatively,**<br>Mole fraction of water = 0.88<br>Mole fraction of ethanol = 1-0.88 = 0.12<br>Therefore 0.12 moles of ethanol are present in 0.88 moles of water.<br>Mass of water = 0.88 x 18 =15.84 g of water.<br>Molality = number of moles of solute (ethanol) present in 1000 g of solvent (water)<br>= 12 x 1000 / 15.84<br>= 7.57 m<br>Molality of ethanol ( $C_2H_5OH$) = 7.57 m | ½<br>½<br>½<br>½<br>½ |
| 7.(a)<br>(b) | Reaction : Hell-Volhard-Zelinsky reaction.<br>IUPAC : 2-Bromopropanoic acid.<br>Reaction : Rosenmund reduction reaction.<br>IUPAC : Benzaldehyde. | ½<br>½<br>½<br>½ |
| | **OR** | |
| | i) 2-Methylbut-2-enal<br><br>$CH_3-CH=\overset{\overset{CH_3}{\vert}}{C}H-CHO$<br>ii) Pent-2-enal<br>$CH_3-CH_2-CH=CH-CHO$ | ½<br>½<br>½<br>½ |
| 8.(a)<br>(b) | Tert-butyl peroxide acts as a free radical generating initiator(catalyst)<br>$CH_2 = CH- CH = CH_2$<br>$C_6H_5 – CH= CH_2$ | **1**<br>½<br>½ |

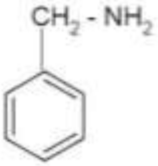
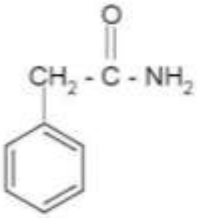
| | | |
|---|---|---|
| 9. | Step 1 : Formation of protonated alcohol. | ½ |
| |  | |
| | Step 2 : Formation of carbocation. | 1 |
| |  | |
| | Step 3: Formation of ethane by elimination of a proton. | ½ |
| |  | |
| 10. | (i) Zero order reaction<br>(ii) Slope represents –k ; Intercept represents $[R]_0$<br>(iii) $mol\,L^{-1}\,s^{-1}$ | ½<br>½+½<br>½ |
| 11.(a) |  | 1 |
| (b) |  | 1 |
| 12.(i) | Since $Ti^{4+}/Ti^{3+}$ has lower reduction potential than $Fe^{3+}/Fe^{2+}$, it cannot be reduced in comparison with $Fe^{3+}/Fe^{2+}$ ions.<br>Hence $Ti^{4+}$ cannot oxidise $Fe^{2+}$ to $Fe^{3+}$. | 1<br>½ |
| (ii) | As the value of reduction potential increases the stability of +2 oxidation increases. Therefore correct order of stability is<br>$Cr^{3+}/Cr^{2+} < Fe^{3+}/Fe^{2+} < Mn^{3+}/Mn^{2+}$ | 1<br>½ |

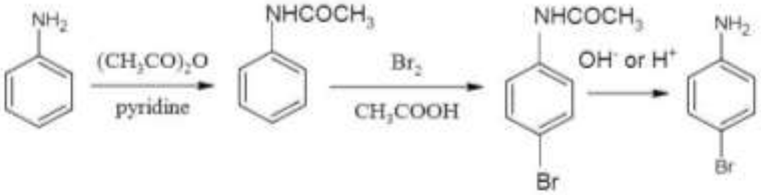
| | **SECTION C** | |
|---|---|---|
| 13. | $r=\frac{\sqrt{3}}{4}a$<br>$143.1=\frac{\sqrt{3}}{4}a$ | ½ |
| | a = 330.4 pm | ½ |
| | $\rho=\frac{zM}{a^3N_A}$ | ½ |
| | $\rho=\frac{2\,\mathbf{x}\,93}{(330.4\,\mathbf{x}\,10^{-10})^3\,\mathbf{x}\,6.023\,\mathbf{x}\,10^{23}}$ | ½ |
| | $\rho=8.58\ g/cm^3$ | ½ + ½ |
| 14.(a) | Molecules of benzoic acid dimerise in benzene, the number of particles are reduced. | **1** |
| (b) | The intermolecular interactions between ethanol and acetone are weaker/ the escaping tendency of ethanol and acetone molecules increases on mixing / the vapour pressure increases. | **1** |
| (c) | Due to osmosis, a bacterium on fruit loses water, shrivels and dies. | **1** |
| 15. |  A : $CH_3-\overset{\overset{CH_3}{\vert}}{C}H-CH_2-OH$ | **1** |
| |  B : $CH_3-\overset{\overset{CH_3}{\vert}}{C}H-COOH$ | ½ |
| |  C : $CH_3-\overset{\overset{CH_3}{\vert}}{C}H=CH_2$ | ½ |
| |  D : $CH_3-\underset{\underset{OH}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}H-CH_3$ | ½ |
| | A and D are position isomers. | ½ |

| | | |
|---|---|---|
| 16. | $C_6H_5CH_2Cl$ will undergo $S_N1$reaction faster.<br>The carbocation formed by $C_6H_5CH_2Cl$ gets stabilized through resonance.<br>Greater the stability of carbocation, greater will be its ease of formation from the respective halide.<br> | ½<br>½<br>1<br>1 |
| | OR | |
| | $CH_3-\overset{\overset{Cl}{\mid}}{C}H-CH_2Cl$<br>$CH_2Cl-CH_2-CH_2Cl$<br>$CH_3-CH_2-CHCl_2$<br>$CH_3-\overset{\overset{Cl}{\mid}}{\underset{\underset{Cl}{\mid}}{C}}-CH_3$<br>The following isomer will exhibit enantiomerism:<br>$CH_3-\overset{\overset{Cl}{\mid}}{C}H-CH_2Cl$<br>IUPAC name: 1,2-Dichloropropane. | ½<br>½<br>½<br>½<br>½<br>½ |
| 17.(a) |  | 1 |
| (b) | HOOC - $CH_2$ - $CH_2$ - $CH_2$ - $CH_2$ – COOH | 1 |

| | | |
|---|---|---|
| (c) |  | 1 |
| 18.(i) | It is unstable at cooking temperature. | 1 |
| (ii) | Excessive hydrogencarbonate can make the stomach alkaline and trigger the production of even more acid. Metal hydroxides being insoluble do not increase the pH above neutrality. | 1 |
| (iii) | Aspirin has anti blood clotting action. | 1 |
| 19.(a) | Amylopectin. | 1 |
| (b) | C- 2 | 1 |
| (c) | Two peptide linkages. | 1 |
| | OR | |
| | (1) Glucose does not give 2,4- DNP test. | 1 |
| | (2) Glucose does not give Schiff's test. | 1 |
| | (3) The pentaacetate of glucose does not react with hydroxylamine. | 1 |
| | (4) Glucose does not form the hydrogensulphite addition product with $NaHSO_3$.<br>(Any three points ) | |
| 20. | $2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$ | |
| | At t = 0   0.5 atm   0 atm   0 atm | |
| | At time t   $0.5-2x$ atm   $2x$ atm   $x$ atm | |
| | $p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$<br>$= =(0.5-2x)+2x+x = =0.5+x$ | ½ |
| | $x = p_t - 0.5$ | |
| | $p_{N_2O_5} = 0.5-2x$<br>$= 0.5-2(p_t-0.5)$<br>$= 1.5 - 2p_t$ | ½ |
| | At t = 100 s ; $p_t = 0.512$ atm<br>$p_{N_2O_5} = 1.5-2\times0.512 = 0.476 atm$ | |
| | $k = \frac{2.303}{t}\log\frac{p_i}{p_A}$ | ½ |
| | $k = \frac{2.303}{100s}\log\frac{0.5 atm}{0.476 atm}$ | ½ |
| | $k = \frac{2.303}{100s}\times0.0216 = 4.98\times10^{-4}s^{-1}$ | 1 |
| | **OR** | 1 |
| | The Arrhenius equation: $k = Ae^{-Ea/RT}$<br>Taking log on both sides: $\log k = \log A - \frac{E_a}{2.303RT}$ | |

| | | |
|---|---|---|
| | For reaction (i) $\log k_1 = \log A - \frac{E_a(1)}{2.303RT}$<br>For reaction (ii) $\log k_2 = \log A - \frac{E_a(2)}{2.303RT}$ | 1 |
| | Subtracting (i) from (ii)<br>$\log \frac{k_1}{k_2} = \frac{E_a(1) - E_a(2)}{2.303RT}$<br>$= \log \frac{k_1}{k_2} = \frac{24.9 \times 1000}{2.303 \times 8.3 \times 300} = 4.342$<br>$\frac{k_1}{k_2} = anti \log(4.342) = 2.198 \times 10^4$ | 1 |
| 21.<br>(a) | Negative charge is developed on the sol.<br>Sol is represented as $AgI / I^-$ | ½<br>½ |
| (b) | Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. | 1 |
| (c) | $Na_3PO_4$<br>Hardy-Schulze rule | ½<br>½ |
| 22.<br>(a) | Leached gold complex is treated with Zinc and gold is recovered by displacement method<br>$2Au[(CN)_2]^-(aq) + Zn(s) \rightarrow 2Au(s) + [Zn(CN)_4]^{2-}(aq)$ | ½<br>½ |
| (b) | Zirconium iodide is decomposed on a tungsten filament; electrically heated to 1800 K. Pure Zr metal is deposited on the filament.<br>$ZrI_4 \rightarrow Zr + I_2$ | ½<br>½ |
| (c) | Silica is added to the ore and heated. It helps to slag off iron oxide as iron silicate<br>$FeO + SiO_2 \rightarrow FeSiO_3(slag)$ | ½<br>½ |
| | **OR** | |
| (a) | NaCN is used as depressants to separate two sulphide ores ( ZnS and PbS) in Froth Floatation Method. | (1) |
| (b) | Carbon monoxide forms a volatile complex of nickel, nickel tetracarbonyl. | (1) |
| (c) | Coke is used as a reducing agent to reduce zinc oxide to zinc. | (1) |
| 23.<br>(a) | $Co^{2+}$ : [Ar]3$d^7$ $Sc^{3+}$ : [Ar]3$d^0$ $Cr^{3+}$ : [Ar]3$d^3$<br>$Co^{2+}$ and $Cr^{3+}$ have unpaired electrons. Thus, they are coloured in aqueous solution.$Sc^{3+}$ has no unpaired electron. Thus it is colourless. | 1 |
| (b) | Metal copper has high enthalpy of atomisation and enthalpy of ionisation. Therefore the high energy required to convert Cu(s) to $Cu^{2+}$(aq) is not balanced by its hydration enthalpy. | 1 |

<table>
<tr><td>(c)</td><td>Due to lanthanoid contraction the size of lanthanoid ion decreases regularly with increase in atomic size. Thus covalent character between lanthanoid ion and $OH^-$ increases from $La^{3+}$ to $Lu^{3+}$. Thus the basic character of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$</td><td>1</td></tr>
<tr><td>24.<br>(a)<br><br>(b)<br>(c)</td><td>Isomer A: $[Cr(NH_3)_4 BrCl]Cl$<br>Isomer B: $[Cr (NH_3)_4 Cl_2]Br$<br>Hybridisation of Cr in isomer A and B is $d^2sp^3$.<br>Number of unpaired electrons in $Cr^{3+}(3d^3)$ is 3<br>Magnetic moment = $\sqrt{n(n+2)}$<br>$= \sqrt{3(3+2)} = 3.87$ BM<br>(deduct half mark for wrong unit/unit not written)</td><td>½<br>½<br>1<br><br>1</td></tr>
<tr><td>25.(a)<br><br><br><br><br><br>(b)<br>(i)<br><br><br>(ii)</td><td>A = $AgNO_2$<br>B = <br>C = <br>D = $CHCl_3$ + KOH , Heat.<br>
<table>
<tr><th>Experiment</th><th>Aniline</th><th>Benzylamine</th></tr>
<tr><td>Azo dye test:<br>Dissolve the amine in HCl, cool it and then add cold aqueous solution of $NaNO_2$ and then solution of $\beta$ - naphthol</td><td>A brilliant orange red dye is observed.</td><td>No dye is formed.</td></tr>
</table>
<table>
<tr><th>Experiment</th><th>Methylamine</th><th>Dimethylamine</th></tr>
<tr><td>Carbylamine test:<br>To the organic compound add chloroform and ethanolic potassium hydroxide and heat</td><td>A foul smelling substance (isocyanide)</td><td>No reaction.</td></tr>
</table>
(or any other suitable test)</td><td>½<br>½<br>½<br>½<br>1<br>1</td></tr>
</table>

| | | |
|---|---|---|
| (c) | A = $CH_3CH_2CH_2NH_2$<br>B = $CH_3CH_2CH_2OH$ | ½<br>½ |
| | **OR** | |
| (a)(i) | In strongly acidic medium, aniline is protonated to form the anilium ion which is meta directing. | 1 |
| (ii) | Aryl halides do not undergo nucleophilc substitution with the anion formed by phthalimide. | 1 |
| (b)(i) | $CH_3\text{- }COOH \xrightarrow{NH_3,\ \Delta} CH_3\text{-}CO\text{-}NH_2 \xrightarrow{NaOH + Br_2} CH_3NH_2$ | 1 |
| (ii) |  | 1 |
| (c) | p- Nitroaniline < Aniline < p- Toludine. | 1 |
| 26.(a) | $E_{cell}$ decreases. | 1 |
| (b) | Anode: $Cl_2 \uparrow$<br>Cathode : $H_2 \uparrow$ | ½<br>½ |
| (c) | $Cu^{2+}(aq.) + Ni(s) \rightarrow Ni^{2+}(aq.) + Cu(s)$ | ½ |
| | $E^0_{cell} = E^0_{cathode} - E^0_{anode}$<br>$E^0_{cell} = 0.34 - (-0.25)$<br>$E^0_{cell} = 0.59V$ | ½ |
| | $E_{cell} = E^0_{cell} - \frac{2.303RT}{nF}\log\frac{[Ni^{2+}]}{[Cu^{2+}]}$ | ½ |
| | $E_{cell} = 0.59 - \frac{0.059}{2}\log\frac{[0.01\ ]}{[0.1\ ]}$ | ½ |
| | $E_{cell} = 0.6195V$ | ½ +½ |
| | **OR** | |
| (a) | $\Lambda^0_{m(CaCl_2)} = \lambda^0_{Ca^{2+}} + 2\lambda^0_{Cl^-}$ | 1 |
| (b) | Conductivity of NaCl decreases on dilution as the number of ions per unit volume decreases. | 1 |

| | | |
|---|---|---|
| | Whereas molar conductivity of NaCl increases on dilution as on dilution the interionic interactions are overcome and ions are free to move. | 1 |
| (c) | $G^* = \kappa R$<br>$\kappa = \frac{1.29}{100} = 0.0129\ S\,cm^{-1}$<br>$\Lambda_m = \frac{1000\ \kappa}{C}$<br>$\Lambda_m = \frac{1000\ x\ 0.0129}{0.1}$<br>$\Lambda_m = 129\,S\,cm^2\ mol^{-1}$ | ½<br>½<br>½<br>½ |
| 27.<br>(a) | (i)S atom in $SF_4$ is not sterically protected as it is surrounded by only four F atoms, so attack of water molecules can take place easily. In contrast, S atom in $SF_6$ is protected by six F aoms. Thus attack by water molecules cannot take place easily. | 1 |
| | (ii) Chlorine water produces nascent oxygen (causes oxidation) which is responsible for bleaching action.<br>$Cl_2 + H_2O \rightarrow 2HCl + [O]$ | 1 |
| | (iii) Due to inert pair effect Bi(V) can accept a pair of electrons to form more stable Bi (III). (+3 oxidation state of Bi is more stable than its +5 oxidation state). | 1 |
| (b) | (i)Phosphorus undergoes disproportionation reaction to form phosphine gas.<br>$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ | 1 |
| | (ii)On partial hydrolysis, $XeF_6$ gives oxyfluoride $XeOF_4$ and HF.<br>$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$ | 1 |
| | **OR** | |
| (a) | N.Bartlett first prepared a red compound $O_2^+PtF_6^-$. He then realised that the first ionisation enthalpy of molecular oxygen was almost identical with Xenon. So he carried out reaction between Xe and $PtF_6$. | 1 |
| (b) | (i) $I_2 < F_2 < Br_2 < Cl_2$<br>(ii) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ | 1<br>1 |
| (c) | (i)<br>$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$ | 1 |
| | (ii)<br>$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$ | 1 |

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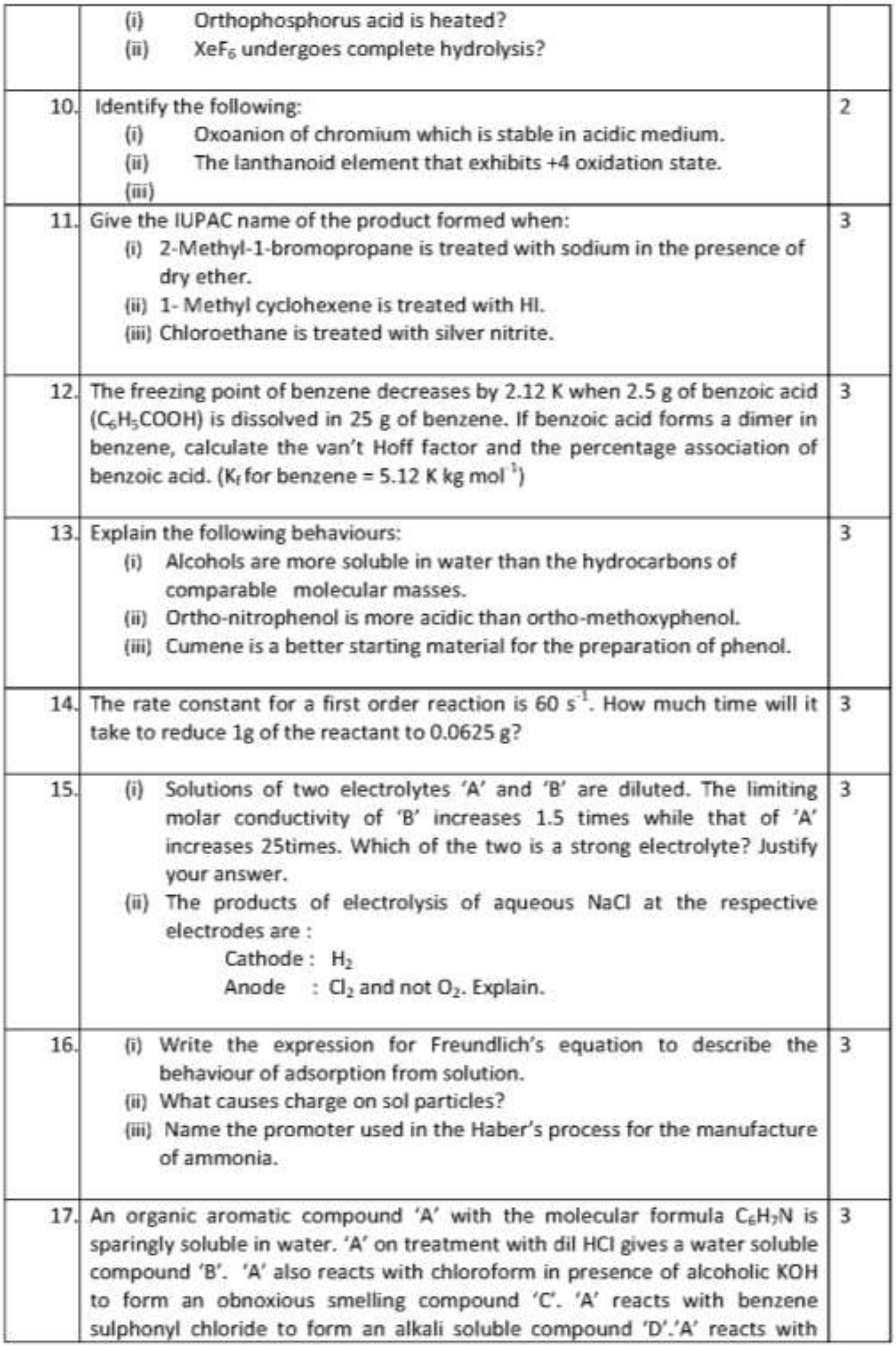


| | | |
|---|---|---|
| | (i) Orthophosphorus acid is heated?<br>(ii) $XeF_6$ undergoes complete hydrolysis? | |
| 10. | Identify the following:<br>(i) Oxoanion of chromium which is stable in acidic medium.<br>(ii) The lanthanoid element that exhibits +4 oxidation state.<br>(iii) | 2 |
| 11. | Give the IUPAC name of the product formed when:<br>(i) 2-Methyl-1-bromopropane is treated with sodium in the presence of dry ether.<br>(ii) 1- Methyl cyclohexene is treated with HI.<br>(iii) Chloroethane is treated with silver nitrite. | 3 |
| 12. | The freezing point of benzene decreases by 2.12 K when 2.5 g of benzoic acid ($C_6H_5COOH$) is dissolved in 25 g of benzene. If benzoic acid forms a dimer in benzene, calculate the van't Hoff factor and the percentage association of benzoic acid. ($K_f$ for benzene = 5.12 K kg $mol^{-1}$) | 3 |
| 13. | Explain the following behaviours:<br>(i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.<br>(ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol.<br>(iii) Cumene is a better starting material for the preparation of phenol. | 3 |
| 14. | The rate constant for a first order reaction is 60 $s^{-1}$. How much time will it take to reduce 1g of the reactant to 0.0625 g? | 3 |
| 15. | (i) Solutions of two electrolytes 'A' and 'B' are diluted. The limiting molar conductivity of 'B' increases 1.5 times while that of 'A' increases 25times. Which of the two is a strong electrolyte? Justify your answer.<br>(ii) The products of electrolysis of aqueous NaCl at the respective electrodes are :<br>Cathode : $H_2$<br>Anode : $Cl_2$ and not $O_2$. Explain. | 3 |
| 16. | (i) Write the expression for Freundlich's equation to describe the behaviour of adsorption from solution.<br>(ii) What causes charge on sol particles?<br>(iii) Name the promoter used in the Haber's process for the manufacture of ammonia. | 3 |
| 17. | An organic aromatic compound 'A' with the molecular formula $C_6H_7N$ is sparingly soluble in water. 'A' on treatment with dil HCl gives a water soluble compound 'B'. 'A' also reacts with chloroform in presence of alcoholic KOH to form an obnoxious smelling compound 'C'. 'A' reacts with benzene sulphonyl chloride to form an alkali soluble compound 'D'.'A' reacts with | 3 |

$NaNO_2$ and HCl to form a compound 'E' which on reaction with phenol forms an orange red dye 'F'. Elucidate the structures of the organic compounds from 'A' to 'F'.

18. (i) Which vitamin deficiency causes rickets? 3
(ii) Name the base that is found in nucleotide of RNA only.
(iii) Glucose on reaction with acetic acid gives glucose penta acetate. What does it suggest about the structure of glucose?

19. Name the type of reaction involved in the formation of the following polymers from their respective monomers 3
(i) PVC.
(ii) Nylon6.
(iii) PHBV.

20. Describe the role of 3
(i) NaCN in the extraction of gold from its ore.
(ii) Cryolite in the extraction of aluminium from pure alumina.
(iii) CO in the purification of Nickel

21. A metal ion $M^{n+}$ having $d^4$ valence electronic configuration combines with three bidentate ligands to form a complex compound. Assuming $\Delta_o > P$: 3
(i) Write the electronic configuration of $d^4$ ion.
(ii) What type of hybridisation will $M^{n+}$ ion has?
(iii) Name the type of isomerism exhibited by this complex.

22. The magnetic moments of few transition metal ions are given below: 3

| **Metal ion** | **Magnetic moment(BM)** |
|---|---|
| $Sc^{3+}$ | 0.00 |
| $Cr^{2+}$ | 4.90 |
| $Ni^{2+}$ | 2.84 |
| $Ti^{3+}$ | 1.73 |

(at no. Sc = 21, Ti =22, Cr = 24, Ni = 28)

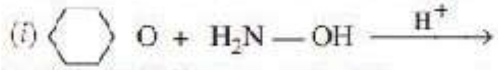
Which of the given metal ions :
(i) has the maximum number of unpaired electrons?
(ii) forms colourless aqueous solution?
(iii) exhibits the most stable +3 oxidation state?

**OR**

Consider the standard electrode potential values ($M^{2+}/M$) of the elements of the first transition series.

| Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|
| -1.63 | -1.18 | -0.90 | -1.18 | -0.44 | -0.28 | -0.25 | +0.34 | -0.76 |

Explain:
(i) $E^\circ$ value for copper is positive.
(ii) $E^\circ$ value of Mn is more negative as expected from the trend.

| | | |
|---|---|---|
| | (iii) $Cr^{2+}$ is a stronger reducing agent than $Fe^{2+}$. | |
| 23. | Ashwin observed that his friend Shubham was staying aloof, not playing with friends and becoming easily irritable for some weeks. Ashwin told his teacher about this, who, in turn, called Shubham's parents and advised them to consult a doctor. Doctor after examining Shubham prescribed antidepressant drugs for him.<br>After reading the above passage, answer the following questions:<br>i) Name two antidepressant drugs.<br>ii) Mention the values shown by Ashwin.<br>iii) How should Shubham's family help him other than providing medicine?<br>iv) What is the scientific explanation for the feeling of depression? | 4 |
| 24. | (a) Arrange the following in the order of property indicated against each set:<br>(i) $F_2, Cl_2, Br_2, I_2$ (increasing bond dissociation enthalpy)<br>(ii) $H_2O$, $H_2S$, $H_2Se$, $H_2Te$ (increasing acidic character)<br>(b) A colourless gas 'A' with a pungent odour is highly soluble in water and its aqueous solution is weakly basic. As a weak base it precipitates the hydroxides of many metals from their salt solution. Gas 'A' finds application in detection of metal ions. It gives a deep blue colouration with copper ions. Identify the gas 'A' and write the chemical equations involved in the following:<br>(i) Gas 'A' with copper ions<br>(ii) Solution of gas 'A' with $ZnSO_4$ solution.<br>**OR**<br>**Answer the following questions**<br>(a) Write the formula of the neutral molecule which is isoelectronic with $ClO^-$.<br>(b) Draw the shape of $H_2S_2O_7$.<br>(c) Nitric acid forms an oxide of nitrogen on reaction with $P_4$. Write the formula of the stable molecule formed when this oxide undergoes dimerisation.<br>(d) Bleaching action of chlorine is permanent. Justify.<br>(e) Write the disproportionation reaction of that oxoacid of nitrogen in which nitrogen is in +3 oxidation state. | 5 |
| 25. | Write the products of the following reactions:<br><br>(ii) $2C_6H_5CHO + \text{conc. } NaOH \longrightarrow$<br>(iii) $CH_3COOH \xrightarrow{Cl_2/P}$<br>(b) Give simple chemical tests to distinguish between the following pairs of | 5 |

compounds:
(*i*) Benzaldehyde and Benzoic acid
(*ii*) Propanal and Propanone

OR

(*a*) Account for the following:
(*i*) $CH_3CHO$ is more reactive than $CH_3COCH_3$ towards reaction with HCN.
(*ii*) 2-Fluorobutanoic acid is a stronger acid than 3-Fluorobutanoic acid.
(*b*) Write the chemical equations to illustrate the following name reactions:
(*i*) Etard reaction.
(ii) Rosenmund's reaction.
(c) Give the mechanism of cyanohydrin formation when carbonyl compounds react with HCN in the presence of alkali.

26. (i) Following is the schematic alignment of magnetic moments: 5

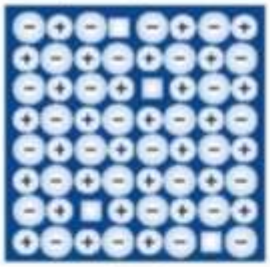
Identify the type of magnetism. What happens when these substances are heated?

(ii) If the radius of the octahedral void is 'r' and radius of the atoms in close packing is 'R'. What is the relation between 'r' and 'R'?

(iii) Tungsten crystallizes in body centred cubic unit cell. If the edge of the unit cell is 316.5 pm. What is the radius of tungsten atom?

**OR**

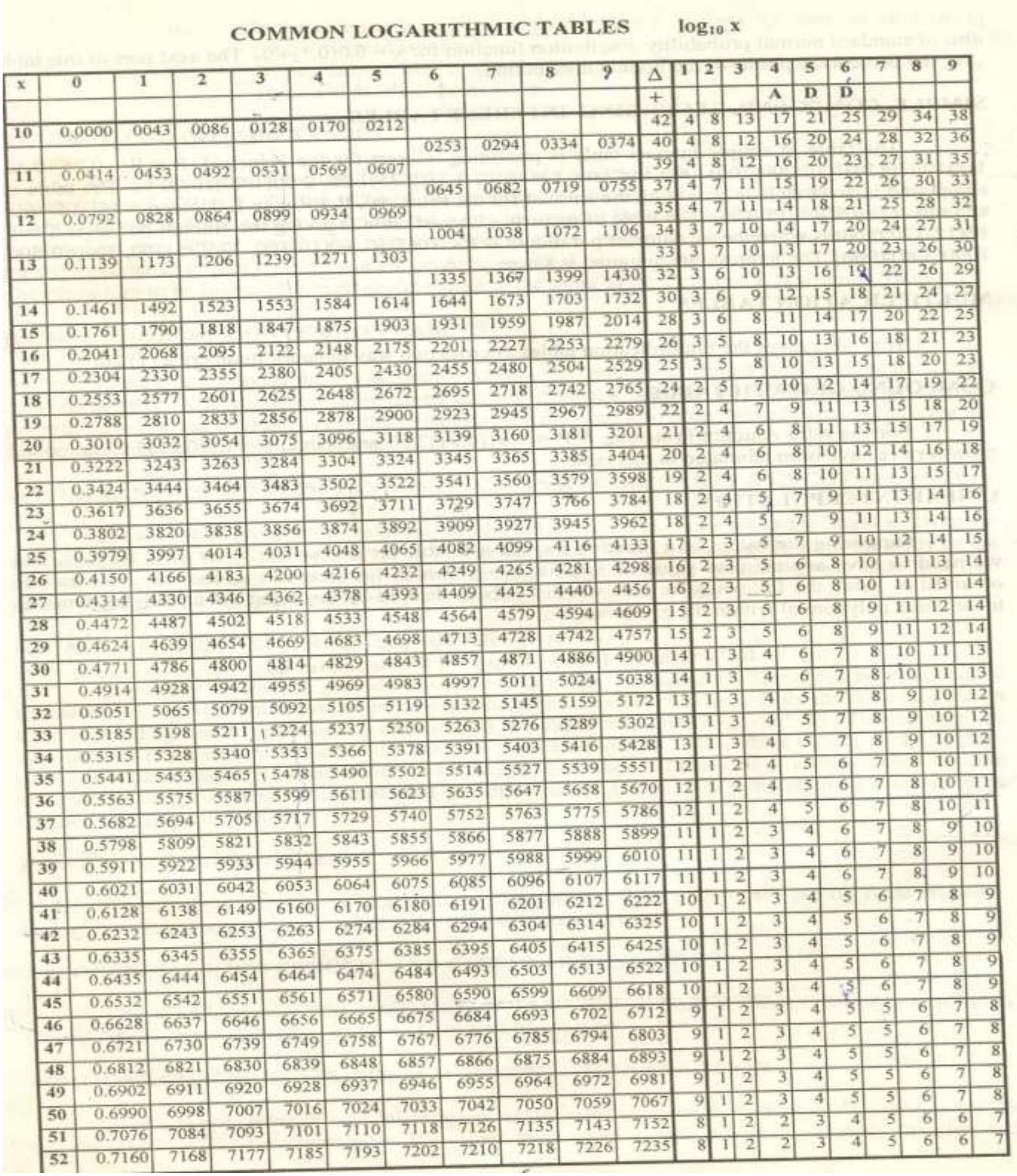
**(i)** Identify the type of defect shown in the following figure:



What type of substances show this defect?

(ii) A metal crystallizes in a body centred cubic structure. If 'a' is the edge length of its unit cell, 'r' is the radius of the sphere. What is the relationship between 'r' and 'a'?

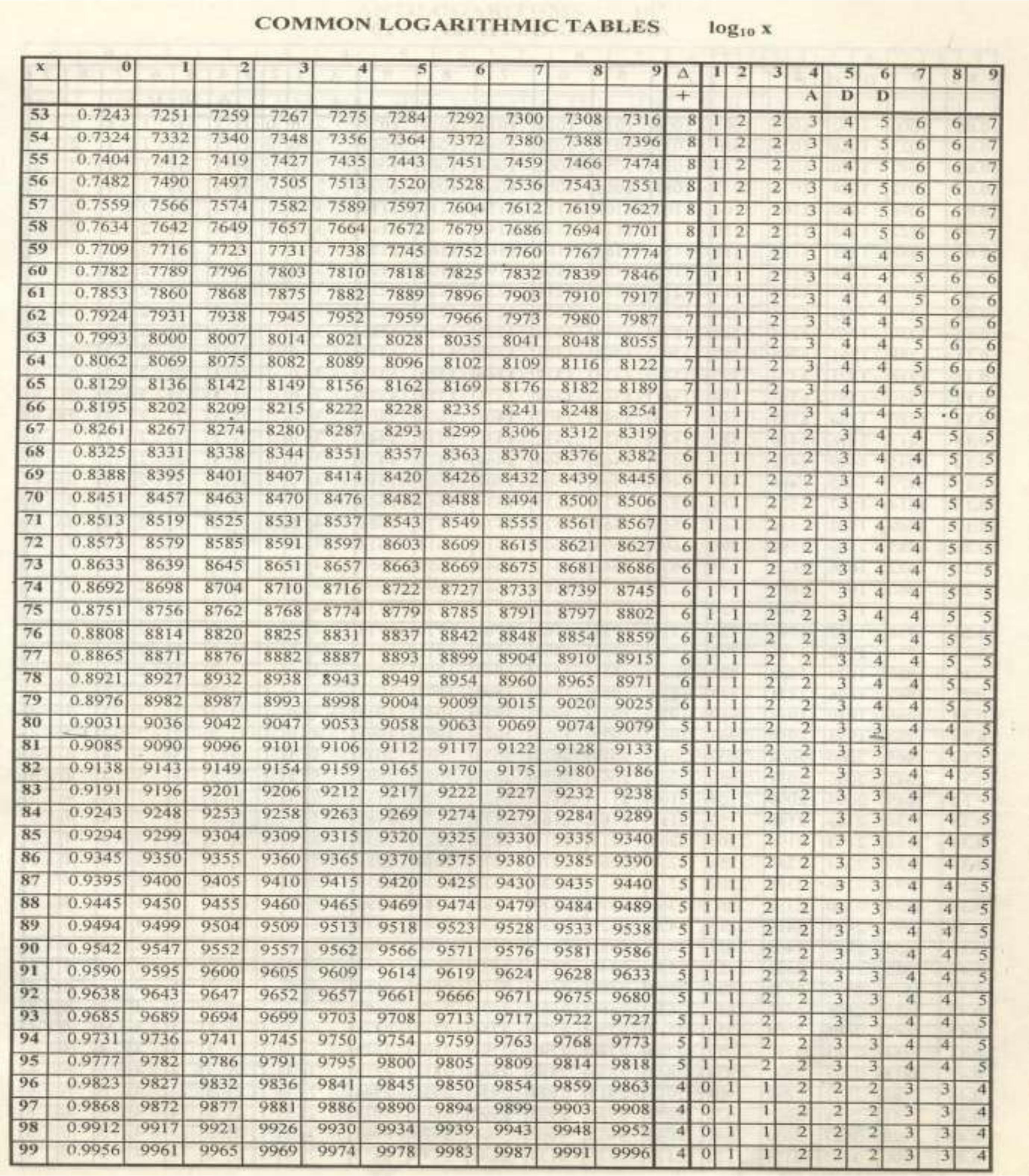
(iii) An element with molar mass 63 g / mol forms a cubic unit cell with edge length of 360.8 pm. If its density is 8.92 g/ cm$^3$. What is the nature of the cubic unit cell?



## COMMON LOGARITHMIC TABLES

$\log_{10} x$

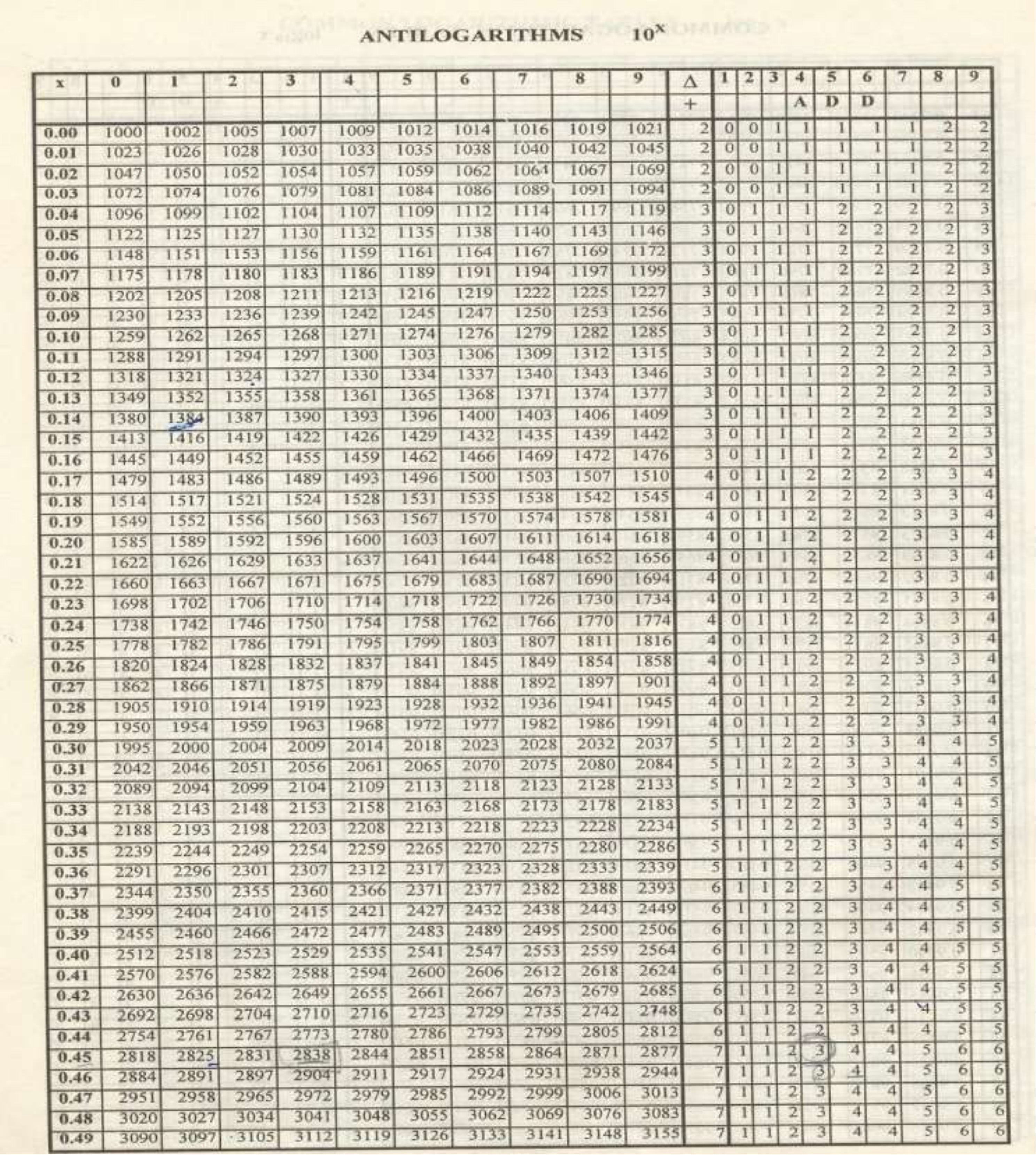
| x | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Δ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  |  |  | + |  |  |  | A | D | D |  |  |  |
| 10 | 0.0000 | 0043 | 0086 | 0128 | 0170 | 0212 |  |  |  |  | 42 | 4 | 8 | 13 | 17 | 21 | 25 | 29 | 34 | 38 |
|  |  |  |  |  |  |  | 0253 | 0294 | 0334 | 0374 | 40 | 4 | 8 | 12 | 16 | 20 | 24 | 28 | 32 | 36 |
| 11 | 0.0414 | 0453 | 0492 | 0531 | 0569 | 0607 |  |  |  |  | 39 | 4 | 8 | 12 | 16 | 20 | 23 | 27 | 31 | 35 |
|  |  |  |  |  |  |  | 0645 | 0682 | 0719 | 0755 | 37 | 4 | 7 | 11 | 15 | 19 | 22 | 26 | 30 | 33 |
| 12 | 0.0792 | 0828 | 0864 | 0899 | 0934 | 0969 |  |  |  |  | 35 | 4 | 7 | 11 | 14 | 18 | 21 | 25 | 28 | 32 |
|  |  |  |  |  |  |  | 1004 | 1038 | 1072 | 1106 | 34 | 3 | 7 | 10 | 14 | 17 | 20 | 24 | 27 | 31 |
| 13 | 0.1139 | 1173 | 1206 | 1239 | 1271 | 1303 |  |  |  |  | 33 | 3 | 7 | 10 | 13 | 17 | 20 | 23 | 26 | 30 |
|  |  |  |  |  |  |  | 1335 | 1367 | 1399 | 1430 | 32 | 3 | 6 | 10 | 13 | 16 | 19 | 22 | 26 | 29 |
| 14 | 0.1461 | 1492 | 1523 | 1553 | 1584 | 1614 | 1644 | 1673 | 1703 | 1732 | 30 | 3 | 6 | 9 | 12 | 15 | 18 | 21 | 24 | 27 |
| 15 | 0.1761 | 1790 | 1818 | 1847 | 1875 | 1903 | 1931 | 1959 | 1987 | 2014 | 28 | 3 | 6 | 8 | 11 | 14 | 17 | 20 | 22 | 25 |
| 16 | 0.2041 | 2068 | 2095 | 2122 | 2148 | 2175 | 2201 | 2227 | 2253 | 2279 | 26 | 3 | 5 | 8 | 10 | 13 | 16 | 18 | 21 | 23 |
| 17 | 0.2304 | 2330 | 2355 | 2380 | 2405 | 2430 | 2455 | 2480 | 2504 | 2529 | 25 | 3 | 5 | 8 | 10 | 13 | 15 | 18 | 20 | 23 |
| 18 | 0.2553 | 2577 | 2601 | 2625 | 2648 | 2672 | 2695 | 2718 | 2742 | 2765 | 24 | 2 | 5 | 7 | 10 | 12 | 14 | 17 | 19 | 22 |
| 19 | 0.2788 | 2810 | 2833 | 2856 | 2878 | 2900 | 2923 | 2945 | 2967 | 2989 | 22 | 2 | 4 | 7 | 9 | 11 | 13 | 15 | 18 | 20 |
| 20 | 0.3010 | 3032 | 3054 | 3075 | 3096 | 3118 | 3139 | 3160 | 3181 | 3201 | 21 | 2 | 4 | 6 | 8 | 11 | 13 | 15 | 17 | 19 |
| 21 | 0.3222 | 3243 | 3263 | 3284 | 3304 | 3324 | 3345 | 3365 | 3385 | 3404 | 20 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| 22 | 0.3424 | 3444 | 3464 | 3483 | 3502 | 3522 | 3541 | 3560 | 3579 | 3598 | 19 | 2 | 4 | 6 | 8 | 10 | 11 | 13 | 15 | 17 |
| 23 | 0.3617 | 3636 | 3655 | 3674 | 3692 | 3711 | 3729 | 3747 | 3766 | 3784 | 18 | 2 | 4 | 5 | 7 | 9 | 11 | 13 | 14 | 16 |
| 24 | 0.3802 | 3820 | 3838 | 3856 | 3874 | 3892 | 3909 | 3927 | 3945 | 3962 | 18 | 2 | 4 | 5 | 7 | 9 | 11 | 13 | 14 | 16 |
| 25 | 0.3979 | 3997 | 4014 | 4031 | 4048 | 4065 | 4082 | 4099 | 4116 | 4133 | 17 | 2 | 3 | 5 | 7 | 9 | 10 | 12 | 14 | 15 |
| 26 | 0.4150 | 4166 | 4183 | 4200 | 4216 | 4232 | 4249 | 4265 | 4281 | 4298 | 16 | 2 | 3 | 5 | 6 | 8 | 10 | 11 | 13 | 14 |
| 27 | 0.4314 | 4330 | 4346 | 4362 | 4378 | 4393 | 4409 | 4425 | 4440 | 4456 | 16 | 2 | 3 | 5 | 6 | 8 | 10 | 11 | 13 | 14 |
| 28 | 0.4472 | 4487 | 4502 | 4518 | 4533 | 4548 | 4564 | 4579 | 4594 | 4609 | 15 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 12 | 14 |
| 29 | 0.4624 | 4639 | 4654 | 4669 | 4683 | 4698 | 4713 | 4728 | 4742 | 4757 | 15 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 12 | 14 |
| 30 | 0.4771 | 4786 | 4800 | 4814 | 4829 | 4843 | 4857 | 4871 | 4886 | 4900 | 14 | 1 | 3 | 4 | 6 | 7 | 8 | 10 | 11 | 13 |
| 31 | 0.4914 | 4928 | 4942 | 4955 | 4969 | 4983 | 4997 | 5011 | 5024 | 5038 | 14 | 1 | 3 | 4 | 6 | 7 | 8 | 10 | 11 | 13 |
| 32 | 0.5051 | 5065 | 5079 | 5092 | 5105 | 5119 | 5132 | 5145 | 5159 | 5172 | 13 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 10 | 12 |
| 33 | 0.5185 | 5198 | 5211 | 5224 | 5237 | 5250 | 5263 | 5276 | 5289 | 5302 | 13 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 10 | 12 |
| 34 | 0.5315 | 5328 | 5340 | 5353 | 5366 | 5378 | 5391 | 5403 | 5416 | 5428 | 13 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 10 | 12 |
| 35 | 0.5441 | 5453 | 5465 | 5478 | 5490 | 5502 | 5514 | 5527 | 5539 | 5551 | 12 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| 36 | 0.5563 | 5575 | 5587 | 5599 | 5611 | 5623 | 5635 | 5647 | 5658 | 5670 | 12 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| 37 | 0.5682 | 5694 | 5705 | 5717 | 5729 | 5740 | 5752 | 5763 | 5775 | 5786 | 12 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| 38 | 0.5798 | 5809 | 5821 | 5832 | 5843 | 5855 | 5866 | 5877 | 5888 | 5899 | 11 | 1 | 2 | 3 | 4 | 6 | 7 | 8 | 9 | 10 |
| 39 | 0.5911 | 5922 | 5933 | 5944 | 5955 | 5966 | 5977 | 5988 | 5999 | 6010 | 11 | 1 | 2 | 3 | 4 | 6 | 7 | 8 | 9 | 10 |
| 40 | 0.6021 | 6031 | 6042 | 6053 | 6064 | 6075 | 6085 | 6096 | 6107 | 6117 | 11 | 1 | 2 | 3 | 4 | 6 | 7 | 8 | 9 | 10 |
| 41 | 0.6128 | 6138 | 6149 | 6160 | 6170 | 6180 | 6191 | 6201 | 6212 | 6222 | 10 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 42 | 0.6232 | 6243 | 6253 | 6263 | 6274 | 6284 | 6294 | 6304 | 6314 | 6325 | 10 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 43 | 0.6335 | 6345 | 6355 | 6365 | 6375 | 6385 | 6395 | 6405 | 6415 | 6425 | 10 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 44 | 0.6435 | 6444 | 6454 | 6464 | 6474 | 6484 | 6493 | 6503 | 6513 | 6522 | 10 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 45 | 0.6532 | 6542 | 6551 | 6561 | 6571 | 6580 | 6590 | 6599 | 6609 | 6618 | 10 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 46 | 0.6628 | 6637 | 6646 | 6656 | 6665 | 6675 | 6684 | 6693 | 6702 | 6712 | 9 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| 47 | 0.6721 | 6730 | 6739 | 6749 | 6758 | 6767 | 6776 | 6785 | 6794 | 6803 | 9 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| 48 | 0.6812 | 6821 | 6830 | 6839 | 6848 | 6857 | 6866 | 6875 | 6884 | 6893 | 9 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| 49 | 0.6902 | 6911 | 6920 | 6928 | 6937 | 6946 | 6955 | 6964 | 6972 | 6981 | 9 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| 50 | 0.6990 | 6998 | 7007 | 7016 | 7024 | 7033 | 7042 | 7050 | 7059 | 7067 | 9 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| 51 | 0.7076 | 7084 | 7093 | 7101 | 7110 | 7118 | 7126 | 7135 | 7143 | 7152 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 52 | 0.7160 | 7168 | 7177 | 7185 | 7193 | 7202 | 7210 | 7218 | 7226 | 7235 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |



## COMMON LOGARITHMIC TABLES $\log_{10} x$

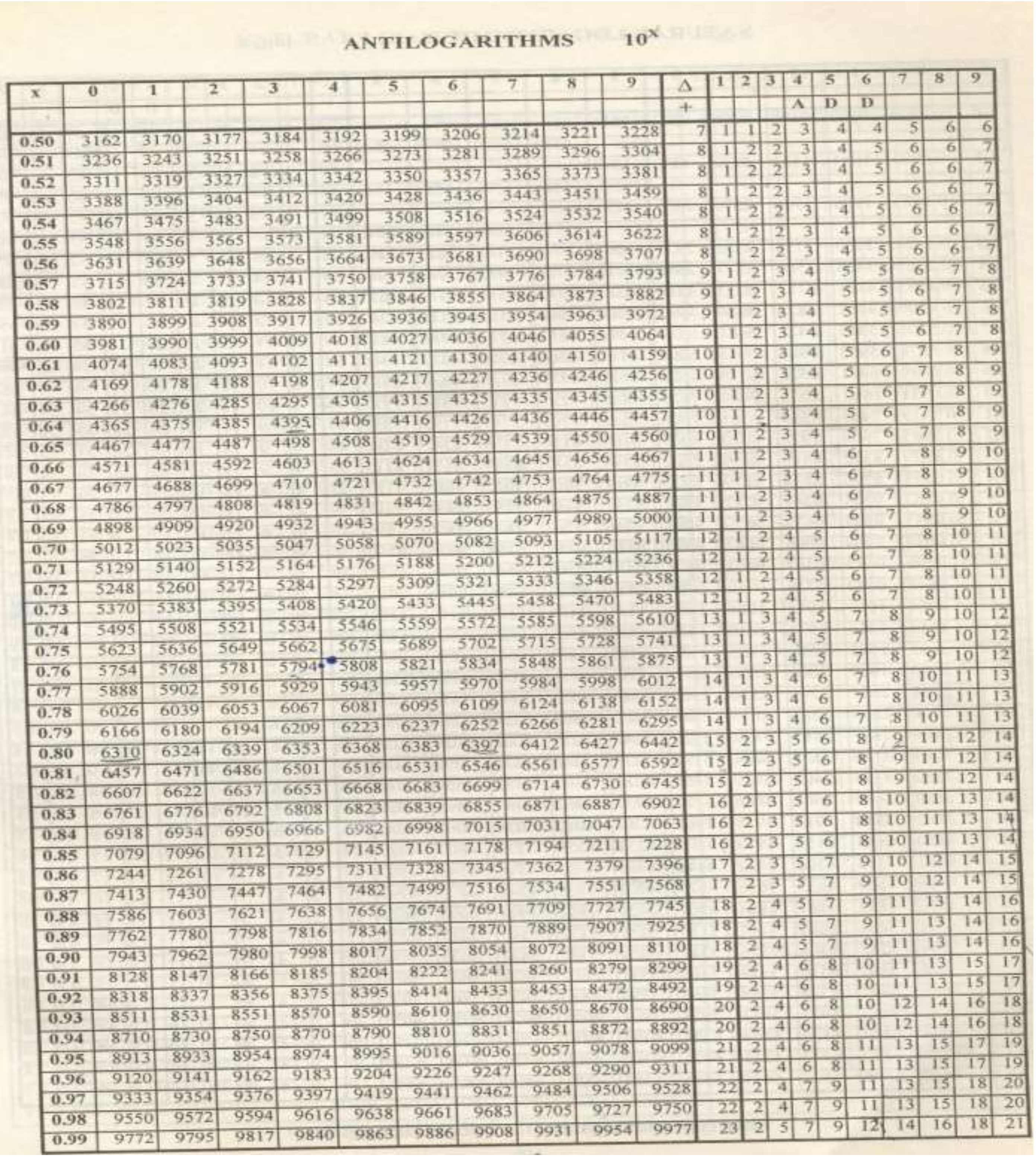
| x | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Δ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | + | | | | A | D | D | | | |
| 53 | 0.7243 | 7251 | 7259 | 7267 | 7275 | 7284 | 7292 | 7300 | 7308 | 7316 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 54 | 0.7324 | 7332 | 7340 | 7348 | 7356 | 7364 | 7372 | 7380 | 7388 | 7396 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 55 | 0.7404 | 7412 | 7419 | 7427 | 7435 | 7443 | 7451 | 7459 | 7466 | 7474 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 56 | 0.7482 | 7490 | 7497 | 7505 | 7513 | 7520 | 7528 | 7536 | 7543 | 7551 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 57 | 0.7559 | 7566 | 7574 | 7582 | 7589 | 7597 | 7604 | 7612 | 7619 | 7627 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 58 | 0.7634 | 7642 | 7649 | 7657 | 7664 | 7672 | 7679 | 7686 | 7694 | 7701 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 59 | 0.7709 | 7716 | 7723 | 7731 | 7738 | 7745 | 7752 | 7760 | 7767 | 7774 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 60 | 0.7782 | 7789 | 7796 | 7803 | 7810 | 7818 | 7825 | 7832 | 7839 | 7846 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 61 | 0.7853 | 7860 | 7868 | 7875 | 7882 | 7889 | 7896 | 7903 | 7910 | 7917 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 62 | 0.7924 | 7931 | 7938 | 7945 | 7952 | 7959 | 7966 | 7973 | 7980 | 7987 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 63 | 0.7993 | 8000 | 8007 | 8014 | 8021 | 8028 | 8035 | 8041 | 8048 | 8055 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 64 | 0.8062 | 8069 | 8075 | 8082 | 8089 | 8096 | 8102 | 8109 | 8116 | 8122 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 65 | 0.8129 | 8136 | 8142 | 8149 | 8156 | 8162 | 8169 | 8176 | 8182 | 8189 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 66 | 0.8195 | 8202 | 8209 | 8215 | 8222 | 8228 | 8235 | 8241 | 8248 | 8254 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 67 | 0.8261 | 8267 | 8274 | 8280 | 8287 | 8293 | 8299 | 8306 | 8312 | 8319 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 68 | 0.8325 | 8331 | 8338 | 8344 | 8351 | 8357 | 8363 | 8370 | 8376 | 8382 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 69 | 0.8388 | 8395 | 8401 | 8407 | 8414 | 8420 | 8426 | 8432 | 8439 | 8445 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 70 | 0.8451 | 8457 | 8463 | 8470 | 8476 | 8482 | 8488 | 8494 | 8500 | 8506 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 71 | 0.8513 | 8519 | 8525 | 8531 | 8537 | 8543 | 8549 | 8555 | 8561 | 8567 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 72 | 0.8573 | 8579 | 8585 | 8591 | 8597 | 8603 | 8609 | 8615 | 8621 | 8627 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 73 | 0.8633 | 8639 | 8645 | 8651 | 8657 | 8663 | 8669 | 8675 | 8681 | 8686 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 74 | 0.8692 | 8698 | 8704 | 8710 | 8716 | 8722 | 8727 | 8733 | 8739 | 8745 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 75 | 0.8751 | 8756 | 8762 | 8768 | 8774 | 8779 | 8785 | 8791 | 8797 | 8802 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 76 | 0.8808 | 8814 | 8820 | 8825 | 8831 | 8837 | 8842 | 8848 | 8854 | 8859 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 77 | 0.8865 | 8871 | 8876 | 8882 | 8887 | 8893 | 8899 | 8904 | 8910 | 8915 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 78 | 0.8921 | 8927 | 8932 | 8938 | 8943 | 8949 | 8954 | 8960 | 8965 | 8971 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 79 | 0.8976 | 8982 | 8987 | 8993 | 8998 | 9004 | 9009 | 9015 | 9020 | 9025 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 80 | 0.9031 | 9036 | 9042 | 9047 | 9053 | 9058 | 9063 | 9069 | 9074 | 9079 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 81 | 0.9085 | 9090 | 9096 | 9101 | 9106 | 9112 | 9117 | 9122 | 9128 | 9133 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 82 | 0.9138 | 9143 | 9149 | 9154 | 9159 | 9165 | 9170 | 9175 | 9180 | 9186 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 83 | 0.9191 | 9196 | 9201 | 9206 | 9212 | 9217 | 9222 | 9227 | 9232 | 9238 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 84 | 0.9243 | 9248 | 9253 | 9258 | 9263 | 9269 | 9274 | 9279 | 9284 | 9289 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 85 | 0.9294 | 9299 | 9304 | 9309 | 9315 | 9320 | 9325 | 9330 | 9335 | 9340 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 86 | 0.9345 | 9350 | 9355 | 9360 | 9365 | 9370 | 9375 | 9380 | 9385 | 9390 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 87 | 0.9395 | 9400 | 9405 | 9410 | 9415 | 9420 | 9425 | 9430 | 9435 | 9440 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 88 | 0.9445 | 9450 | 9455 | 9460 | 9465 | 9469 | 9474 | 9479 | 9484 | 9489 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 89 | 0.9494 | 9499 | 9504 | 9509 | 9513 | 9518 | 9523 | 9528 | 9533 | 9538 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 90 | 0.9542 | 9547 | 9552 | 9557 | 9562 | 9566 | 9571 | 9576 | 9581 | 9586 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 91 | 0.9590 | 9595 | 9600 | 9605 | 9609 | 9614 | 9619 | 9624 | 9628 | 9633 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 92 | 0.9638 | 9643 | 9647 | 9652 | 9657 | 9661 | 9666 | 9671 | 9675 | 9680 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 93 | 0.9685 | 9689 | 9694 | 9699 | 9703 | 9708 | 9713 | 9717 | 9722 | 9727 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 94 | 0.9731 | 9736 | 9741 | 9745 | 9750 | 9754 | 9759 | 9763 | 9768 | 9773 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 95 | 0.9777 | 9782 | 9786 | 9791 | 9795 | 9800 | 9805 | 9809 | 9814 | 9818 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 96 | 0.9823 | 9827 | 9832 | 9836 | 9841 | 9845 | 9850 | 9854 | 9859 | 9863 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 97 | 0.9868 | 9872 | 9877 | 9881 | 9886 | 9890 | 9894 | 9899 | 9903 | 9908 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 98 | 0.9912 | 9917 | 9921 | 9926 | 9930 | 9934 | 9939 | 9943 | 9948 | 9952 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 99 | 0.9956 | 9961 | 9965 | 9969 | 9974 | 9978 | 9983 | 9987 | 9991 | 9996 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |


विद्यया च विमुच्यते
SANSKRITI
THE CIVIL SERVICES SCHOOL



## ANTILOGARITHMS $10^x$

| x | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Δ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  |  |  | + |  |  |  | A | D | D |  |  |  |
| 0.00 | 1000 | 1002 | 1005 | 1007 | 1009 | 1012 | 1014 | 1016 | 1019 | 1021 | 2 | 0 | 0 | 1 | 1 | 1 | 1 | 1 | 2 | 2 |
| 0.01 | 1023 | 1026 | 1028 | 1030 | 1033 | 1035 | 1038 | 1040 | 1042 | 1045 | 2 | 0 | 0 | 1 | 1 | 1 | 1 | 1 | 2 | 2 |
| 0.02 | 1047 | 1050 | 1052 | 1054 | 1057 | 1059 | 1062 | 1064 | 1067 | 1069 | 2 | 0 | 0 | 1 | 1 | 1 | 1 | 1 | 2 | 2 |
| 0.03 | 1072 | 1074 | 1076 | 1079 | 1081 | 1084 | 1086 | 1089 | 1091 | 1094 | 2 | 0 | 0 | 1 | 1 | 1 | 1 | 1 | 2 | 2 |
| 0.04 | 1096 | 1099 | 1102 | 1104 | 1107 | 1109 | 1112 | 1114 | 1117 | 1119 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.05 | 1122 | 1125 | 1127 | 1130 | 1132 | 1135 | 1138 | 1140 | 1143 | 1146 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.06 | 1148 | 1151 | 1153 | 1156 | 1159 | 1161 | 1164 | 1167 | 1169 | 1172 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.07 | 1175 | 1178 | 1180 | 1183 | 1186 | 1189 | 1191 | 1194 | 1197 | 1199 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.08 | 1202 | 1205 | 1208 | 1211 | 1213 | 1216 | 1219 | 1222 | 1225 | 1227 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.09 | 1230 | 1233 | 1236 | 1239 | 1242 | 1245 | 1247 | 1250 | 1253 | 1256 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.10 | 1259 | 1262 | 1265 | 1268 | 1271 | 1274 | 1276 | 1279 | 1282 | 1285 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.11 | 1288 | 1291 | 1294 | 1297 | 1300 | 1303 | 1306 | 1309 | 1312 | 1315 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.12 | 1318 | 1321 | 1324 | 1327 | 1330 | 1334 | 1337 | 1340 | 1343 | 1346 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.13 | 1349 | 1352 | 1355 | 1358 | 1361 | 1365 | 1368 | 1371 | 1374 | 1377 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.14 | 1380 | 1384 | 1387 | 1390 | 1393 | 1396 | 1400 | 1403 | 1406 | 1409 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.15 | 1413 | 1416 | 1419 | 1422 | 1426 | 1429 | 1432 | 1435 | 1439 | 1442 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.16 | 1445 | 1449 | 1452 | 1455 | 1459 | 1462 | 1466 | 1469 | 1472 | 1476 | 3 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| 0.17 | 1479 | 1483 | 1486 | 1489 | 1493 | 1496 | 1500 | 1503 | 1507 | 1510 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.18 | 1514 | 1517 | 1521 | 1524 | 1528 | 1531 | 1535 | 1538 | 1542 | 1545 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.19 | 1549 | 1552 | 1556 | 1560 | 1563 | 1567 | 1570 | 1574 | 1578 | 1581 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.20 | 1585 | 1589 | 1592 | 1596 | 1600 | 1603 | 1607 | 1611 | 1614 | 1618 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.21 | 1622 | 1626 | 1629 | 1633 | 1637 | 1641 | 1644 | 1648 | 1652 | 1656 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.22 | 1660 | 1663 | 1667 | 1671 | 1675 | 1679 | 1683 | 1687 | 1690 | 1694 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.23 | 1698 | 1702 | 1706 | 1710 | 1714 | 1718 | 1722 | 1726 | 1730 | 1734 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.24 | 1738 | 1742 | 1746 | 1750 | 1754 | 1758 | 1762 | 1766 | 1770 | 1774 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.25 | 1778 | 1782 | 1786 | 1791 | 1795 | 1799 | 1803 | 1807 | 1811 | 1816 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.26 | 1820 | 1824 | 1828 | 1832 | 1837 | 1841 | 1845 | 1849 | 1854 | 1858 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.27 | 1862 | 1866 | 1871 | 1875 | 1879 | 1884 | 1888 | 1892 | 1897 | 1901 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.28 | 1905 | 1910 | 1914 | 1919 | 1923 | 1928 | 1932 | 1936 | 1941 | 1945 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.29 | 1950 | 1954 | 1959 | 1963 | 1968 | 1972 | 1977 | 1982 | 1986 | 1991 | 4 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| 0.30 | 1995 | 2000 | 2004 | 2009 | 2014 | 2018 | 2023 | 2028 | 2032 | 2037 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 0.31 | 2042 | 2046 | 2051 | 2056 | 2061 | 2065 | 2070 | 2075 | 2080 | 2084 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 0.32 | 2089 | 2094 | 2099 | 2104 | 2109 | 2113 | 2118 | 2123 | 2128 | 2133 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 0.33 | 2138 | 2143 | 2148 | 2153 | 2158 | 2163 | 2168 | 2173 | 2178 | 2183 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 0.34 | 2188 | 2193 | 2198 | 2203 | 2208 | 2213 | 2218 | 2223 | 2228 | 2234 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 0.35 | 2239 | 2244 | 2249 | 2254 | 2259 | 2265 | 2270 | 2275 | 2280 | 2286 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 0.36 | 2291 | 2296 | 2301 | 2307 | 2312 | 2317 | 2323 | 2328 | 2333 | 2339 | 5 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 0.37 | 2344 | 2350 | 2355 | 2360 | 2366 | 2371 | 2377 | 2382 | 2388 | 2393 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 0.38 | 2399 | 2404 | 2410 | 2415 | 2421 | 2427 | 2432 | 2438 | 2443 | 2449 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 0.39 | 2455 | 2460 | 2466 | 2472 | 2477 | 2483 | 2489 | 2495 | 2500 | 2506 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 0.40 | 2512 | 2518 | 2523 | 2529 | 2535 | 2541 | 2547 | 2553 | 2559 | 2564 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 0.41 | 2570 | 2576 | 2582 | 2588 | 2594 | 2600 | 2606 | 2612 | 2618 | 2624 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 0.42 | 2630 | 2636 | 2642 | 2649 | 2655 | 2661 | 2667 | 2673 | 2679 | 2685 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 0.43 | 2692 | 2698 | 2704 | 2710 | 2716 | 2723 | 2729 | 2735 | 2742 | 2748 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 0.44 | 2754 | 2761 | 2767 | 2773 | 2780 | 2786 | 2793 | 2799 | 2805 | 2812 | 6 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 0.45 | 2818 | 2825 | 2831 | 2838 | 2844 | 2851 | 2858 | 2864 | 2871 | 2877 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 0.46 | 2884 | 2891 | 2897 | 2904 | 2911 | 2917 | 2924 | 2931 | 2938 | 2944 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 0.47 | 2951 | 2958 | 2965 | 2972 | 2979 | 2985 | 2992 | 2999 | 3006 | 3013 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 0.48 | 3020 | 3027 | 3034 | 3041 | 3048 | 3055 | 3062 | 3069 | 3076 | 3083 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 0.49 | 3090 | 3097 | 3105 | 3112 | 3119 | 3126 | 3133 | 3141 | 3148 | 3155 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |



## ANTILOGARITHMS $10^x$

| x | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Δ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | + | | | | A | D | D | | | |
| 0.50 | 3162 | 3170 | 3177 | 3184 | 3192 | 3199 | 3206 | 3214 | 3221 | 3228 | 7 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 0.51 | 3236 | 3243 | 3251 | 3258 | 3266 | 3273 | 3281 | 3289 | 3296 | 3304 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 0.52 | 3311 | 3319 | 3327 | 3334 | 3342 | 3350 | 3357 | 3365 | 3373 | 3381 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 0.53 | 3388 | 3396 | 3404 | 3412 | 3420 | 3428 | 3436 | 3443 | 3451 | 3459 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 0.54 | 3467 | 3475 | 3483 | 3491 | 3499 | 3508 | 3516 | 3524 | 3532 | 3540 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 0.55 | 3548 | 3556 | 3565 | 3573 | 3581 | 3589 | 3597 | 3606 | 3614 | 3622 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 0.56 | 3631 | 3639 | 3648 | 3656 | 3664 | 3673 | 3681 | 3690 | 3698 | 3707 | 8 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 0.57 | 3715 | 3724 | 3733 | 3741 | 3750 | 3758 | 3767 | 3776 | 3784 | 3793 | 9 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| 0.58 | 3802 | 3811 | 3819 | 3828 | 3837 | 3846 | 3855 | 3864 | 3873 | 3882 | 9 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| 0.59 | 3890 | 3899 | 3908 | 3917 | 3926 | 3936 | 3945 | 3954 | 3963 | 3972 | 9 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| 0.60 | 3981 | 3990 | 3999 | 4009 | 4018 | 4027 | 4036 | 4046 | 4055 | 4064 | 9 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| 0.61 | 4074 | 4083 | 4093 | 4102 | 4111 | 4121 | 4130 | 4140 | 4150 | 4159 | 10 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 0.62 | 4169 | 4178 | 4188 | 4198 | 4207 | 4217 | 4227 | 4236 | 4246 | 4256 | 10 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 0.63 | 4266 | 4276 | 4285 | 4295 | 4305 | 4315 | 4325 | 4335 | 4345 | 4355 | 10 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 0.64 | 4365 | 4375 | 4385 | 4395 | 4406 | 4416 | 4426 | 4436 | 4446 | 4457 | 10 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 0.65 | 4467 | 4477 | 4487 | 4498 | 4508 | 4519 | 4529 | 4539 | 4550 | 4560 | 10 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 0.66 | 4571 | 4581 | 4592 | 4603 | 4613 | 4624 | 4634 | 4645 | 4656 | 4667 | 11 | 1 | 2 | 3 | 4 | 6 | 7 | 8 | 9 | 10 |
| 0.67 | 4677 | 4688 | 4699 | 4710 | 4721 | 4732 | 4742 | 4753 | 4764 | 4775 | 11 | 1 | 2 | 3 | 4 | 6 | 7 | 8 | 9 | 10 |
| 0.68 | 4786 | 4797 | 4808 | 4819 | 4831 | 4842 | 4853 | 4864 | 4875 | 4887 | 11 | 1 | 2 | 3 | 4 | 6 | 7 | 8 | 9 | 10 |
| 0.69 | 4898 | 4909 | 4920 | 4932 | 4943 | 4955 | 4966 | 4977 | 4989 | 5000 | 11 | 1 | 2 | 3 | 4 | 6 | 7 | 8 | 9 | 10 |
| 0.70 | 5012 | 5023 | 5035 | 5047 | 5058 | 5070 | 5082 | 5093 | 5105 | 5117 | 12 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| 0.71 | 5129 | 5140 | 5152 | 5164 | 5176 | 5188 | 5200 | 5212 | 5224 | 5236 | 12 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| 0.72 | 5248 | 5260 | 5272 | 5284 | 5297 | 5309 | 5321 | 5333 | 5346 | 5358 | 12 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| 0.73 | 5370 | 5383 | 5395 | 5408 | 5420 | 5433 | 5445 | 5458 | 5470 | 5483 | 12 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| 0.74 | 5495 | 5508 | 5521 | 5534 | 5546 | 5559 | 5572 | 5585 | 5598 | 5610 | 13 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 10 | 12 |
| 0.75 | 5623 | 5636 | 5649 | 5662 | 5675 | 5689 | 5702 | 5715 | 5728 | 5741 | 13 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 10 | 12 |
| 0.76 | 5754 | 5768 | 5781 | 5794 | 5808 | 5821 | 5834 | 5848 | 5861 | 5875 | 13 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 10 | 12 |
| 0.77 | 5888 | 5902 | 5916 | 5929 | 5943 | 5957 | 5970 | 5984 | 5998 | 6012 | 14 | 1 | 3 | 4 | 6 | 7 | 8 | 10 | 11 | 13 |
| 0.78 | 6026 | 6039 | 6053 | 6067 | 6081 | 6095 | 6109 | 6124 | 6138 | 6152 | 14 | 1 | 3 | 4 | 6 | 7 | 8 | 10 | 11 | 13 |
| 0.79 | 6166 | 6180 | 6194 | 6209 | 6223 | 6237 | 6252 | 6266 | 6281 | 6295 | 14 | 1 | 3 | 4 | 6 | 7 | 8 | 10 | 11 | 13 |
| 0.80 | 6310 | 6324 | 6339 | 6353 | 6368 | 6383 | 6397 | 6412 | 6427 | 6442 | 15 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 12 | 14 |
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| 0.84 | 6918 | 6934 | 6950 | 6966 | 6982 | 6998 | 7015 | 7031 | 7047 | 7063 | 16 | 2 | 3 | 5 | 6 | 8 | 10 | 11 | 13 | 14 |
| 0.85 | 7079 | 7096 | 7112 | 7129 | 7145 | 7161 | 7178 | 7194 | 7211 | 7228 | 16 | 2 | 3 | 5 | 6 | 8 | 10 | 11 | 13 | 14 |
| 0.86 | 7244 | 7261 | 7278 | 7295 | 7311 | 7328 | 7345 | 7362 | 7379 | 7396 | 17 | 2 | 3 | 5 | 7 | 9 | 10 | 12 | 14 | 15 |
| 0.87 | 7413 | 7430 | 7447 | 7464 | 7482 | 7499 | 7516 | 7534 | 7551 | 7568 | 17 | 2 | 3 | 5 | 7 | 9 | 10 | 12 | 14 | 15 |
| 0.88 | 7586 | 7603 | 7621 | 7638 | 7656 | 7674 | 7691 | 7709 | 7727 | 7745 | 18 | 2 | 4 | 5 | 7 | 9 | 11 | 13 | 14 | 16 |
| 0.89 | 7762 | 7780 | 7798 | 7816 | 7834 | 7852 | 7870 | 7889 | 7907 | 7925 | 18 | 2 | 4 | 5 | 7 | 9 | 11 | 13 | 14 | 16 |
| 0.90 | 7943 | 7962 | 7980 | 7998 | 8017 | 8035 | 8054 | 8072 | 8091 | 8110 | 18 | 2 | 4 | 5 | 7 | 9 | 11 | 13 | 14 | 16 |
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| 0.93 | 8511 | 8531 | 8551 | 8570 | 8590 | 8610 | 8630 | 8650 | 8670 | 8690 | 20 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| 0.94 | 8710 | 8730 | 8750 | 8770 | 8790 | 8810 | 8831 | 8851 | 8872 | 8892 | 20 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| 0.95 | 8913 | 8933 | 8954 | 8974 | 8995 | 9016 | 9036 | 9057 | 9078 | 9099 | 21 | 2 | 4 | 6 | 8 | 11 | 13 | 15 | 17 | 19 |
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| 0.97 | 9333 | 9354 | 9376 | 9397 | 9419 | 9441 | 9462 | 9484 | 9506 | 9528 | 22 | 2 | 4 | 7 | 9 | 11 | 13 | 15 | 18 | 20 |
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