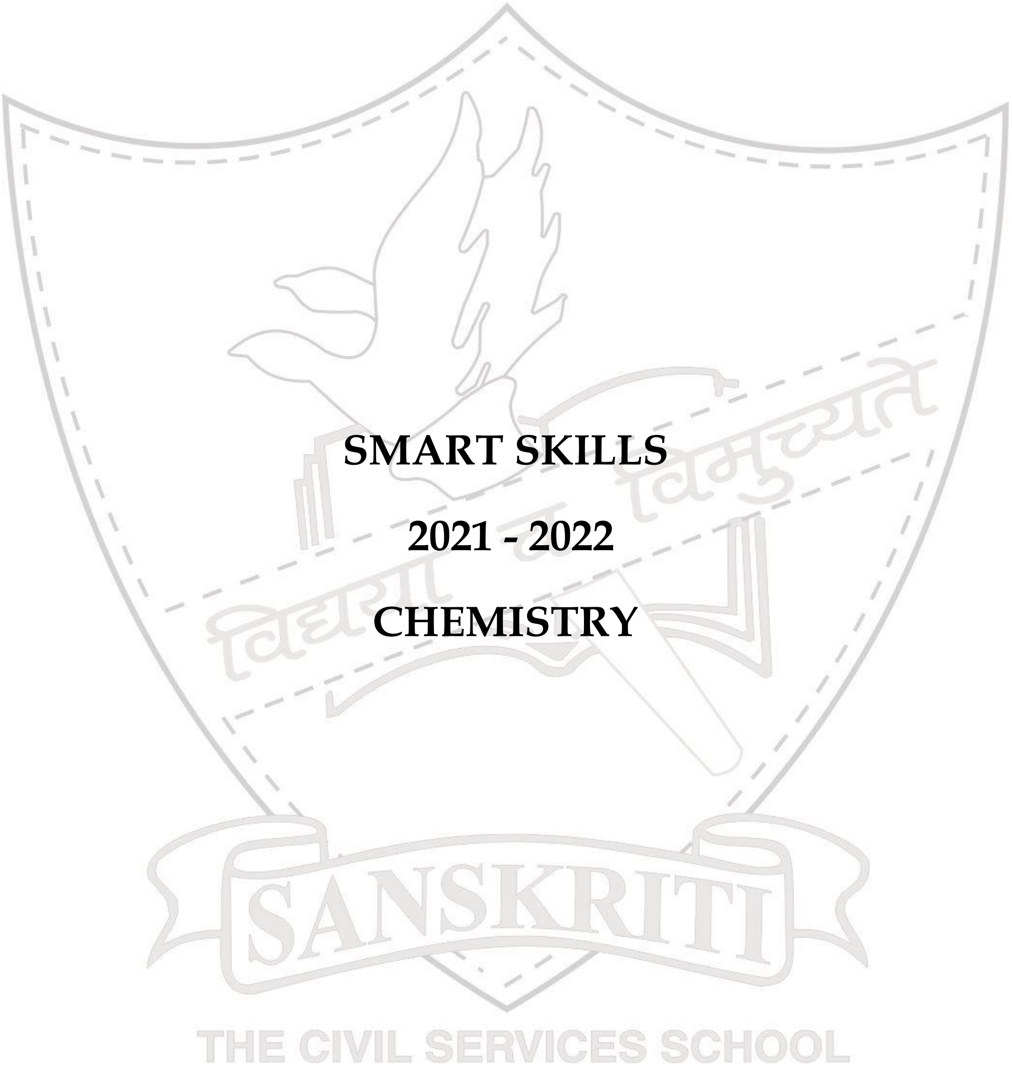


SMART SKILLS

2021 - 2022

CHEMISTRY

INDEX

CBSE SYLLABUS

Unit I: Solid State 10 Periods

Classification of solids based on different binding forces: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea). Unit cell in two dimensional and three dimensional lattices, calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell, point defects, electrical and magnetic properties. Band theory of metals, conductors, semiconductors and insulators and n and p type semiconductors.

Unit II: 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 III: 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 IV: 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 V: 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 VI: 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 VII: p-Block Elements 12 Periods

Group 15 elements: General introduction, electronic configuration, occurrence, oxidation states, trends in physical and chemical properties; nitrogen - preparation, properties and uses; compounds of nitrogen: preparation and properties of ammonia and nitric acid, oxides of nitrogen (structure only); Phosphorous-allotropic forms; compounds .of phosphorous: preparation and properties of phosphine, halides (PCI3, PCls) and oxoacids (elementary idea only)

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 VIII: "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 IX: 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 X: 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 XI: 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 XII: 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 XIII: 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 XIV: 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 XV: 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.

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 (HCl) 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-}; C2O42_ $CH_3COO^{-,}$

(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

Unit III: 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 IV: 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);

MONTH : JUNE, JULY

Unit IV: Chemical Kinetics (continued)

concept of collision theory (elementary idea, no mathematical treatment), Activation energy, Arrhenious equation

Unit II: 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 I: Solid State 10 Periods

Classification of solids based on different binding forces: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea). Unit cell in two dimensional and three dimensional lattices, calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell, point defects, electrical and magnetic properties.

Band theory of metals, conductors, semiconductors and insulators and n and p type semiconductors.

Unit V: Surface Chemistry

Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, colloids 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 X: 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 XI: 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.

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 : AUGUST

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

Unit XIII: 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.

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

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

MONTH: SEPTEMBER- OCTOBER

Unit VI: p-Block Elements (Periods 14)

Group 15 elements: General introduction, electronic configuration, occurrence, oxidation states, trends in physical and chemical properties; nitrogen - preparation, properties and uses; compounds of nitrogen: preparation and properties of ammonia and nitric acid, oxides of nitrogen (structure only); Phosphorous-allotropic forms; compounds .of phosphorous: preparation and properties of phosphine, halides (PCl_3, PCls) and oxoacids (elementary idea only)

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.

Unit IX: 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 VIII: 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. 11,12

Preparation of Potassium Ferric Oxalate.

EXPERIMENT No.: 13-18

Tests for the functional groups present in organic compounds:

Alcoholic, phenolic, aldehydic, ketonic, carboxylic and amino (primary) groups.

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.: 20-21

Preparation of one lyophilic and one lyophobic sol.

(a) Lyophilic sol- starch

(b) Lyophobic sol- ferric hydroxide.

EXPERIMENT No.: 21-23

Characteristic tests of carbohydrates, fats and proteins in pure samples and their detection in given food stuffs.

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

MONTH: NOVEMBER

Unit VI: 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 XV: 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.

Unit XVI: 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.

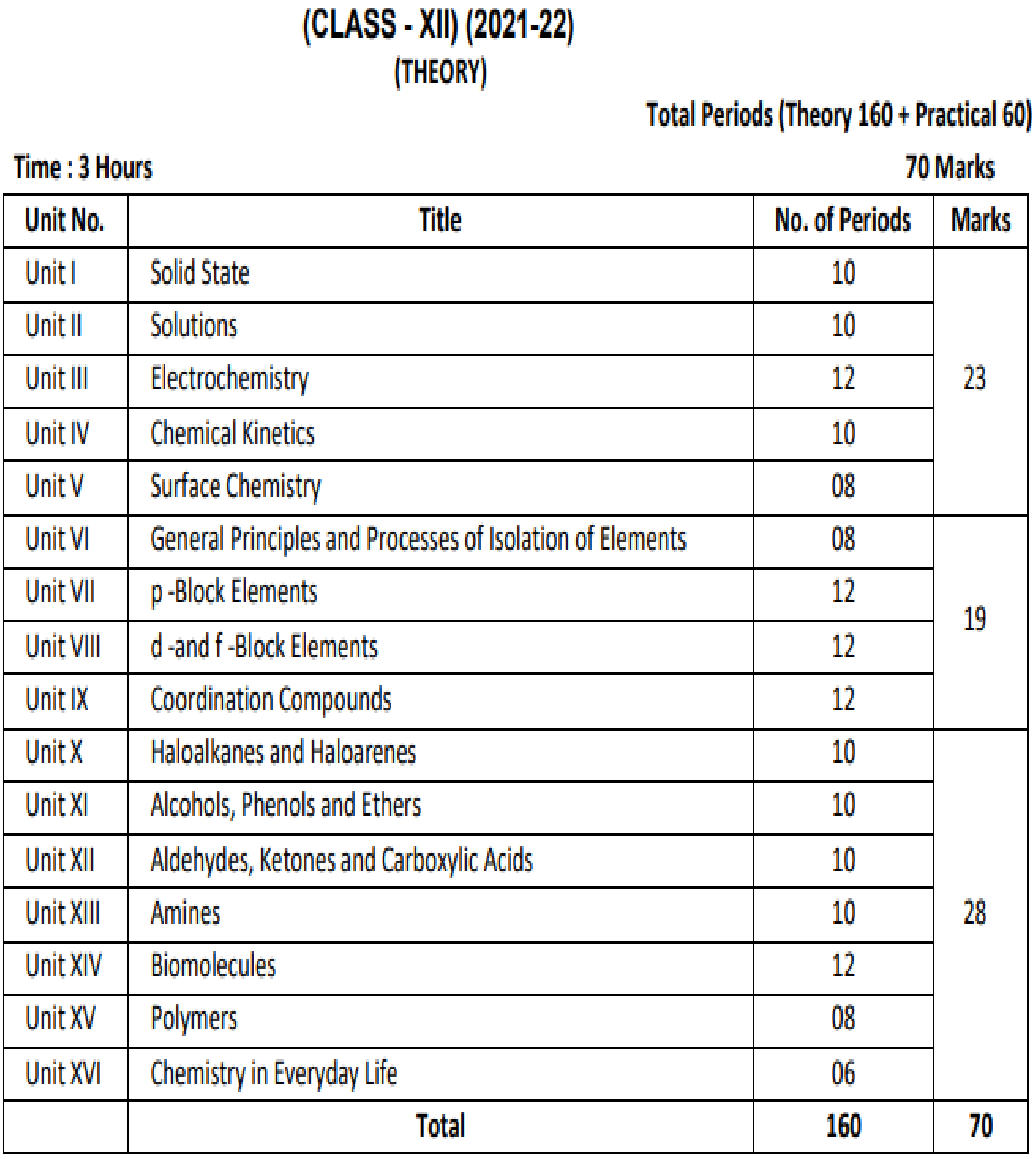
Cleansing agents - soaps and detergents, cleansing action

Unit XIV: 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.



(CLASS - XII) (2021-22)

(THEORY)

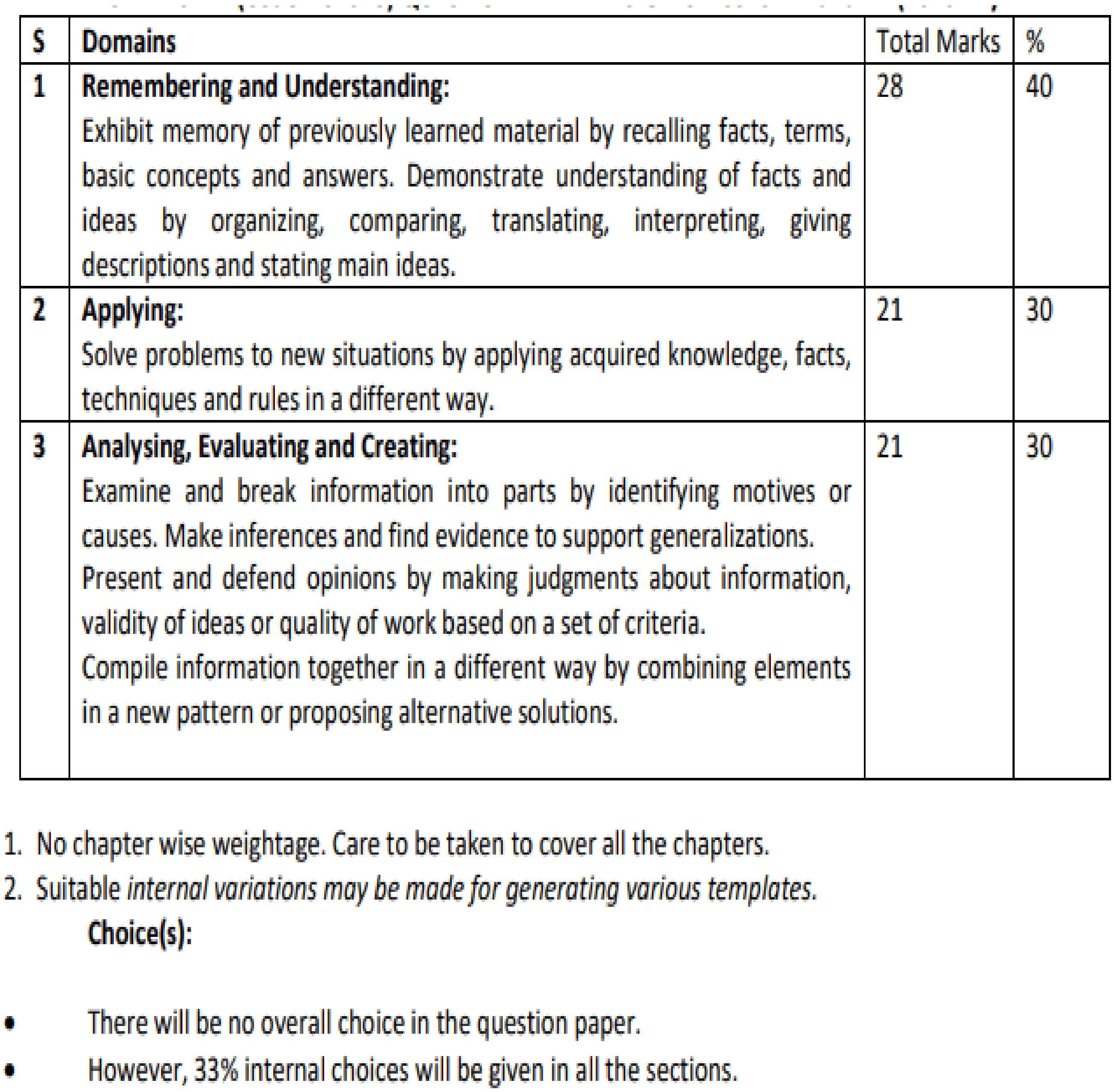
Total Periods (Theory 160 + Practical 60)

Time : 3 Hours **70 Marks**

Unit No.	Title	No. of Periods	Marks
Unit I	Solid State	10	23
Unit II	Solutions	10	
Unit III	Electrochemistry	12	
Unit IV	Chemical Kinetics	10	
Unit V	Surface Chemistry	08	
Unit VI	General Principles and Processes of Isolation of Elements	08	19
Unit VII	p -Block Elements	12	
Unit VIII	d -and f -Block Elements	12	
Unit IX	Coordination Compounds	12	
Unit X	Haloalkanes and Haloarenes	10	28
Unit XI	Alcohols, Phenols and Ethers	10	
Unit XII	Aldehydes, Ketones and Carboxylic Acids	10	
Unit XIII	Amines	10	
Unit XIV	Biomolecules	12	
Unit XV	Polymers	08	
Unit XVI	Chemistry in Everyday Life	06	
	Total	**160**	**70**

CHEMISTRY (CODE-043)
QUESTION PAPER DESIGN
CLASS - XII (2021-22)

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



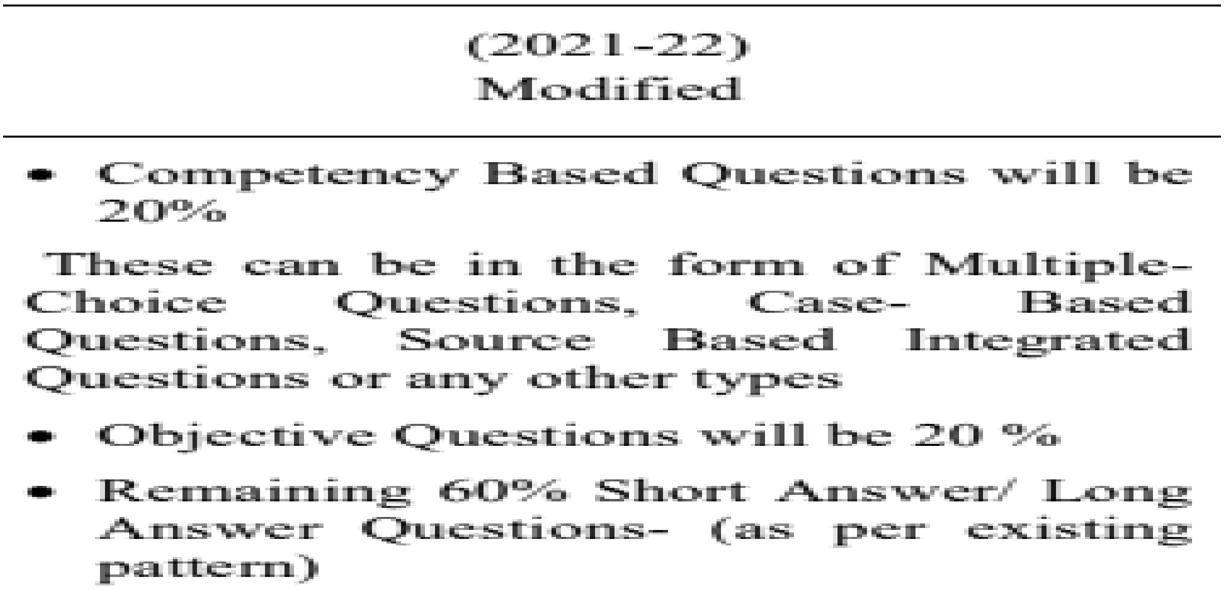
S	Domains	Total Marks	%
1	**Remembering and Understanding:** Exhibit memory of previously learned material by recalling facts, terms, basic concepts and answers. Demonstrate understanding of facts and ideas by organizing, comparing, translating, interpreting, giving descriptions and stating main ideas.	28	40
2	**Applying:** Solve problems to new situations by applying acquired knowledge, facts, techniques and rules in a different way.	21	30
3	**Analysing, Evaluating and Creating:** Examine and break information into parts by identifying motives or causes. Make inferences and find evidence to support generalizations. Present and defend opinions by making judgments about information, validity of ideas or quality of work based on a set of criteria. Compile information together in a different way by combining elements in a new pattern or proposing alternative solutions.	21	30

1. No chapter wise weightage. Care to be taken to cover all the chapters.
2. Suitable *internal variations may be made for generating various templates.*

Choice(s):

- There will be no overall choice in the question paper.
- However, 33% internal choices will be given in all the sections.

QUESTION WISE BREAK UP



(2021-22)
Modified

- Competency Based Questions will be 20%

These can be in the form of Multiple-Choice Questions, Case- Based Questions, Source Based Integrated Questions or any other types

- Objective Questions will be 20 %
- Remaining 60% Short Answer/ Long Answer Questions- (as per existing pattern)

Assignment
Chapter 1: Solid State

Learning Outcomes: The learners-

- communicates the findings and conclusions effectively, of different types of solids based on its classification
- exhibits creativity in designing models of solids
- derives formulae, and does calculations
- calculates using the data given
- describes importance of solid state in daily life
- describes general characteristic s of solid state;
- distinguishes between amorphous and crystalline solids;
- classifies crystalline solids on the basis of the nature of binding forces;
- defines crystal lattice and unit cell;
- distinguish between unit cells of different types of crystal lattices;
- explains close packing of particles

1. In which pair most efficient packing is present?
(i) hcp and bcc
(ii) hcp and ccp
(iii) bcc and ccp
(iv) bcc and simple cubic cell

2. Which kind of defects are introduced by doping?
(i) Dislocation defect
(ii) Schottky defect
(iii) Frenkel defects
(iv) Electronic defects

3. (a) An element has atomic mass 93 g mol–1 and density 11.5 g cm–3. If the edge length of its unit cell is 300 pm, identify the type of unit cell.
(b) Write any two differences between amorphous solids and crystalline solids.

4. (a) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a f.c.c. structure. (Atomic mass of Al = 27 g mol–1)
(b) Give reasons :
(i) In stoichiometric defects, NaCl exhibits Schottky defect and not Frenkel defect.
(ii) Silicon on doping with Phosphorus forms n-type semiconductor.
(iii) Ferrimagnetic substances show better magnetism than antiferromagnetic substances.

5. What is the maximum possible coordination number of an atom in
(a) hcp crystal structure
(b) ccp crystal structure of an element?

6. a) What is meant by 'doping' in a semiconductor?
b) Account for the following:
(i) Impurity doped silicon is a semiconductor.
(ii) alkali metal halides sometimes coloured, which are otherwise colourless

7. Which point defect in crystals
(i) does not alter the density of the solid
(ii) decreases the density of the solid
(iii) Increases the density of the solid?

8.Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.
a) tetra phosphorus decaoxide (P_4O_{10}) (c) Graphite
b) Brass (d) Ammonium Phosphate
e) Rb (f) SiC

9. Examine the illustration of a portion of the defective crystal given below and answer the following questions.
(a) What are these type of vacancy defects called?
(b) How is the density of a crystal affected by these defects?
(c) What type of ionic substances show such defect?
(d) How is the stoichiometry of the compound affected?

10 . In an ionic compound the anion (N-) form cubic close type of packing. While the cation (M+) ions occupy one third of the tetrahedral voids. Deduce the empirical formula of the compound and the coordination number of (M+) ions.

11. What is the formula of a compound in which the element Y forms the ccp lattice and atom X occupy 1/3rd of the tetrahedral voids?

12. (i) What type of magnetism is shown in the following alignment of magnetic moment?
↑ ↓↑↓ ↑ ↓↑↓ ↑↓
(ii) What type of semiconductor is produced when boron is doped with silicon?
(iii) What type of magnetism is shown by a substance if magnetic moments of domains are arranged in same direction ?

13. 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? (r = 137 pm)

14. An element with density 11.2 gcm^{-3} forms a f.c.c. lattice with edge length of 4 X 10-8 cm. Calculate the atomic mass of the element. (Given: $N_A = 6.022 \times 10^{23}$ mol^{-1})

15. An element crystallizes in a f.c.c. lattice with cell edge of 250 pm. Calculate the density if 300 g of this element contain 2 X 10^{-24} atoms.

16. Analysis shows that metal oxide has the formula $M_{0.96}O$. What fractions of metal exist as M^{+2} and M^{+3} ions? (M^{2+} =0.916; M^{3+} = 0.08)

17. Iron has a body centred cubic unit cells with cell edge of 286.65 pm. The density of iron is 7.874 g cm^{-3}. Use this information to calculate Avogadro's number. (At. Mass of Fe = 55.845 $gmol^{-1}$) (6.02×10^{23} mol^{-1})

18. Which of the following is an amorphous solid?

a) Graphite (C)
b) Quartz (SiO2)

c) Chrome alum
d) Silicon carbide (SiC)

19. Iodine molecules are held in the crystal lattice by :

a) London Forces
b) dipole-dipole interactions
c) covalent bonds
d) coulombic forces

20. Cations are present in the interstitial sites in

a) Frenkel defect
b) Schottky defect
c) vacancy defect
d) metal deficiency defect

21. Silicon doped with electron rich impurity forms

a) p-type semiconductor
b) n- type semiconductor
c) intrinsic semiconductor
d) insulator

In the following questions, a statement of assertion (A) is given followed by a corresponding statement of reason (R) just below it. Choose the correct answer out of the following choices:

(a)Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b)Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c)Assertion is correct statement but reason is wrong statement.
(d)Assertion is wrong statement but reason is correct statement

22. Assertion: The total number of atoms present in a simple cubic unit cell is one.

Reason: Simple cubic unit cell has atoms at its corners, each of which is shared between eight adjacent unit cells.

23 Assertion: Graphite is a good conductor of electricity however diamond belongs to the category of insulators.

Reason: Graphite is soft in nature on the other hand diamond is very hard and brittle.

24. Assertion: The packing efficiency is maximum for the fcc structure.

Reason: The coordination number is 12 in fcc structures.

More Practice
Solid State

1. The well known mineral fluorite is chemically calcium fluoride. It is known that in one unit cell of this mineral there are 4 Ca2+ ions and 8F- ions and that Ca^{2+} ions are arranged in a fcc lattice. The F- ions fill all tetrahedral holes in the face centred cubic lattice of Ca^{2+} ions. The edge of the unit cell is $5.46X10^{-8}$ cm in length. The density of the solid is 3.18g cm^{-3}. Use this I information to calculate Avogadro's number (Molar mass of Ca F_2 = 78.08 g mol-1)

2. Analysis shows that Nickel oxide has the formula Ni0.98O. What fractions of metal exist as Ni^{+2} and Ni^{+3} ions?

3. Aluminium metal forms a ccp crystal structure. Its atomic radius is 125 x 10^{-12} m.

i) Calculate the length of the side of the unit cell.
ii) How many such unit cells are there in 1.00 m^3 of Aluminium?

4. An element has a body centered cubic structure with a cell edge of 288 pm. The density of the element is 7.2g/cm^3. Calculate the number of atoms present in 208 g of the element.

5. Sodium has a bcc structure with nearest neighbor distance 365.9pm. Calculate its density.(Na = 23u)

Assignment
Chapter 2: Solutions

Learning Outcomes

- explains processes and different methods of measuring concentration.
- Learners will be able to understand the Concentration of solution in different units
- measures concentration of solutions using appropriate apparatus, instruments, methods and formulaes,
- Differentiate between different types of solutions
- applies learning to hypothetical situations - knowledge of colligative properties to finding molar mass of electrolytes
- will be able to draw connections between their previous knowledge of solubility and apply it to solubility of solids and gases in liquids.
- calculates using the data given,
- exhibits values of honesty, objectivity, rational thinking, while sharing experimental results and doing numerical calculations
- understand and classify solutions as ideal and non-ideal on the basis of Raoult's law
- explain Henry's law and Raoult's law and find difference and similarity between the two.
- Describe colligative properties of solutions and calculate the molar masses of the solutes

1. An ideal solution of two liquids is a solution in which each component obeys Raoult's law which states that the vapour pressure of any component in the solution depends on the mole fraction of that component in the solution and the vapour pressure of that component in the pure state. However, there are many solutions which do not obey Raoult's law. In other words, they show deviations from ideal behavior which may be positive or negative. However, in either case, corresponding to a particular composition, they form constant boiling mixtures called azeotropes.

   (a) Give an example of a mixture showing positive deviation and negative deviation from Raoult's law?

   (b) When an azeotropic solution of two liquids has boiling point lower than either of the two liquids, what type of azeotrope will it be?

   (c) A solution has a 1:4 mole ratio of pentane to hexane. The vapour pressures of the pure hydrocarbons at 20^{o}C are 440mm of Hg for pentane and 120mm of Hg for hexane in the vapour phase. Calculate the mole fraction of pentane in the vapour phase? (0.478)

2. van't Hoff factors x,y,z for association, dissociation and no change of solute in the solution respectively are n the order:

   (a) $x < y < z$ (b) $x > z > y$ (c) $x < z < y$ (d) $x > y > z$

3. At equilibrium the rate of dissolution of a solid solute in a volatile liquid solvent is:

   a) Less than the rate of crystallization

b) Greater than the rate of crystallization

c) Equal to the rate of crystallization

d) Zero.

4. Value of Henry's constant K_H:

a) Increases with increase in temperature

b) Decreases with increase in temperature

c) Remains constant

d) First increases then decreases

In the following questions, a statement of assertion (A) is given followed by a corresponding statement of reason (R) just below it. Choose the correct answer out of the following choices:

(a)Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b)Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c)Assertion is correct statement but reason is wrong statement.

(d)Assertion is wrong statement but reason is correct statement

5. Assertion: 0.1 M solution of glucose has higher increment in the freezing point than 0.1 M solution of urea.

Reason: K_f for both has different values.

6. Assertion: Molarity of a solution in liquid state changes with temperature.

Reason: The volume of a solution changes with change in temperature.

7. Assertion: When methyl alcohol is added to water, boiling point of water increases

Reason: When a volatile solute is added to a volatile solvent, elevation in boiling point is observed.

8. Assertion: When NaCl is added to water a depression in freezing point is observed .

Reason: The lowering of vapour pressure of a solution causes depression in the freezing point.

9. Assertion: When a solution is separated from the pure solvent by a semipermeable membrane, the solvent molecules pass through it from pure solvent side to the solution side.

   Reason: Diffusion of solvent occurs from a region of high concentration solution to a region of low concentration solution.

10. 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)

11. 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.

12. 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})

13. 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.

14. 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?

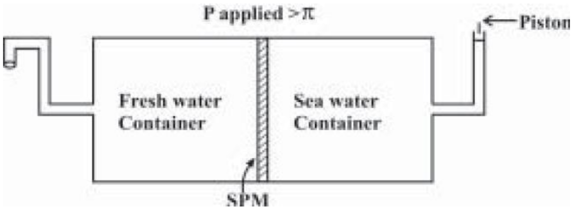
15. (a) Why is the vapour pressure of a solution of glucose in water lower than that of water?

    (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)

16. 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.

17. 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.

18. 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})

19. 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 ?

20. 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 ΔH_{mix} for positive deviation?

21. 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)

22. 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})

23. 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 $80.31^\circ C$. Determine the molar mass of this compound. (B.P. of pure benzene = $80.10^\circ C$ and K_b for benzene = $2.53^\circ C$ kg mol^{-})

    (152.21 g/mol)

24. A 1.00 molal aqueous solution of trichloroacetic acid (CCl_3COOH) is heated to its boiling point. The solution has the boiling point of $100.18^\circ C$. 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 25^0C. 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 25^0C.
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 25^0C, 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. (iii) 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 3: Electrochemistry

Learning Outcomes: The learner-

- draws labelled diagrams, flow charts and concept maps of commercial cells.
- Derive relation between standard potential of the cell, Gibbs energy and its equilibrium constant and solve numericals
- derives formulae and laws of conductance and electrochemical cells
- plans and conducts experiments to arrive at and verify the facts, principles, phenomena or to seek answers to queries on their own, such as factors affecting rusting and relate the various types of conductance on the basis of a formulae and verify it.
- communicates the findings and conclusions effectively and calculates using the data given,
- will be able to understand to calculate the emf of galvanic cell and .Gibbs energy of reaction and its equilibrium constant.
- exhibits values of honesty, objectivity, rational thinking, while sharing experimental results and doing numerical calculations.
- Define resistivity, conductivity , molar conductivity, conductivity at infinite dilution and solve related numerical. Enunciate Kohlrausch law and learn its applications.
- will be able to understand the variation of conductivity and molar conductivity of solutions with change in their concentration

1. If the E^o_{cell} for a given reaction has a negative value, then which of the following gives the correct relationships for the values of ΔG^0 and K_{eq}?

   (a) $\Delta G^0 > 0$; $K_{eq} < 1$ (b) $\Delta G^0 > 0$; $K_{eq} > 1$ (c) $\Delta G^0 < 0$; $K_{eq} > 1$ (d) $\Delta G^0 < 0$; $K_{eq} < 1$

2. The metal that cannot be obtained by electrolysis of an aqueous solution of its salt is
   (a) Ag (b) Na (c) Cu (d) Hg

In Q3 and Q4, a statement of assertion (A) is given followed by a corresponding statement of reason (R) just below it. Of the statements mark the correct answer as:
(i) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(ii) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(iii) Assertion is a correct statement but reason is wrong.
(iv) Assertion and reason both are incorrect statements.
(v) Assertion is wrong statement but reason is correct statement

3. **Assertion**: Conductivity of all electrolytes decreases on dilution.
   Reason: On dilution, number of ions per unit volume decreases.
4. **Assertion**:Current stops flowing when Ecell=0.
   Reason: Equilibrium of the cell reaction is attained.

5. 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)

6. For the reaction

$$2AgCl\ (s) + H_2\ (g)\ (1\ atm) \longrightarrow 2Ag(s) + 2\ H^+(0.1M) + 2Cl^-\ (0.1M)$$

$\triangle G^0 = -43600$ J at 25°C. Calculate the emf of the cell.

(0.344 V)

7. 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.

8. 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})

9. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2mol^{-1}. Given $\lambda^o(H^+) = 349.6$ $Scm^2mol^{-1}$and $\lambda^o(CH_3COO^-) = 40.9$ $Scm^2\ mol^{-1}$

10.
   i. Define molar conductivity and conductivity of a solution and write their units and the relation between the two.
   ii. How does molar conductivity change with change in concentration of solution for weak and strong electrolyte. Why does the conductivity of an electrolyte solution decrease with the decrease in concentration?
   iii. Define limiting molar conductivity.

11. 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.

12. 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 the Apollo Space Programme ?
   (iii) Which cell is used in automobiles and inverters ?
   (iv) Which cell does not have long life ?

13. 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 $0.146X10^{-3}$ Scm^{-1}? (0.219 cm^{-1})

14. 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.

15. 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.

16. 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.

17.

$Cu^{2+} + 2e^- \longrightarrow Cu \quad E^o = +0.34\ V$

$Ag^+ + e^- \longrightarrow Ag \quad E^o = +0.80\ V$

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.)

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

19. 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.

20. Following reactions occur at the cathode during the electrolysis of aqueous silver chloride solution:

$Ag^+ + e^- \longrightarrow Ag \quad E^o = +0.80\ V$

$H^+ + e^- \longrightarrow \frac{1}{2} H_2 \quad E^o = +0.00\ V$

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 3: Electrochemistry

1. Conductivity of 0.00241 M acetic acid is 7.896 X 10^{-5} Scm^{-1}. Calculate its molar conductivity. If Λo 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 ΔG^0 for the reaction.

   (given: $E^0_{Ag+/Ag}$ = 0.80 V , $E^0_{Zn2+/Zn}$ = -0.76 V) (E=1.56 V, ΔG^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 4: Chemical Kinetics

Learning Outcomes: The learners -

- performs experiments and collects data for different concentration of solutions, w.r.t., temperature or rate constants.
- will be able to Understand the Integrated rate expression for zero and first order reaction
- calculates rate constant of zero order and first order reaction and activation using the data given and also calculate half life
- analyses and interprets graphs and figures
- draws graphs using the given data.
- communicates the findings and conclusions effectively, such as, order of a reaction or activation energy or rate constant
- exhibits values of honesty, objectivity, rational thinking, while sharing experimental results and doing numerical calculations
- Explain the dependence of rate or reactions on concentration, temperature and catalyst
- Distinguish between elementary and complex reactions.
- Differentiate between the molecularity and order of a reaction

1. Which of the following statements is not correct for the catalyst?
(a) It catalyses the backward and forward reaction to the same extent.
(b) It alters ΔG of the reaction.
(c)It is a substance that does not change the equilibrium constant of a reaction.
(d)It provides an alternate mechanism by reducing activation energy between reactants and products.

2. Rate law for the reaction, $A + 2B \rightarrow C$ is found to be Rate = k[A][B]. Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be
(a)the same (b)doubled (c) quadrupled (d) halved

In Q3 and Q4, a statement of assertion (A) is given followed by a corresponding statement of reason (R) just below it. Of the statements mark the correct answer as:
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3. **Assertion**: The hydrolysis of methyl acetate by dilute HCl is a pseudo first order reaction.
Reason: HCl acts as a catalyst for hydrolysis.

4. **Assertion**: The order of a reaction can have fractional value.
Reason: The order of reaction cannot be written from the balanced chemical equation.

5. For the reaction:

$2N_2O_5(g)$ □ $4NO_2(g) + O_2(g)$

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

6. 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)

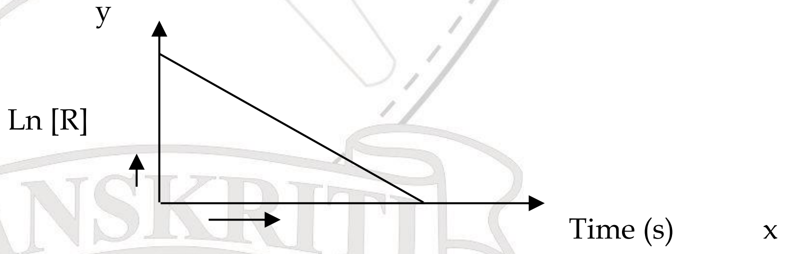
7. For a reaction R --> P, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction ?

8. 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.

9. 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.

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

11. 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)

12. For the reaction
$2\,NO_{(g)} + Cl_2(g) \longrightarrow 2NOCl\,(g)$
The following data 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 the 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}]

13. 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(mol L-1s-1)
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 $l^2 mol^{-2} s^{-1}$)

(iv) write the expression for the rate of reaction in terms of A and C.

14. For an elementary reaction

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

the rate of appearance of C at time 't' is 1.3×10^{-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 mol/l/s, (ii) 8.66 x 10^{-5} mol/l/s) }

15. 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)

16. 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 reaction if A is present in large excess.

17. 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 $JK^{-1}mol^{-1}$)

18. 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)

19. 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. (1859.8 years)

20.

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

For hydrolysis of methyl acetate, the following data were obtained

(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.
(0.005 mol L-1s-1)

Hands-on/ IT Enabled work:

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

More Practice

Chapter 4: Chemical Kinetics

1. Following data are obtained for the reaction :

N2O5□? $2NO_2 + \frac{1}{2}O_2$

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

(a) Show that it follows first order reaction.

(b) Calculate the half-life.

(calculate its concentration after 2 min, if rate costant is 5×10^{-4} s^{-1}

(Given log 2 = 0.3010 log 4 = 0.6021)

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

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

4. For the reaction :

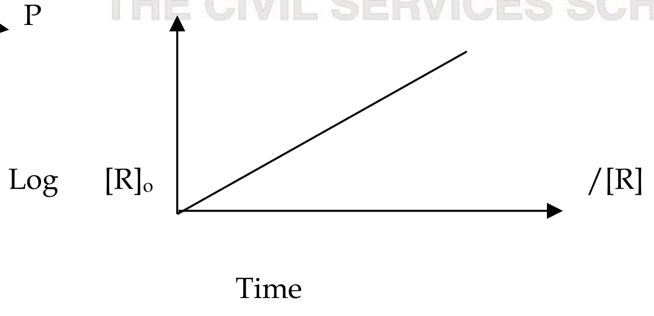
$Cl_2\,(g) + 2\,NO\,(g) \longrightarrow 2NOCl\,(g)$

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 2×10^{-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?

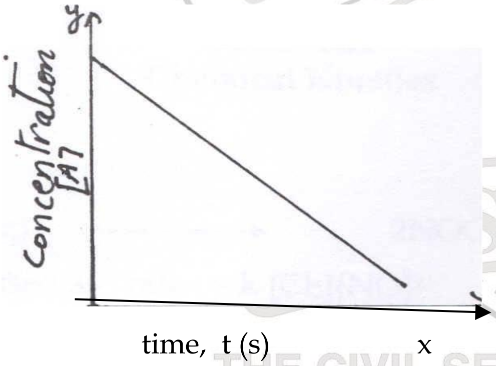
8. At elevated temperatures, HI decomposes according to the chemical equation;
$2HI(g) \longrightarrow H_2(g) + I_2(g)$ at 443°C. The rate of the reaction increases with concentration of HI, as shown in the following table:

HI (mol/ l)	0.005	0.01	0.02
Rate (mol/l/s)	7.5×10^{-4}	3.0×10^{-3}	1.2×10^{-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 reactant, 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 5: 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 adsorbate are held on the surface of the solid adsorbent.

Entropy decreases, i.e. ΔS is negative

➢ $\Delta G = \Delta H - T\Delta S$

For the process of adsorption to occur, ΔG must be negative which is possible only when, ΔS keeps on decreasing and $T\Delta S$ keeps on increasing till ultimately ΔH 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 vanderwaal 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 Vanderwaals' forces of attraction between adsorbate and adsorbent.
  (vii) It has low enthalpy of adsorption (20 – 40 kJ mol-1).
  (viii) Low temperature is favorable.
  (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 favorable.
(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.

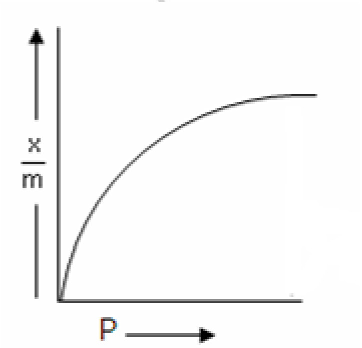
c. Specific area of the adsorbent: The greater the specific area more will be the extent of adsorption. That is why porous or finely divided forms of adsorbents adsorb larger quantities of adsorbate. The pores should be large enough to allow the gas molecules to enter.

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 increase with increase in pressure at low pressure but becomes independent of pressure at high pressure.

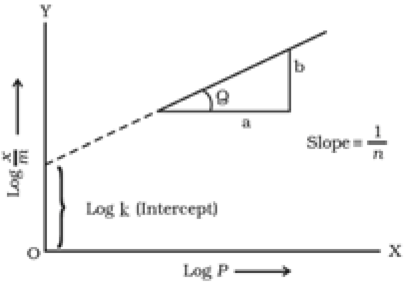


Taking logarithm on both sides, we get,

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

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 is 1/n and 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 they remain chemically and quantitatively unchanged after the reaction and 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.'

- <u>Types of catalysis</u>:
- 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**:
4. 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.

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

5. ***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 catalyze one particular reaction only. It may fail to catalyze 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 catalysts

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

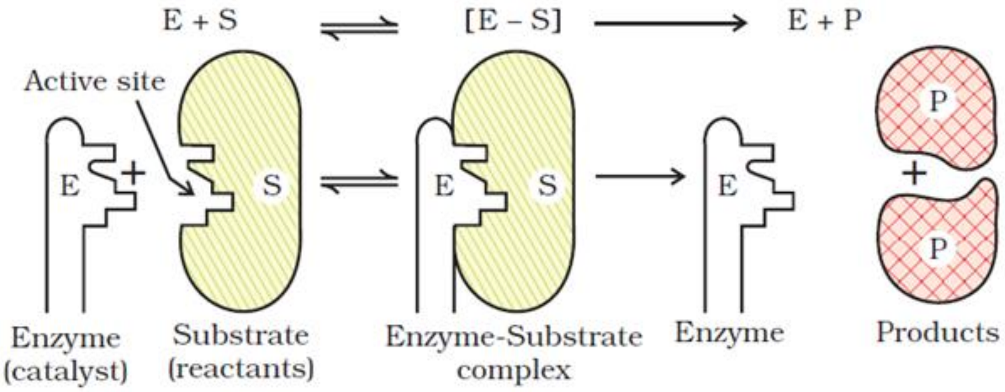
Glucose ethyl alcohol + gas

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

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 is 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 higher concentrations due to the formation of aggregated particles of colloidal dimensions. Such substances are also referred to as associated colloids.

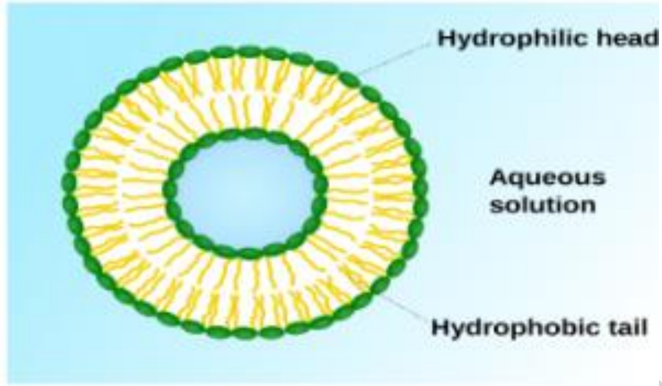
- Kraft Temperature (Tk): Micelles are formed only above a certain temperature called Kraft temperature.

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

- Soaps: These are 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:

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

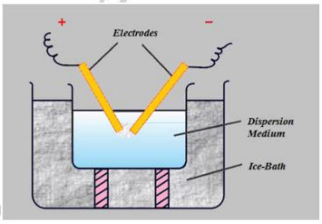
$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S(sol) + 2H_2O$$

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

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

Bredig's method:

An electric arc is struck between two metallic electrodes immersed in dispersion medium. The arc produced vaporizes the metal which on further 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 – Hemoglobin (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 neutralize 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 neutralization 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/flocculating ion as it neutralizes 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

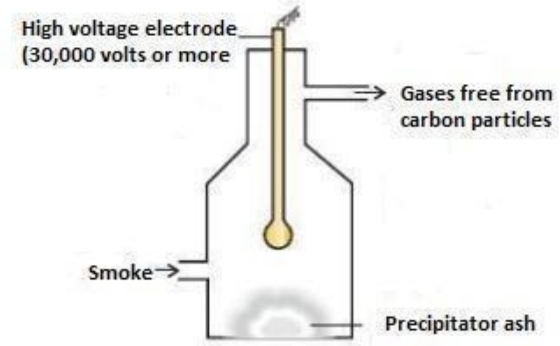
- Demulsification: It is the process of breaking an emulsion into its constituent liquids by freezing, boiling, centrifugation or some chemical methods.

  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

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 5: Surface Chemistry

Learning Outcomes: The learners-

- explains the cause and effect of adsorption and relationship between the terms in freundlich adsorption isotherm.
- will be able to understand the differences between physical and chemical adsorption
- take initiative to know about scientific phenomena related to colloids around us , analyse it and give reason for it.
- classifies and compares different types of colloids.
- will be able to understand the various types of catalysis - homogeneous and heterogeneous
- explains adsorption process and phenomena,
- understand the applications of adsorption in daily life.
- Describe preparation, properties and purification of colloids

1. Extent of physisorption of a gas increases with ___________.

(i) increase in temperature.
(ii) decrease in temperature.
(iii) decrease in surface area of adsorbent.
(iv) decrease in strength of van der Waals forces.

2. In Physisorption adsorbent does not show specificity for any particular gas because:

○ Involved vander Waals forces are universal
○ Gases involved behave like idal gases
○ Enthalpy of adsorption is low
○ It is a reversible process.

3. Which of the following is an example of absorption?

a) Water on silica gel
b) Water on calcium chloride
c) Hydrogen on finely divided nickel
d) Oxygen on metal surface

4. At high concentration of soap in water, soap behaves as ____________.

(i) molecular colloid
(ii) associated colloid
(iii) macromolecular colloid
(iv) lyophilic colloid

In the following questions, a statement of assertion (A) is given followed by a corresponding statement of reason (R) just below it. Choose the correct answer out of the following choices:

(a)Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b)Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c)Assertion is correct statement but reason is wrong statement.
(d)Assertion is wrong statement but reason is correct statement

5. Assertion : Coagulation power of Al^{3+} is more than Na^+ .
Reason : Greater the valency of the flocculating ion added, greater is its power to cause precipitation (Hardy Schulze rule).

6. Assertion : Colloidal solutions do not show brownian motion.
Reason : Brownian motion is responsible for stability of sols.

7. Assertion: An ordinary filter paper impregnated with collodion solution stops the flow of colloidal particles.
Reason: Pore size of the filter paper becomes more than the size of colloidal particle.

8. Assertion: Colloidal solutions show colligative properties.
Reason: Colloidal particles are large in size.

9. Assertion: Detergents with low CMC are more economical to use.
Reason: Cleansig action of detergent involves in the formation of micelles. These are formed when the concentration of detergent becomes equal to CMC.

10. 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.

11. (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.

12. Write one difference in each of the following :

(i) Lyophobic sol and Lyophilic sol
(ii) Solution and Colloid

13. (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?

(d) 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?

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

15. What causes Brownian movement in a colloidal solution?

16. 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 entropy, still it is a spontaneous process.

e) Enzyme catalysts are highly specific in their action.

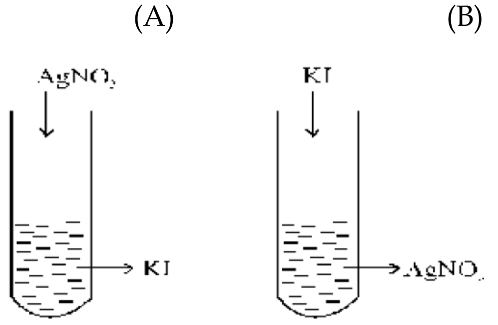
f) The enthalpy in case of chemisorption is usually higher than that of physisorption.

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.

17. (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 ?

18. A colloidal solution of AgI is prepared by two different methods shown below:-



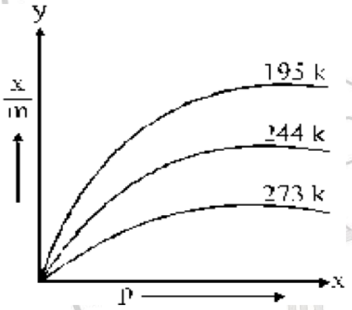
(a) What is the charge of AgI colloidal particles in the two test tubes (A) and (B)?
(b) Give reasons for the origin of charge.

19. What are the two classes of emulsion? Give one example of each class.

20. 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

21. 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.

22 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.

23. 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 -6
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.

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

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

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

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

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

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)

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

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

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. $CaCO_3 \qquad\qquad CaO + CO_2$

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.

$ZnS + O_2 \qquad\qquad ZnO + SO_2$

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.

$MxOy + yC \qquad\qquad xM + yCO$

Extraction of iron from its oxides

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

(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)

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

The oxide is then reduced to metallic copper using coke.

$Cu_2O + C \qquad\qquad 2Cu + CO$

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.**

$FeO + SiO_2 \qquad\qquad FeSiO_3$ (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:

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

$FeO + SiO_2 \qquad\qquad FeSiO_3$

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

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

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.

$$ZnO \quad + \quad C \quad {}^{\text{coke, 673K}} \qquad Zn \quad + \quad CO$$

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 $T\Delta S$ would increase ($\Delta H < T\Delta S$) and $\Delta H<T\Delta S$) 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

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

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

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

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

The resultant will have ΔG as negative.

According to Ellingham diagram, the ΔG^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 [$\Delta G(C, CO) < \Delta G(Fe, FeO)$]. 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 $\quad Cu^{2+} + 2e^-$

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

$Ni + 4CO \quad {}^{330-350\ K} \quad Ni(CO)_4$

volatile complex- nickel tetracarbonyl

At higher temperature,

$Ni(CO)_4 \quad {}_{450-470\ K} \quad Ni + 4CO$

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.

$Zr + 2I_2 \qquad ZrI_4$

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

$ZrI_4 \quad {}_{\Delta} \quad Zr + 2I_2$

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.

<u>EXTRACTION OF ALUMINIUM</u>:

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.

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

Reactions at electrodes are:

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

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

C(s) + $2O^{2-}$ (melt) 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 $Fe_2O_3.3H_2O$

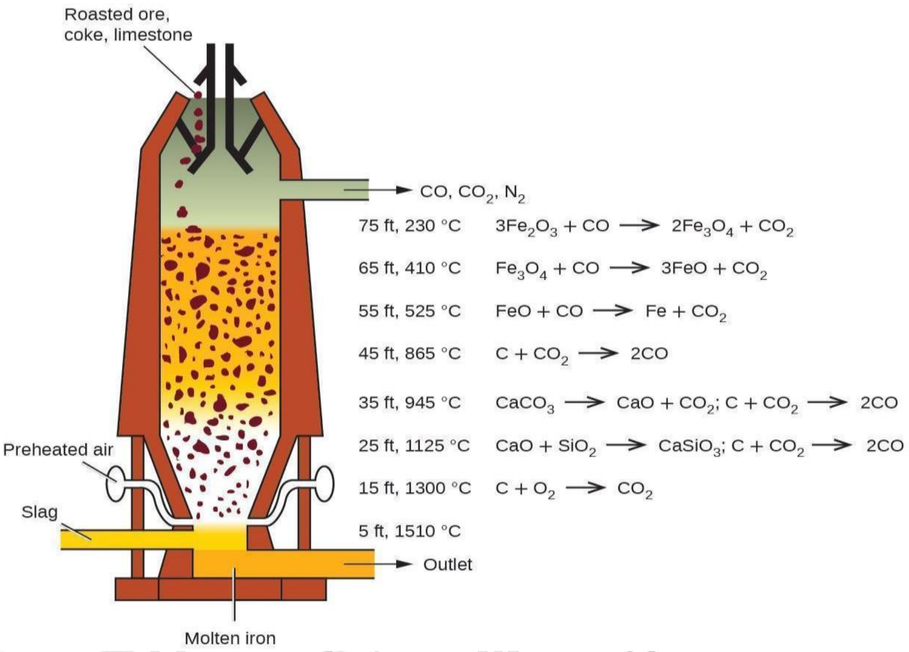
Iron Pyrites FeS_2

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.

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

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

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

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

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

   $CaCO_3 \qquad CaO + CO_2$

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

   $CaO + SiO_2 \qquad CaSiO_3$

   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.

   $FeO + CO \qquad Fe + CO_2$

   $3Fe_2O_3 + CO \qquad 2Fe_3O_4 + CO_2$

$$Fe_3O_4 + 4CO \qquad 3Fe + 4CO_2$$

$$Fe_2O_3 + CO \qquad 2FeO + CO_2$$

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

At lower hotter part, reaction is

$FeO + C \qquad Fe + CO$.

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.

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

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.
      $S + O_2 \qquad SO_2$
      $P_4 + 5O_2 \qquad 2P_2O_5$
      $4As + 3O_2 \qquad 2As_2O_3$
      $4Sb + 3O_2 \qquad 2Sb_2O_3$
   c) Copper pyrites is converted to ferrous sulphide (FeS) and cuprous sulphide (Cu_2S)
      $2CuFeS_2 + O_2 \qquad Cu_2S + FeS + SO_2$
      $2FeS + 3O_2 \qquad 2FeO + 2SO_2$
      $2Cu_2S + 3O_2 \qquad 2Cu_2O + 2SO_2$
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.
      $2FeS + 3O_2 \qquad 2FeO + 2SO_2$
      $FeO + SiO_2 \qquad FeSiO_3$ (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
      $2Cu_2S + 3O_2 \qquad 2Cu_2O + 2SO_2$

$Cu_2O + FeS \qquad Cu_2S + FeO$ (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.

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

      $FeO + SiO_2 \qquad FeSiO_3$ (slag)
   b) Copper sulphide is oxidized to cuprous oxide which further reacts with remaining copper sulphide to form copper and sulphur dioxide.

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

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

      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: $Cu \qquad Cu^{2+} + 2e^-$

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

   The impurities of Zn, Ni, Fe etc. gets collected below as <u>anode mud.</u>

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.

   $2ZnS + 3O_2 \qquad 2ZnO + 2SO_2$
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.

$ZnO + C \qquad ^{coke,\ 673K}\, Zn + CO$

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) $2OH^-$ (aq.) + H_2(g) + Cl_2(g)

ΔG^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)

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

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

Similarly for Silver

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

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

Hands-on/ IT Enabled work

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

Assignment
Chapter 6: General Principles and Processes of Isolation of Elements

Learning Outcomes: The learner

- differentiates between different types of, phenomena of concentration of ores, methods to prepare oxides, based on properties or characteristics of ores of metals.
- classifies between different methods of refining based on properties and characteristics of metals obtained
- Understand the principles of oxidation and reduction and apply to the extraction procedures
- describes scientific discoveries and inventions, such as economical metallurgical processes
- Apply the thermodynamic concepts like that of Gibbs energy and entropy to the principles of extraction of Al, Cu, Fe & Zn.
- explains why specific reducing agents , like CO, are used for the reduction purposes,

1. In the extraction of copper from its sulphide ore, the metal is formed by the reduction of Cu_2O with

(a)FeS (b) CO (c) Cu_2 (d) SO_2

2. In the metallurgy of aluminium….

(a)Al^{3+} is oxidized to Al(s)
(b)graphite anode is oxidized to carbon monoxide and carbon dioxide.
(c)oxidation state of oxygen changes in the reaction at anode
(d)oxidation state of oxygen changes in the overall reaction involved in the process

3. In the extraction of chlorine by electrolysis of brine….

a) Oxidation of Cl- ion to Chlorine gas occurs
b) Reduction of Cl- ion to Chlorine gas occurs
c) For overall reaction ΔG0 has negative value
d) A displacement reaction takes place

4. When copper ore is mixed with silica, in a reverberatory furnace copper matte is produced. The copper matte contains

a) sulphides of copper (II) and iron (II)
b) sulphides of copper (II) and iron (III)
c) sulphides of copper (I) and iron (II)
d) sulphides of copper (I) and iron (III)

In the following questions, a statement of assertion (A) is given followed by a corresponding statement of reason (R) just below it. Choose the correct answer out of the following choices:

(a)Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b)Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c)Assertion is correct statement but reason is wrong statement.
(d)Assertion is wrong statement but reason is correct statement

5. **Assertion**: Ag and Au are extracted by leaching their ores with a dilute solution of NaCN.

   Reason: Impurities associated with these ores dissolve in NaCN.

6. **Assertion**: Carbonate and hydroxide ores are concentrated by froth floatation process.

   Reason: In froth floatation process, mineral oil is used because it preferentially wets the gangue particles.

7. **Assertion:** Sulphide ores are concentrated by froth floatation method.

   Reason: Cresols stabilize the froth in froth floatation method.

8. **Assertion:** Zone refining method is very useful for producing semiconductors

   Reason: Semiconductors are of high purity.

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

10. (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?

11. What do you understand by the following terms?

    (a) Roasting (b) Flux (c) Calcination (d) Smelting (e) Slag

12. a) In the extraction of Al, 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?

13. Write the reactions occurring in the different zones of blast furnance during extraction of iron from concentrated Haemetite ore.

14. Explain Hall Heroult process of reduction of aluminium oxide. What is the role of graphite and cryolite in electrometallurgy of aluminium?

15. (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?

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

17. 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

18. a) Indicate the principle behind the method used for refining of zinc.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?

b) 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 15

N	$2s^2 2p^3$	Non Metals	• Solids and show allotropic modifications • s-orbitals in these elements are completely filled and p-orbitals are half filled, making their electronic configuration extra stable.
P	$3s^2 3p^3$		
As	$4s^2 4p^3$	Metalloids	
Sb	$5s^2 5p^3$		
Bi	$6s^2 6p^3$	Metal	

Down the group covalent radii increases and electro negativity decreases, Ionization energy decreases and hence metallic nature increases. Nitrogen has maximum electro negativity.

There is considerable increase in covalent radius from N to P. However from As to Bi only a small increase in covalent radius is observed.

Successive ionization enthalpy: $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$

Boiling point (bp) increases from top to bottom, but mp increases upto As and decreases upto Bi.

Except N all elements show allotropy.

Chemical properties of group 15

Oxidation State and Trends in group 15

N	-3, +3	• Covalent character decreases down the group.
P	-3, +3, +5	

As	-3, +3, +5	Most common oxidation state are -3, +3 and +5 -3 O.S decreases down the group due to increase in size and metallic nature.
Sb	+3, +5	
Bi	+3, +5	

- The stability of +5 O.S decreases due to inert pair effect down the group. Only Bi(V) compound is BiF_5
- Nitrogen exhibits +1, +2 and +4 O.S also when it reacts with oxygen. All these O.S tend to disproportionate in acid solution.E.g
  $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$
- Nitrogen is restricted to a maximum covalency of 4 since 4 orbitals (ons s and three p) are available for bonding.
- Phosphorous exhibits nearly all intermediate O.S from +5 and -3.
- The heavier elements have vacant d-orbitals which can be used for bonding as in PF_6^-

Anomalous properties of nitrogen

- Nitrogen differs from the rest of the members of this group due to its smaller size, high electro negativity, high ionization enthalpy and non-availability of d-orbitals.
- Nitrogen can form pπ-pπ multiple bond.
- Nitrogen exists as diatomic molecule with a triple bond.
- Heavier elements do not form pπ-pπ bonds as their atomic orbitals are so large and differs that they cannot have effective overlapping.
- P, As and Sb form P-P, As-As and Sb-Sb single bonds whereas Bi forms metallic bonds. However, N-N single bond is weaker than P-P single bond, because of high inter electronic repulsion of non-bonding electrons owing to small bond length.
- Catenations tendency is weaker in N as N-N bond is much weaker than P-P, As-As and Sb-Sb due to inter electronic repulsions because of small bond length.
- Except nitrogen, the heavier elements can form dπ-pπ bonds, e.g $R_3P{=}O$ or $R_3P{=}CH_2$ and also when transition elements like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands; they form dπ-dπ bonds.

1) Reactivity towards hydrogen: Form hydrides of formula EH_3
    - Structure pyramidal
    - Bond angle decreases down the group due to decrease in electro negativity.
    - Stability decreases due to increase in size.
    - Reducing character increases due to decrease in stability. NH_3 is a mild reducing agent while BiH_3 is strongest.
    - Basic character decreases in the order: $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.
2) Reactivity towards oxygen: Form two types of oxides of the formula: E_2O_3 and E_2O_5. The oxide in the higher oxidation is more acidic than that of lower oxidation state. Acidic character decreases down the group.
   N_2O_3, P_2O_3 □ Acidic
   As_2O_3, Sb_2O_3 □ Amphoteric
   Bi_2O_3 □ Basic oxide
3) Reactivity towards halogens: They form halides of the formula: EX_3 and EX_5.
    - Nitrogen does not form pentahalide due to absence of the d orbitals.
    - Pentahalides are more covalent than trihalides.
    - All trihalides except those of nitrogen are stable. Only NF_3 is stable. Trihalides except BiF_3 are predominantly covalent.

4) Reactivity towards metals: All these elements react with metals to form their binary compounds exhibiting –3 oxidation state, such as, Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As_2 (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

Dinitrogen

Preparation

1. Dinitrogen is prepared commercially by the liquefaction and fractional distillation of air.
2. In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.
   $NH_4CI(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl\ (aq)$
3. $(NH_4)_2Cr_2O_7$ Heat $N_2 + 4H_2O + Cr_2O_3$
4. Pure nitrogen is obtained by the thermal decomposition of sodium or barium azide.
   $Ba(N_3)_2 \rightarrow Ba + 3N_2$
   $2NaN_3 \rightarrow 2Na + 3N_2$

Properties

1. Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.
2. It is inert at room temperature because of the high bond enthalpy of N ≡ N bond.
3. At high temperature, it directly combines with some metals to form ionic nitrides and with non-metals to form covalent nitrides.
   $6Li + N_2$ Heat $2Li_3N$
   $3Mg + N_2$ Heat $2Mg_3N_2$
4. It combines with hydrogen at about 773 K to form ammonia:
   $N_2(g) + 3H_2\ (g)$ 773K $2NH_3(g)$; $\Delta_f H^o = –46.1$ kJmol–1
5. It combines with dioxygen only at about 2000 K to form nitric oxide, NO.
   $N_2 + O_2(g)$ Heat $2NO(g)$

   Thermal decomposition of sodium azide gives dinitrogen gas. ($2NaN_3$ □$2Na + 3N_2$)

Ammonia

Preparation

Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.

$$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

On a small scale ammonia is obtained from ammonium salts which decompose when treated with caustic soda or lime.

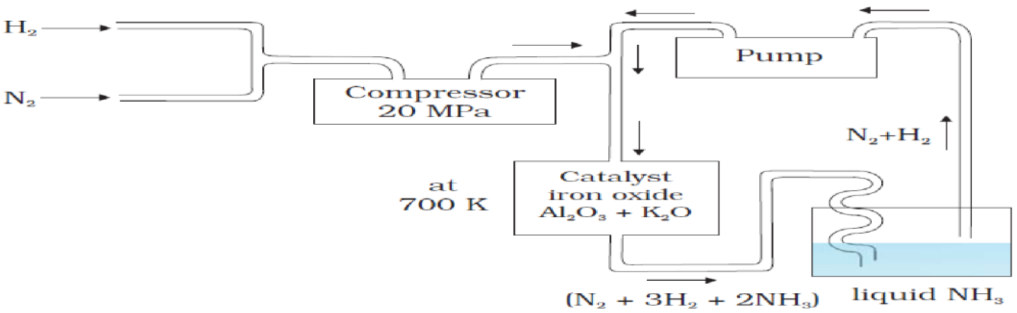
$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$$

$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

On a large scale, ammonia is manufactured by Haber's process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \qquad \Delta_f H^\ominus = -46.1 \text{ kJ mol}^{-1}$$

The optimum conditions are a pressure of 200×10^5 Pa (about 200 atm), a temperature of ~ 700 K with iron oxide and small amount of K_2O and Al_2O_3 as catalyst.



HABER'S PROCESS

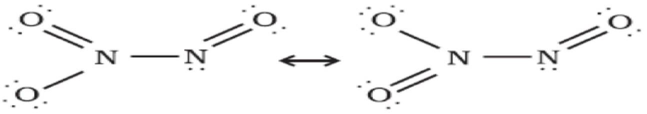
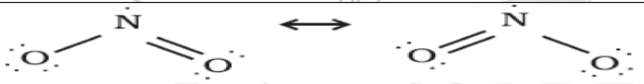
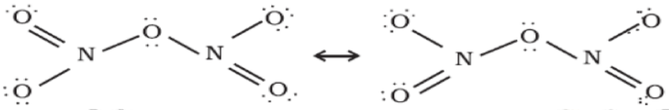
Properties

1. Ammonia is a colourless gas with a pungent odour.
2. In the solid and liquid state there exists H-bond, which accounts for its higher melting and boiling points.
3. It is trigonal bipyramidal with three bond pairs and 1 lone pair.
4. Highly soluble
   $$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
   (weakly basic in aq. Solution)
5. Forms ammonium salts with acids, e.g., NH_4Cl, $(NH_4)_2SO_4$, etc. It precipitates the hydroxides of many metals from their salt solutions. For example,
   $$2FeCl_3(aq) + 3NH_4OH(aq) \rightarrow \underset{\text{(brown ppt)}}{Fe_2O_3.xH_2O(s)} + 3NH_4Cl(aq)$$
   $$ZnSO_4(aq) + 2NH_4OH(aq) \rightarrow \underset{\text{(white ppt)}}{Zn(OH)_2(s)} + (NH_4)_2SO_4(aq)$$
6. Presence of a lone pairs makes it a Lewis base. It donates the electron pair and forms linkage with metal ions.
   $$\underset{\text{(blue)}}{Cu^{2+}(aq)} + 4NH_3(aq) \rightleftharpoons \underset{\text{(deep blue)}}{[Cu(NH_3)_4]^{2+}(aq)}$$
   $$\underset{\text{(colourless)}}{Ag^+(aq) + Cl^-(aq)} \rightarrow \underset{\text{(white ppt)}}{AgCl(s)}$$
   $$\underset{\text{(white ppt)}}{AgCl(s)} + 2NH_3(aq) \rightarrow \underset{\text{(colourless)}}{[Ag(NH_3)_2]Cl(aq)}$$

Uses

To produce nitrogenous fertilizers and manufacture of inorganic nitrogen compounds. Liquid ammonia is also used as a refrigerant.

Oxides of Nitrogen

Formula	Oxidation state	Resonance Structures	Common Methods of Preparation
N_2O	+1	$\ddot{N}=N=\ddot{O} \longleftrightarrow :N\equiv N-\ddot{O}:$	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$
NO	+2	$:N=\ddot{O}: \longleftrightarrow :\dot{N}=\ddot{O}:$	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4$ $\rightarrow Fe_2(SO_4)_3 + 2NaHSO_4$ $+ 2H_2O + 2NO$
N_2O_3	+3		$2NO + N_2O_4 \xrightarrow{250\,K} 2N_2O_3$
NO_2	+4		$2Pb(NO_3)_2 \xrightarrow{673\,K}$ $4NO_2 + 2PbO$
N_2O_4	+4		$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$
N_2O_5	+5		$4HNO_3 + P_4O_{10}$ $\rightarrow 4HPO_3 + 2N_2O_5$

NITRIC ACID

Preparation

1. In the laboratory, nitric acid is prepared by heating KNO_3 or $NaNO_3$ and concentrated H2SO4 in a glass retort.
   $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$
2. On a large scale it is prepared mainly by Ostwald's process.
   $$\underset{\text{(from air)}}{4NH_3(g) + 5O_2(g)} \xrightarrow[500\,K,\ 9\,bar]{Pt/Rh\ gauge\ catalyst} 4NO(g) + 6H_2O(g)$$
3. $2NO(g) + O_2(g) \qquad 2NO_2(g)$
4. $3NO_2(g) + H_2O(l)$ □ $2HNO_3(aq) + NO(g)$
5. NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4.

Properties

1. A colourless liquid. In gaseous state it has a planar structure.
2. In aq. Solution, behaves as a strong acid.
   HNO_3 (aq) + H_2O (l) H_3O^+ (aq) + NO_3^- (aq)
3. Conc. HNO_3 is a strong oxidizing agent and can react with metals and non-metals.
   $3Cu + 8HNO_3$ (dil) $Cu(NO_3)_2 + 2NO + H_2O$
   $Cu + 4HNO_3$ (conc) $\rightarrow$ $Cu(NO_3)_2 + 2NO_2 + 2H_2O$
   $4Zn + 10HNO_3$ (dil) $\rightarrow$ $4Zn(NO_3)_2 + 5H_2O + N_2O$
   $Zn + 4HNO_3$ (conc) $\rightarrow$ $Zn(NO_3)_2 + 2H_2O + 2N_2O$

   <u>With Non-metals</u>

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10\,NO_2 + 4H_2O$$
$$C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$$
$$S_8 + 48HNO_3(\text{conc.}) \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$
$$P_4 + 20HNO_3(\text{conc.}) \rightarrow 4H_3PO_4 + 20\,NO_2 + 4H_2O$$

<u>Brown Ring Test</u>: Aq. Solution of nitrate ion + dil. $FeSO_4$ solution + conc. H_2SO_4 along the sides of the test tube.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$
$$[Fe(H_2O)_6]^{2+} + NO \rightarrow \underset{\text{(brown)}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

PHOSPHORUS

Occurrence: Occurs as fluoroapatite $Ca_5(PO_4)_3F$ and hydroxyapatire $ca_5(PO_4)_3(OH)$

Preparation:

- Calcination of phosphate rock.
- Reduction with coke and sand

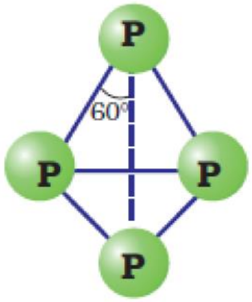
$2Ca(PO_4)_3 + 6SiO_2 + 10C \xrightarrow{1773K, \text{ electric arc}} P_4 + 6\,CaSiO_3 + 10CO$

Vapours condensed to solid under water

Allotropes:

1. **White Phosphorus**:

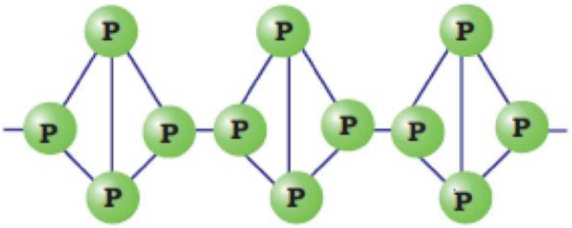
Condensation of gaseous or liquid state. It glows in dark (chemiluminescence). It is a waxy solid, insoluble in water, soluble in CS_2 and benzene. It is stored under water as it ignites spontaneously in air. It shows phosphopescence.

	● Each 'P' located at the corner of a tetrahedron is attached to 3 other 'P' atoms. ● Angle is 60°. P_4 units face lot of angle strain. ● It readily catches fire in air to give white dense fumes of P_4O_{10} $P_4 + 5O_2 \rightarrow P_4O_{10}$ ● It dissolves in NaOH (boiling) to give phosphine. $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ (sodium hypophosphite)

2. **Red Phosphorus**:

White P $\xrightarrow{570K, \text{inert atm.}}$ Red P

It is insoluble in water and CS_2.
It does not glow in the dark.
It has a high melting point (870K), amorphorus, less reactive.
Red P is less reactive than white P.
Safe to handle and shows a polymeric structure.



3. **Black Phosphorus**:

It has two forms: α-black phosphorus and β-black phosphorus.

Red P 803k Black P (α-form)
White P 473k, high pressure Black P (β-form)

It is the most stable variety with an extended layer structure

Uses:

In the form of phosphatic fertilizers.
Manufacture of food grade phosphates.
Detergents, pharmaceuticals, water industry.
Manufacture of organo phosphorus compounds used as pesticides.

Compounds: Hydrides: (MH_3)

NH_3 – Ammonia, most stable, shows H-bonding. Therefore, soluble in water

PH_3 – Phosphine : When pure, it is non inflammable but becomes inflammable owing to the presence of P_2H_4 or P_4 vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

$$PH_4I + KOH \rightarrow KI + H_2O + PH_3$$

AsH_3
SbH_3 no H-bond insoluble in water. Strong reducing agent and poisonous.
BiH_3

Preparation of PH_3:

$Ca_3P_2 + 6HCl \quad 3CaCl_2 + 2PH_3$
$Ca_3P_2 + 6H_2O \quad 2PH_3 + 3Ca(OH)_2$
$P_4 + 3KOH\ 3H_2O \quad PH_3 + 3KH_2PO_2$ (Potassium hypophosphite)
/NaOH /$3NaH_2PO_2$

Preparation of AsH_3, SbH_3:

M=As, Sb
$Zn_3M_2 + 6HCl \quad 2MH_3(g) + 3ZnCl_2$

- Basic character of hydrides decrease down the group due to decrease in charge density. NH_3 is the most basic whereas ASH_3, SbH_3, BiH_3 do not show any basic properties.
- Thermal stability decreases down the group as the size of the central atom increases and the tendency to form stable M-H bond decreases.
- Reducing character increases down the group, because thermal stability of hydrides decreases.

Properties of Phosphine:

It is a colourless gas with rotten fish smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.

$PH_3(aq)$ light Red P + H_2

$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$
$3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$
(mercury chloride)

Phosphine is weakly basic and gives phosphonium compounds with acids e.g.,

$PH_3 + HBr \rightarrow PH_4Br$

Halides:

MX_3 (known for all) MX_5 (except N)

N: $2s^22p^3$, It can easily form 3 covalent bonds and 1 coordinate bond. Thus total 4 bonds.

Since there is non-availability of d-orbital, it cannot extend its coordination number beyond 4.

However, for P and other group 15 elements, 5 covalent bonds can also be formed due to availability of d orbitals. (sp^3d hybridization).

MX_3	
NX_3 AsX_3 Covalent SbX_3 BiX_3 – ionic	● Ionic character increases down the group, because of increased size of central atom, the electro positive character increases. ● MX_3 have pyramidal structure. ● They are hydrolysed by water. (except NX_3)

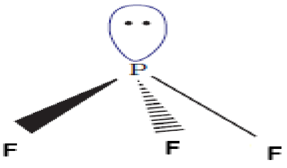
Preparation:

$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

$P_4 + 6X_2 \quad 4PX_3$;

PF_3 is pyramidal

(in gas phase)



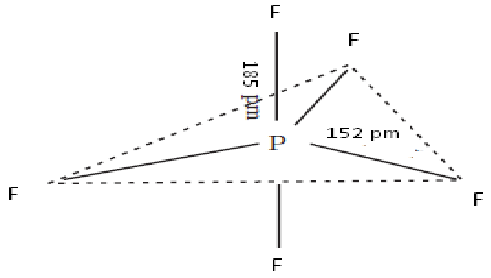
$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$ (gives fumes)

PCl_3 fumes in moisture due to formation of HCl(g)

$2PCl_3 + O_2 \quad 2POCl_3$ (phosphoryl chloride)

$3CH_3COOH + PCl_3 \quad 3CH_3COCl + H_3PO_3$

$3C_2H_5OH + PCl_3 \quad 3C_2H_5Cl + H_3PO_3$

MX_5 PX_5 PF_5 PCl_5 PBr_5 AsX_5 AsF_5 $AsCl_5$ SbX_5 SbF_5 $SbCl_5$ BiX_5 BiF_5	 Structure: Trigonal bipyramid

PF_5 exist as PF_5 molecule in gas and solid state. There are 2 kinds of bond lengths, 3 equatorial and 2 axial bonds.

PCl_5 exist as PCl_5 molecule in gas or liquid and as $[PCl_4]^+$ $[PCl_6]^-$ in solid state.

PCl_5 reacts with organic compounds.

$C_2H_5OH + PCl_5 \quad C_2H_5Cl + POCl_3 + HCl$
$CH_3COOH + PCl_5 \quad CH_3COCl + POCl_3 + HCl$

Finely divided metals on heating with PCl5 give corresponding chlorides.

$2Ag + PCl_5 \quad 2AgCl + PCl_3$
$Sn + 2PCl_5 \quad SnCl_4 + 2PCl_3$

Preparation:

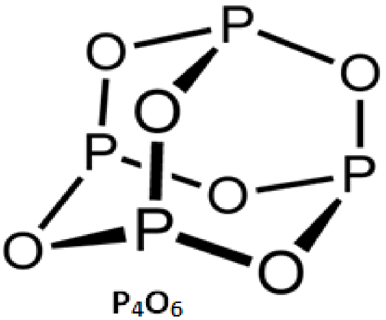
$PCl_3 + Cl_2 \quad PCl_5$
$P_4 + 10Cl_2 \quad 4PCl_5$

Hydrolysis:

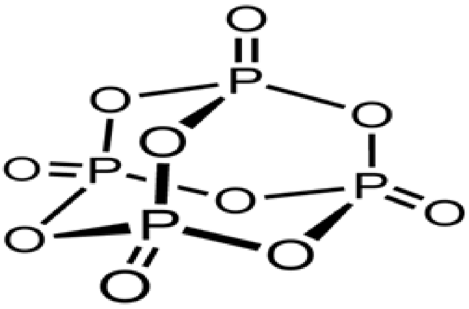
$PCl_5 + H_2O \quad POCl_3 + 2HCl$
$PCl_5 + 3H_2O$ (excess) $\quad H_3PO_3 + 2HCl$

Oxides:

E_2O_3 and E_2O_5 [E=P to Bi]
But due to the reluctance of P-Bi to form pπ-pπ bonding, they actually form dimers E_4O_6 and E_4O_{10}



P_4O_6



P_4O_{10}

- Bi_4O_{10} is unstable.
- Basic character increases down the group with atomic number.
- P_4O_6 – Acidic $\quad$ As_4O_6 – Acidic
- Sb_4O_6 – Amphoteric $\quad$ Bi_4O_6 – Basic

$Bi_2O_3 + 6HNO_3 \quad 2Bi(NO_3)_3 + 3H_2O$

Preparation:

$P_4 + 3O_2 \quad P_4O_6$

$P_4 + 5O_2 \quad P_4O_{10}$

They dissolve in water to give acids.

$P_4O_6 + 6H_2O \quad 4H_3PO_3$

$P_4O_{10} + 6H_2O \quad 4H_3PO_4$

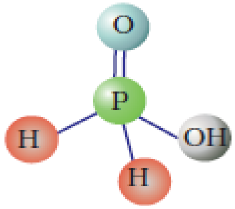
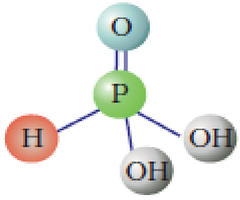
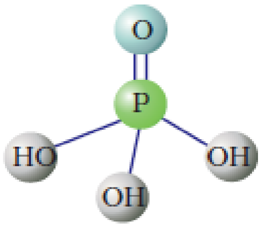
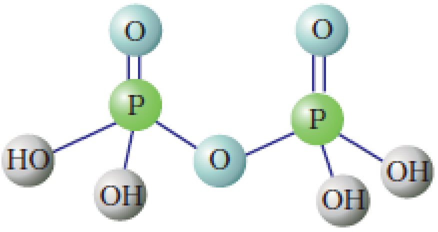
Due to affinity of P_4O_{10} for H_2O, it is a good dehydrating agent.

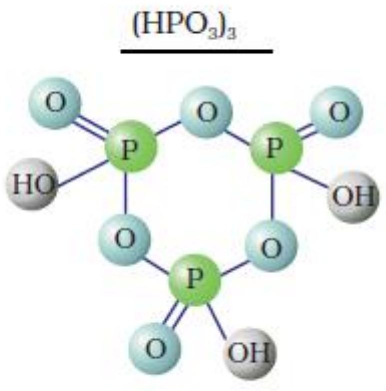
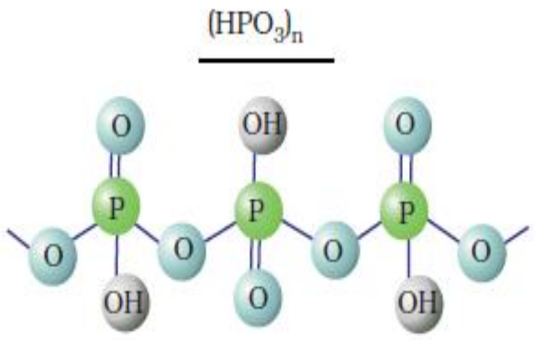
$P_4O_{10} + 4HNO_3 \quad 2N_2O_5 + 4HPO_3$

$P_4O_{10} + 6H_2SO_4 \quad 6SO_3 + 4H_3PO_4$

Oxoacids:

All oxoacids have at least oneP=O and one P-OH bond. They have cyclic or linear structure.

H_3PO_2  - Monoprotic acid - Hypophosphorous or Phosphinic acid	H_3PO_3  - Phosphorus acid - Diprotic acid, forms 2 series of salts: NaH_2PO_3 & Na_2HPO_3
H_3PO_4  - Orthophosphoric acid - Triprotic acid, Na_2HPO_4, NaH_2PO_4, Na_3PO_4 - Used for manufacture of phosphatic fertilizers.	$H_4P_2O_7$  - Diphosphonic acid or Pyrophosphoric acid

 - Cyclotrimetaphosphoric acid	 - Polymetaphosphoric acid

+3 oxidation state

$4H_3PO_3 \quad 3H_3PO_4 + PH_3$

The acids with P – H bond have strong reducing properties.

$4AgNO_3 + 2H_2O + H_3PO_2 \quad 4Ag + 4HNO_3 + H_3PO_4$

That is why H_3PO_2 imparts reducing characteto the acid as it has 2H atoms bonded to P.

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	**1. All of them exhibit Allotropy.**
Se, Te - Metalloids	**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.**
Po - Metal	

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 **H_2S** **H_2Se** **H_2Te** **H_2Po**	**1. Acidic nature increases from H_2O to H_2Te due to decrease in bond dissociation enthalpy.** **2. Thermal Stability decreases from H_2O to H_2Po.** **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.

$$2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g); \qquad 2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$$
$$2HgO(s) \rightarrow 2Hg(l) + O_2(g)\,; \qquad 2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$$

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 :
   $2Ca + O_2 \quad 2CaO$
   $4Al + 2O_2 \quad 2Al_2O_3$
   $P_4 + 5O_2 \quad P_4O_{10}$
   $C + O_2 \quad CO_2$
   $2ZnS + 3O_2 \quad 2ZnO + 2SO_2$
   $CH_4 + 2O_2 \quad CO_2 + 2H_2O$
4. Some compounds are catalytically oxidized.
   $2SO_2 + O_2 \; V_2O_5 \quad 2SO_3$
   $4HCl + O_2 \; CuCl_2 \quad 2H_2O$

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)

$SO_2 + H_2O \qquad H_2SO_3$ (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)

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

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

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

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

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.

$3O_2 \quad 2O_3$ (ΔH=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.
   $PbS + 4O_3 \qquad PbSO_4 + 4O_2$
   $2I^- + H_2O + O_3 \qquad 2OH^- + I_2 + O_2$
   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.
   $NO + O_3 \qquad NO_2 + O_2$
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 $KMnO_4$.

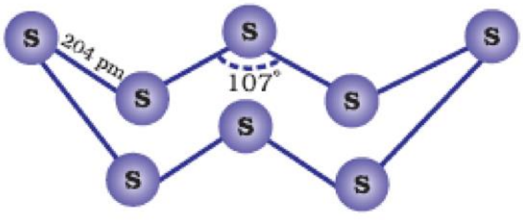
SULPHUR

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.



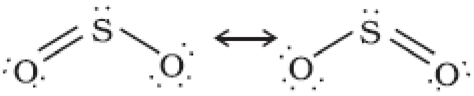
SULPHUR DIOXIDE

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.
   $4FeS_2 + 11O_2(g) \qquad 2Fe_2O_3(s) + 8SO_2(g)$

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. $SO_2(g) + H_2O(l)$ $H_2SO_3(aq)$ (sulphurous acid)
5. $NaOH + SO_2$ Na_2SO_3 (sodium sulphite) + H_2O
   $Na_2SO_3 + H_2O + SO_2$ $2NaHSO_3$ (sodium hydrogen sulphite)
6. Reacts with chlorine in the presence of charcoal as catalyst to give sulphuryl chloride.
   $SO_2(g) + Cl_2(g)$ $SO_2Cl_2(l)$
7. Oxidised to sulphur trioxide in the presence of V_2O_5
   $2SO_2(g) + O_2(g)$ V_2O_5 $2SO_3(g)$
8. Moist SO_2 behaves as reducing agent. Converts Iron(III) ions to Iron(II) ions and
   $2Fe^{3+} + SO_2 + 2H_2O$ $2Fe^{2+} + SO_4^{2-} + 4H^+$
   decolourizes acidified $KMnO_4$ solution
   $5SO_2 + 2MnO_4^- + 2H_2O$ $5SO_4^{2-} + 4H^+ + 2Mn^{2+}$
9. SO_2 is angular.

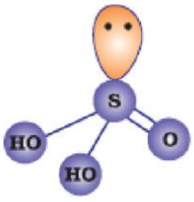


Uses of SO_2:

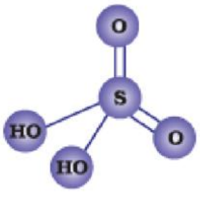
1. In refining petroleum.
2. In bleaching wool and silk.
3. As an anti-colour, disinfectant and preservative.
4. Sulphuric acid, $NaHSO_3$ and $Ca(HSO_3)_2$ are manufactured from sulpur dioxide.
5. Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.

OXOACIDS OF SULPHUR

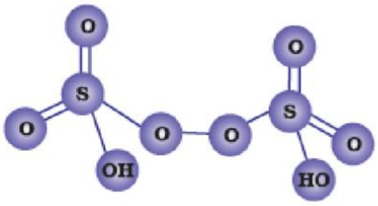
Forms oxoacids of the formula H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$ (x=2 to 5), H_2SO_4, $H_2S_2O_7$, H_2SO_5, $H_2S_2O_8$.



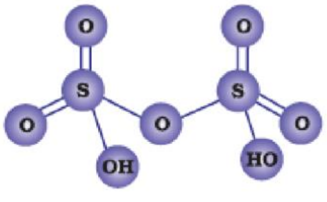
Sulphurous acid (H_2SO_3)



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.
   $S + O_2$ SO_2

$4FeS_2$ (Iron pyrites) + $11O_2$ $2Fe_2O_3 + 8SO_2$

2. Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of catalyst V_2O_5.
   $2SO_2(g) + O_2(g) \quad V_2O_5 \quad 2SO_3(g) \quad \Delta H^o = -196.6 KJmol^{-1}$
   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 ($H_2S_2O_7$).
   $SO_3 + H_2SO_4 \qquad H_2S_2O_7$
4. Dilution of oleum with water to get desired concentration of sulphuric acid.
   $H_2S_2O_7 + H_2O \qquad 2\,H_2SO_4$ (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.

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

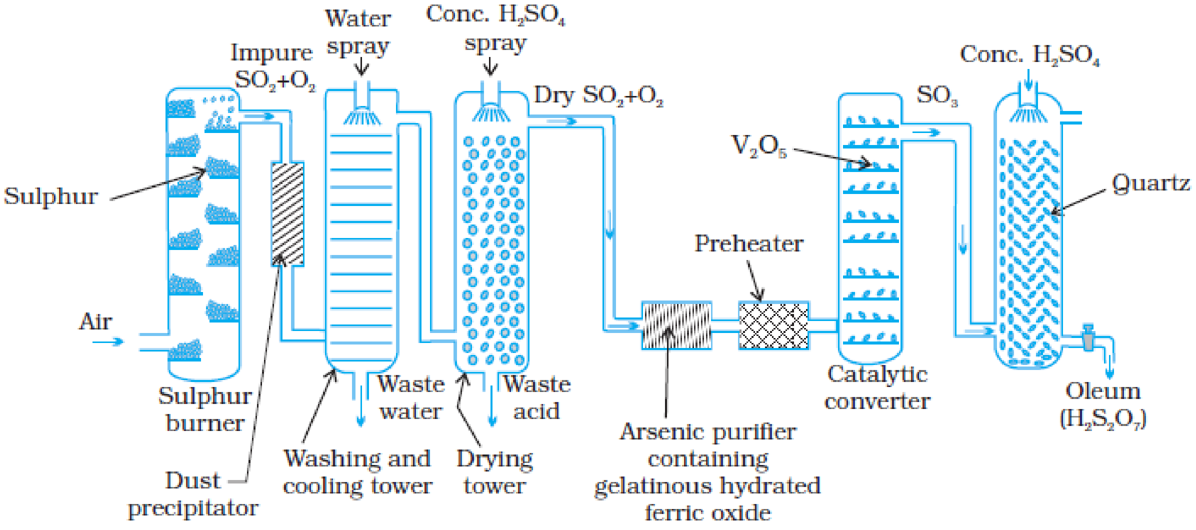
The reaction is exothermic and reversible.

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. **<u>Testing Box</u>**: The purifies gases are tested by passing a strong beam of light. Impurities present will scatter the light.
4. **<u>Contact Chamber or Converter</u>**: 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. **<u>Absorption tower</u>**: 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.
   $H_2SO_4 + SO_3 \qquad H_2S_2O_7$ (oleum)
   Oleum is then diluted with calculated amount of water to get acid of desired concentration.
   $H_2S_2O_7 + H_2O \qquad 2H_2SO_4$

<u>PROPERTIES OF H_2SO_4</u>:

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:
   $H_2SO_4(aq) + H_2O(l) \qquad H_3O^+(aq) + HSO_4^-(aq) \quad K_{a1}$=very large (>10)
   $H_2SO_4^-(aq) + H_2O(l) \qquad H_3O^+(aq) + SO_4^{2-}(aq) \quad K_{a2}=1.2x10^{-2}$
   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.
   $2MX + H_2SO_4 \qquad 2HX + M_2SO_4$ (X=F,Cl, NO_3)
7. Acts as dehydrating agent. Can dry gases and also removes water from organic compounds.
   $C_{12}H_{22}O_{11} \quad H_2SO_4 \quad 12C + 11H_2O$
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.) $\qquad CuSO_4 + SO_2 + 2H_2O$
   $3S + 2H_2SO_4$ (conc.) $\qquad 3SO_2 + 2H_2O$
   $C + 2H_2SO_4$ (conc.) $\qquad CO_2 + 2SO_2 + 2H_2O$

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

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

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

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

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

By oxidation of NaCl

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

Trends in Group 17:

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

Oxidizing Action:

$F_2 > Cl_2 > H_2SO_4 > Br_2 > I_2$

$F_2 + 2X^- \qquad 2F^- + X_2$ (X=Cl, Br, I)

$Cl_2 + 2X^- \qquad 2Cl^- + X_2$ (X=Br, I)

$Br_2 + 2I^- \qquad 2Br^- + I_2$

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.

$NaBr + H_2SO_4 \qquad HBr \qquad Br_2$

$NaI + H_2SO_4 \qquad HI \qquad I_2$

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:

$2F_2(g) + 2H_2O(l) \qquad 4H^+(aq) + 4F^- + O_2(g)$

$X_2(g) + H_2O(l) \qquad HX(aq) + HOX(aq)$ (Where X= Cl or Br)

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

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

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. $Mg + Br_2 \quad MgBr_2$

$Xe + 3F_2 \qquad XeF_6$

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

Low O.S of M MCl_2
High O.S of M 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.

$Pu + 3O_2F_2 \qquad PuF_6 + 3O_2$ (removed as PuF_6)

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:

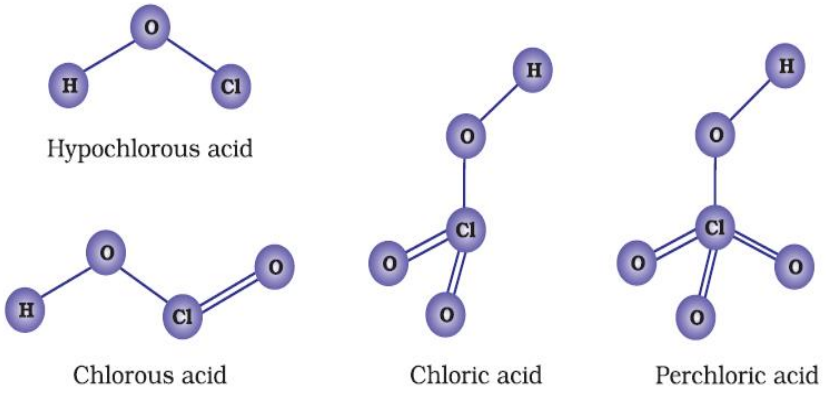
Halogens react with metals to form metal halides. $Mg(s) + Br_2(l) \qquad MgBr_2(s)$

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)**	**–** **–**	**HOCIO** **(chlorous acid)**	**–** **–**	**–** **–**
Halic (V) acid **(Halic acid)**	**–** **–**	**$HOCIO_2$** **(chloric acid)**	**$HOBrO_2$** **(bromic acid)**	**$HOIO_2$** **(iodic acid)**
Halic (VII) acid **(Perhalic acid)**	**–** **–**	**$HOCIO_3$** **(perchloric acid)**	**$HOBrO_3$** **(perbromic acid)**	**$HOIO_3$** **(periodic acid)**



Hypochlorous acid

Chlorous acid

Chloric acid

Perchloric 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.,

$$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{437\text{K}} 2ClF;$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573\text{K}} 2ClF_3;$$

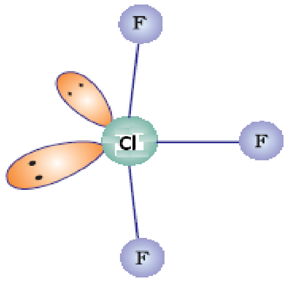
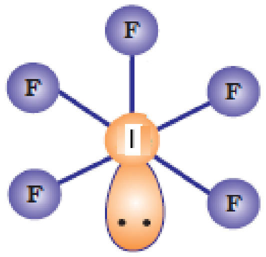
$$\underset{\text{(equimolar)}}{I_2 + Cl_2} \rightarrow 2ICl;$$

$$I_2 + \underset{\text{(excess)}}{3Cl_2} \rightarrow 2ICl_3$$

$$\underset{\text{(diluted with water)}}{Br_2 + 3F_2} \rightarrow 2BrF_3$$

$$Br_2 + \underset{\text{(excess)}}{5F_2} \rightarrow 2BrF_5$$

Properties:

XX'	**ClF, BrF, IF (unstable), BrCl, ICl, IBr**	
XX'$_3$	**ClF$_3$ (Bent T-Shaped,, because it is sp3d hybridized)** **BrF$_3$ (Bent T-Shaped,, because it is sp3d hybridized)** **IF$_3$ (Bent T-Shaped,, because it is sp3d hybridized)** **ClF$_3$ (Bent T-Shaped,, because it is sp3d hybridized)**	
XX'$_5$	**IF$_5$ (Square pyramid)** **BrF$_5$ (Square pyramid)** **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.

$2Al + 3Cl_2 \quad 2AlCl_3$

$2Na + Cl2 \quad 2NaCl$

$2Fe + 3Cl_2 \quad 2FeCl$

$P_4 + 6Cl_2 \quad 4PCl_3$

$S_8 + 4Cl_2 \quad 4S_2Cl_2$

3. Can react with hydrogen to form HCl.

$H_2 + Cl_2 \qquad 2HCl$

$H_2S + Cl_2 \qquad 2HCl + S$

$C_{10}H_{16} + 8Cl_2 \qquad 16HCl + 10C$

4. With excess of NH_3, chlorine gives nitrogen and ammonium chloride while with excess of chlorine, nitrogen trichloride is formed.

$8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_2$; $\qquad NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$

(excess) $\qquad$ (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,

$CH_4 + Cl_2 \quad \text{UV} \quad CH_3Cl + HCl$

$C_2H_4 + Cl_2 \quad \text{Room temp.} \quad C_2H_4Cl_2$

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.

$NaCl + H_2SO_4$ 420K $NaHSO_4 + HCl$

$NaHSO_4 + NaCl$ 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. $HCl(g) + H_2O(l)$ $H_3O^+(aq) + Cl^-(aq)$
   Its aqueous solution is called hydrochloric acid.
3. Reacts with NH_3 and gives white fumes. $NH_3 + HCl$ NH_4Cl
4. 3 parts of conc. HCl and 1 part of con. HNO_3 forms aqua regia.
   $Au + 4H^+ + NO_3^- + 4Cl^-$ $AuCl_4^- + NO + 2H_2O$
   $3Pt + 16H^+ + 4NO_3^- + 18Cl^-$ $3PtCl_6^{2-} + 4NO + 8H_2O$
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. ● 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. ● Used as disinfectant for sterilizing drinking water. ● Used in production of organic compounds- PVC, chlorinated hydrocarbons, pharmaceuticals. ● 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 $1s^2$ **Ne $2s^22p^6$** **Ar $3s^23p^6$** **Kr $4s^24p^6$** **Xe $5s^25p^6$** **Rn $6s^26p^6$**	● **Atmospheric abundance of the noble gases in dry air ~1% by volume of which Ar is major constituent.** ● **Helium or Neon is also found in radioactive minerals, e.g. pitchblende, monazite, cleveite.** ● **Natural gas is commercial source of helium.** ● **Radon is obtained as decay product of ^{226}Ra.** $^{226}_{88}\mathbf{Ra}$ $^{222}_{86}\mathbf{Rn} + ^{4}_{2}\mathbf{He}$

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 is 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.

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

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

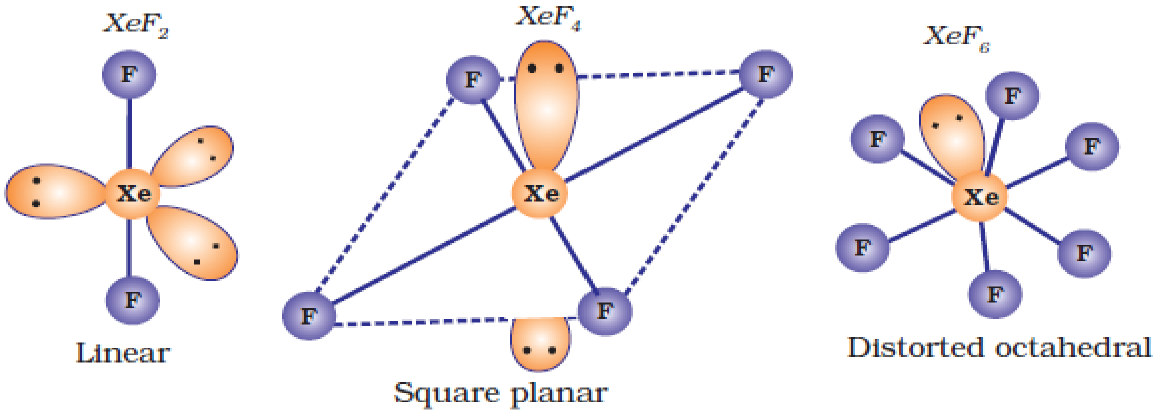
Xenon-fluorine compounds

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

$Xe\ (g) + F_2\ (g) \quad 673k,\ 1bar \quad XeF_2\ (s)$
(Xe in excess)
$Xe\ (g) + 2F_2\ (g) \quad 873k,\ 7bar \quad XeF_4\ (s)$
(1:5 ratio)
$Xe\ (g) + 3F_2\ (g) \quad 573k,\ 60\text{-}70bar \quad XeF_6\ (s)$
(1:20 ratio)

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

Structure:



Linear

Square planar

Distorted octahedral

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.

$XeF_2 + PF_5 \rightarrow [XeF]^+ [PF_6]^-$; $\quad XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$
$XeF_6 + MF \rightarrow M^+ [XeF_7]^-$ (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.

$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$
$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

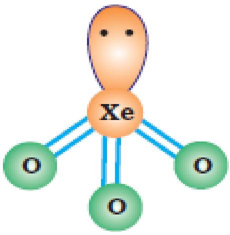
Partial hydrolysis of XeF_6 gives oxyfluorides

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$
$XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

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

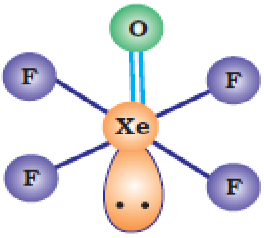
Structure:

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 7: p -Block Elements

Learning Outcomes: The learners -

- classifies elements in different groups based on properties and characteristics.
- plans and conducts experiments to arrive at principles of various processes of preparation of compounds
- relate the structures of compounds to the theories learnt
- uses scientific conventions to represent reactions taking place in p-block elements using symbols, formulae, and equations,
- takes initiative to know about scientific processes for preparation of compounds, such as , sulphuric acid, nitric acid and ammonia.
- plans and conducts investigations to arrive at and verify the facts, principles, and properties or to seek answers to queries on their own
- Know the chemistry and describe the interhalogen compounds and oxoacids of halogens, nitrogen and phosphorus.
- Appreciate the importance of these elements and their compounds in our day to day life.

1. The reactions of Cl_2 with cold dilute and hot concentrated NaOH in water give sodium salts of two different oxoacids of chlorine P and Q respectively. The Cl_2 gas reacts with SO_2 gas, in presence of charcoal, to give a product R.

   (a)Identify P, Q and R.
   (b)Write the balanced chemical equations for the above mentioned reactions.

2. The compound with two lone pairs of electrons on the central atom is

   (a)BrF_5 (b) SO_2 (c) XeF_4 (d) SF_4

In the following questions, a statement of assertion (A) is given followed by a corresponding statement of reason (R) just below it. Choose the correct answer out of the following choices:

(a)Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b)Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c)Assertion is correct statement but reason is wrong statement.
(d)Assertion is wrong statement but reason is correct statement

3. **Assertion**: SF_6 cannot be hydrolysed but SF4 can be.

   Reason: Six F atoms in SF_6 prevent the attack of H_2O on sulphur atom of SF_6.

4. **Assertion:** HI cannot be prepared by the reaction of KI with concentrated H_2SO_4.

Reason: HI has lowest H-X bond strength among halogen acids.

5. (a) Give reasons:
   - When Cl_2 reacts with excess of F_2, ClF_3 is formed and not FCl_3.
   - Dioxygen is a gas while sulphur is a solid at room temperature.

   (b) Draw the structures of the following:
   - i. $HClO_3$
   - ii. $H_2S_2O_7$
   - iii. XeF_6

6. (a) Arrange the following in the decreasing order of their reducing character:
   HF, HCl, HBr, HI

   (b) Complete the following reaction:
   (i) $XeF_4 + SbF_5$
   (ii)$NH_3 + 3Cl_2$(excess) ----->
   (iii) $XeF_6 + 2H_2O$ ----->

7. Give reasons:

   (i) Thermal stability decreases from H_2O to H_2Te.
   (ii) Fluoride ion has higher hydration enthalpy than chloride ion.

8. 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.
   q) Solid PCl_5 is ionic in nature.
   r) NH_3 is stronger base than phosphine.

s) SbF_5 is more stable than BiF_5 .
t) PH_3 has a lower boiling point than NH_3.

9. (a) Write the reaction of preparation of XeF_4, XeF_6, XeO_3
(b) What happens when (i) PCl_5 is heated
(ii) H_3PO_3 is heated

10. 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 m) H_3PO_3 n) H_3PO_2

11. Complete the equations:

a. $XeF_2 + PF_5 \rightarrow$

b. $F_2 (g) + H_2O (l) \rightarrow$

c. $I^-(aq.) + H_2O(l) + O_3(g) \rightarrow$

d. $XeF_4 + O_2F_2 \rightarrow$

e. $Xe(g)$ (excess)+ $F_2(g)$ 673K, 1bar

f. $P_4(s)$ + $NaOH(aq.)$ + H2O(l) □

12. (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?

13. 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.
(c)

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

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

16. Complete the following reactions :
(i) $NH_3 + 3Cl_2$(excess) ----->
(ii) $XeF_6 + 2H_2O$ ----->

What happens when
(i) $(NH_4)_2Cr_2O_7$ is heated ?
(ii) H_3PO_3 is heated ?
Write the equations.

17. Arrange the following in the increasing order of property mentioned :

(a)H_3PO_3, H_3PO_4, H_3PO_2 (Reducing character)
(b) NH_3, PH_3, AsH_3, SbH_3, BiH_3 (Base strength)

18. On adding NaOH to ammonium sulphate, a colourless gas with pungent odour is evolved which forms a blue coloured complex with Cu^{2+} ion. Identify the gas.

19. Draw the structures of white phosphorus and red phosphorus. Which one of these two types of phosphorus is more reactive and why?

20. Which one of PCl_4^+ and PCl_4^- is not likely to exist to exist and why?

21. Which of the following elements can be involved in pπ-dπ bonding?

a) Carbon
b) Nitrogen
c) Phosphorus
d) Boron

22 Which of the following acids form three series of salts?

a) H_3PO_2
b) H_3BO_3
c) H_3PO_4
d) H_3PO_3

23 Maximum covalency of Nitrogen is:

a) 3
b) 4
c) 5
d) 6

24 Which of the following statements is wrong?

a) Single N-N bond is strongr than the single P-P bond
b) PH_3 can act as a ligang in the formation of coordination compound with transition elements
c) NO_2 is paramagnetic in nature.
d) Covalency of nitrogen in N_2O_5 is four.

More Practice
Chapter 7: 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 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
$3d^1 4s^2$	$3d\ ^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

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
$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^2$	$4d^5 s^1$	$4d^6 5s^1$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$

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.

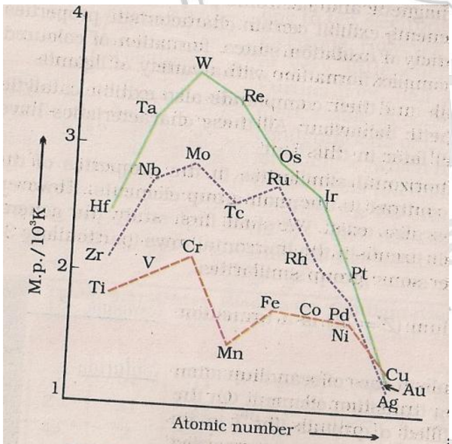


Fig. 8.1: Trends in melting points of transition elements

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 +3 +4	+2 +3 +4 +5	+2 +3 +4 +5 +6	+2 +3 +4 +5 +6 +7	+2 +3 +4 +6	+2 +3 +4	+2 +3 +4	+1 +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 X 10^3 kJ/mol
$Pt \rightarrow Pt^{+2} + 2e^-$ I.E = 2.66 X 10^3 kJ/mol

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

$Ni \rightarrow Ni^{+4} + 4e^-$ I.E = 8.80 X10^3 kJ/mol
$Pt \rightarrow Pt^{+4} + 4e^-$ I.E = 6.70 X 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, ΔH_{sub} , ΔH_{hyd} energy, explain the stability of a particular oxidation state.

1) M(s) M(g) $\Delta_{sub}H^0$
2) M(g) $M^+(g) + e^-$ 1. E $\Delta H = \Delta_{sub} H + I.E + \Delta_{hyd} H$
3) $M^+(g)+nH_2O$ $M^+(aq)$ $\Delta_{hyd} H$

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) The ability of fluorine to stabilize the highest oxidation state is due to its high electronegativity and higher lattice energy as in CoF_3 of high bond enthalpy for high covalent compounds as in VF_5 or CrF_6.
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 but MnO_3F is known.
f) V(V)is shown by VFs only . Other halides undergoing hydrolysis form oxo halides VOX_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) Copper(I) compounds are unstable in aqueous solutions and undergo disproportionation.
   $2Cu^+ \rightarrow Cu^{2+} + Cu.$
i) 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 states in Mn_2O_7.Mangnese forms highest oxidation state fluorides as MnF_4 whereas the highest oxide is Mn_2O_7.This 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 MO_4^{-2} ions are also known for V(V),Cr(VI), Mn(VI) and Mn(VII).

Formation of colored ions-

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 transitions. 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-

μ = Magnetic moment in Bohr magnetron (μ_b) units

($\mu_b = eh/4m = 9.27 \times 10^{-24}$ Am^2 or Jt^{-1})

μ increase with the increasing number of unpaired

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 compounds 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_2CrO4 and $H_2Cr_2O_7$

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.

$4\ FeCr_2O_4 + \underset{\text{Excess}}{Na_2CO_3} + 7O_2 \qquad 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$.

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

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

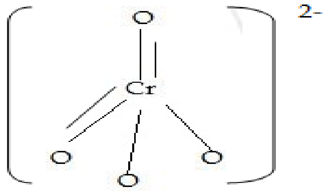
Chromates and dichromates are interchangeable in aqueous solution depending upon pH of the solution.

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

$\underset{(+6)}{2CrO_4^{2-}} + 2H^+ \qquad \underset{(+6)}{Cr_2O_7^{2-}} + H_2O$

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

Chromate ion



Dichromate ion

$Na_2Cr_2O_7$& $K_2Cr_2O_7$: Strong oxidizing agents

Chemical properties of $K_2Cr_2O_7$:-

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

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

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)

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

$3\ H_2S \qquad 6H^+ + 3S + 6e-$

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

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

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

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

Uses – In leather industry, preparation of azo dyes.

Potassium Permanganate ($KMnO_4$)

Preparation –

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

$3MnO_4^{2-} + 4H^+ \qquad 2MnO_4^- + MnO_2 + 2H_2O$

(+6 (+7) (+4)

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

$$MnO_2 \xrightarrow[\text{Oxidize with air or KNO3}]{\text{Fuse with KOH}} MnO_4^{2-}$$

$$MnO_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic oxidation}} MnO_4^-$$

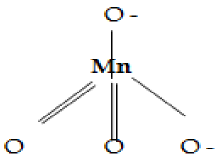
In the laboratory manganese (II) ion salt is oxidized by peroxodisulplate to permanganate

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

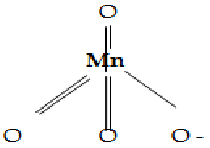
Properties-

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

   $2KMnO_4 \qquad K_2MnO_4 + MnO_2 + O_2$



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-

COO-

5 $\qquad 10CO_2 + 10e^-$

COO-

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

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

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

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

<u>Acidic solutions –</u>

$10I^- + 2MnO_4^- + 16H^+$ $2Mn^{+2} + 8H_2O + 5I_2$ (iodides to KI)
$5C_2O_4^{2-} + 2MnO_4^- + 16H$ $2Mn^{+2} + 8H_2O + 10CO_2$ (oxalate ions to CO_2)
$5Fe^{2+} + MnO_4^- + 8H$ $Mn^{+2} + 4H_2O + 5Fe^{2+}$ (Fe^{2+}(green) to Fe^{3+} (yellow))
$5S^{2-} + 2MnO_4^- + 16H^+$ $2Mn^{+2} + 8H_2O + 5S$ (H_2S to S)
$5SO_3^{2-} + 2MnO_4^- + 6H^+$ $2Mn^{+2} + 3H_2O + 5SO_4^{2}$ (sulphites to sulphates)
$5NO_2^- + 2MnO_4^- + 6H^+$ $2Mn^{+2} + 3H_2O + 5NO_3^-$ (nitrites to nitrates)

<u>Neutral medium</u> -

$2MnO_4^- + H_2O + I^-$ $MnO_2 + OH^- + IO_3^-$ (iodides to iodates)
$8MnO_4^- + H_2O + 3S_2O_3^{2-}$ $8MnO_2 + 2OH^- + 6SO_4^{2}$ (thiosulphates to sulphates)
$MnO_4^- + 2H_2O + 3Mn^{2+}$ $4H^+ + 5MnO_2$ (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 4*f* 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 behaviour

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- Ln(s)

Ln_2O_3 H_2

Burns in O_2 with acids

Heated with S with halogens

Ln_2S_3 Ln LnX_3

Heated with H_2O

N_2

$Ln(OH)_3 + H_2$

Ln N C 2773K

Ln C_2

$$Ln + C \xrightarrow{\Delta} Ln_3C + Ln_2C_3 + LnC_2 \text{ (carbides)}$$

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 Boiling water $M_xO_y + MH_n$

moderate temp
Actinoid + Non metal Corresponding compound
Actinoid + HCl M_xO_y oxide layer
Actinoid + HNO_3 M_xO_y
Actinoid + Alkali 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 8: d -and f -Block Elements

Learning Outcomes- The learner

a) communicates the findings and conclusions regarding the properties of d- and f- block elements effectively and can give reason to the findings.
b) draws flow charts and concept maps, to explain and apply the physiochemical properties learnt
c) differentiates different compounds, based on, properties and characteristics,
d) derives equations
e) describe scientific facts about the d-and f- block compounds and explain the properties.
f) Describe the preparation, properties, structures and uses of $K_2Cr_2O_7$ & $KMnO_4$
g) appreciates the role and impact of d- and f- block elements towards the improvement of quality of human life.
h) Understand the general horizontal and group trends in the d- and f- block elements
i) Describe the properties of the f- block elements

1. The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$. Which of the following is correct?

   (i) Cu(II) is more stable
   (ii) Cu(II) is less stable
   (iii) Cu(I) and Cu(II) are equally stable
   (iv) Stability of Cu(I) and Cu(II) depends on nature of copper salts

2. Which of the following reactions are disproportionation reactions?

   (a) $Cu^+ \rightarrow Cu^{2+} + Cu$
   (b) $3MnO_4^- + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$
   (c) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
   (d) $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$
   (i) a, b (ii) a, b, c (iii) b, c, d (iv) a, d

3. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because

   a) CO_2 is formed as the product
   b) Reaction is exothermic
   c) MnO_4^- catalyses the reaction
   d) Mn^{2+} acts as autocatalyst

4. There are 14 elements in actinoid series. Which of the following does not belong to this series?

   a) U
   b) Np

c) Tm
d) Fm

In the following questions, a statement of assertion (A) is given followed by a corresponding statement of reason (R) just below it. Choose the correct answer out of the following choices:

(a)Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b)Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c)Assertion is correct statement but reason is wrong statement.
(d)Assertion is wrong statement but reason is correct statement

5. Assertion : Cu cannot liberate hydrogen from acids.
Reason : Because it has positive electrode potential.

6. Assertion : Separation of Zr and Hf is difficult.
Reason : Because Zr and Hf lie in the same group of the periodic table.

7. Assertion: Cu^{2+} iodide is not known.
Reason: Cu^{2+} oxidizes I^- to Iodine.
8. Assertion: The highest oxidation state of Osmium is +8

Reason: Osmium is a 5d- block element.

9. Complete and balance the following equations:

(i) $Fe^{2+} + MnO_4^- + H^+ \rightarrow$

(ii) $MnO_4^- + H_2O + I^- \rightarrow$

10. Give reason:

(i) E^0value 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.

11. 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+}.

12. (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?

(iv) Write the formula of an oxo-anion of Manganese (Mn) in which it shows the oxidation state equal to its group number

13. Describe the general characteristics of transition elements with special reference to the following :

(i) Variable oxidation states
(ii) Formations of coloured ions.

14. (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.

15. How is it that several transition metals act as catalysts? Give two examples of reactions catalyzed by them?

16. Complete the following reactions:

(a) $Cr_2O_7^{2-}(aq.) + I^-(aq.) + H^+$

(b) $MnO_4^- (aq.) + Fe^{2+}(aq.) + H^+(aq.)$

(c) $MnO_4^- (aq.) + S_2O_3^{2-}(aq.) + H_2O(l)$

(d) $5NO_2^-(aq.) + 2MnO_4^-(aq.) + 6H^+(aq.)$

(e) $Cr_2O_7^{2-}(aq.) + H_2S(g) + H^+(aq.)$

(f) $Cr_2O_7^{2-}(aq.) + Fe^{2+}(aq.) + H^+(aq.)$

(g) $MnO_2(s) + KOH(aq.) + O_2$

(h) $2CrO_4^{2-} + 2H^+$

(i) $Cr_2O_7^{2-}(aq.) + 3Sn^{2+} + 14 H^+$

17. (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.

18. 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).

19. 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.

20. 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?

21. 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.

22. 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 8: 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:

   (i) Ce^{3+} can be easily oxidized to Ce^{4+} (At. no. of Ce =58).

   (ii) Zr (Z=40) and Hf (Z=70) have very close value of atomic radii.

   (iii) The lowest oxidation state of manganese is basic while the highest is acidic.

   (iv) 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 9: Coordination Compounds

Learning Outcomes

- communicates the findings and conclusions effectively,, such as, applications of the coordination compounds
- takes initiative to know about scientific discoveries and theories of bonding of the coordination compounds
- apply learning of theories to explain properties, structures and bonding in various compounds.
- understand the theories and correlates the theories to the processes and phenomenon, structures and properties of the complex compounds
- understand the rules of Nomenclature and write the names of the compounds on his own.
- appreciates the role and impact of coordination compounds towards the improvement of quality of human life

1. The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?

   (i) $[Fe(CO)_5]$

   (ii) $[Fe(CN)_6]^{3-}$

   (iii) $[Fe(C_2O_4)_3]^{3-}$

   (iv) $[Fe(H_2O)_6]^{3+}$

2. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent?

   (i) thiosulphato

   (ii) oxalate

   (iii) glycinato

   (iv) ethane-1,2-diamine

3. The compounds $[Co(SO4)(NH_3)_5]Br$ and $[Co(SO_4)(NH_3)_5]Cl$ represent:

   a) Linkage isomerism

   b) Ionization isomerism

   c) Coordination isomerism

   d) No isomerism

4. Which of the following is not expected to be a ligand.

j) NO

k) NH_4^+

l) $NH_2CH_2CH_2NH_2$

m) CO

In the following questions, a statement of assertion (A) is given followed by a corresponding statement of reason (R) just below it. Choose the correct answer out of the following choices:

(a)Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b)Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c)Assertion is correct statement but reason is wrong statement.
(d)Assertion is wrong statement but reason is correct statement

5. Assertion : ($[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
Reason : Because it has d^2sp^3 type hybridisation.

6. Assertion : Linkage isomerism arises in coordination compounds containing ambidentate ligand.
Reason : Ambidentate ligand has two different donor atoms.

7. Assertion : Toxic metal ions are removed by the chelating ligands.
Reason: Chelate complexes tend to be more stable.

8. Assertion: Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism
Reason: Geometrical isomerism is not shown by complexes of coordination number 6.

9. Write the coordination number and oxidation state of Platinum in the complex $[Pt(en)_2Cl_2]$

10. (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 $[CoF_6]^{3-}$

11. (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)

(iv) Write the IUPAC name of the following complex : $[Co(NH_3)_5(CO_3)]Cl$.

12. 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) $[CrCl_2(en)_2]Cl$

13. Write the formulas in the following cases.

1) Tetrahydroxozincate(II), 2) Hexaamminecobalt(III) sulphate

3) Hexaammineplatinum(IV) 4) Pentaamminenitrito-N-cobalt(III)

14. 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.

15. 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?

16. When a coordination compoundcr$Cl_3.6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipated per mole of the compound. Write

(i) Structural formula of the complex

(ii) IUPAC name of the complex.

17. 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 $[Pt(en)_2Cl_2]^{2+}$ which is optically active.

18. Show the possible isomers of the following coordination entities?

(i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[Co(NH_3)_3Cl_3]$ (iii) $[Co(en)_2Cl_2]Cl$

19. 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.

20. How many ions are produced from the complex $[Co(NH_3)_6]Cl_2$ in aqueous phase.

21. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

22. (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 Δ^o and P.

(ii) On the basis of CFT, write the electronic configuration of d^4 ion if $\Delta_0 > P$.

23. 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.

24. 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)

25. 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.

26. (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)

27. Explain the following:

(a) The π-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.

More Practice

Chapter 9: 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) Dichloridobis (ethane-1,2-diamine) platinum (IV) nitrate

Chapter 10- Haloalkanes and Haloarenes

POLYHALOGEN COMPOUNDS

1. **CH_2 CL_2 (Methylene Chloride) / (Dichloromethane)**

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.

Light

$CHCl_3 \quad + \quad O_2 \qquad\qquad 2COCl_2 \quad + \quad 2HCl$

(Carbonyl chloride)

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 (Iodoform/ 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- $CCl_4 \quad + \quad 2\,AgF\,/\,SbF_2 \qquad CCl_2F_2$ (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 10: Haloalkanes and Haloarenes

Learning Outcomes: The Learner

- draws, flow charts, concept maps, to understand and apply the physical and chemical properties.
- will be able to know how to write the trivial and IUPAC name of various organic compounds
- will be able to Understand the Preparation & properties of the organic compounds.
- uses scientific conventions, symbols, and equations to represent various chemical equations and predict the products.
- Distinguish between various organic compounds by giving chemical tests
- make an effort to conserve the environment using the knowledge and harmful effects of polyhalogen compounds such as CFCs.
- exhibit rational thinking towards while taking decisions and respect life with the knowledge and harmful effects of alcohol and compounds
- explain organic reactions using mechanisms
- will be able to perform the test to distinguish between the primary, secondary and tertiary amines amines, aldehydes and ketones, alcohols and phenols, haloalkanes and haloarenes, etc.
- plans and conducts investigations to arrive at and verify the facts, principles, phenomena or to seek answers to queries on their own,

1. Which of the following reactions is most suitable for the preparation of n-propyl benzene?

   (a)Friedel-Crafts alkylation (b) Wurtz reaction (c) Wurtz-Fittig reaction (d) Grignard reaction

2. S_N1 reaction of optically active alkyl halides leads to,

   (a)retention of configuration (b) racemization (c) inversion of configuration (d) none of these

3. Which of the following is not correctly matched with its IUPAC name?

   (a) $CHF_2CBrClF$: 1-Bromo-1-chIoro-1, 2, 2-trifluoroethane

   (b) $(CCl_3)_3CCl$: 2-(Trichloromethyl)-1, 1, 2, 3, 3-heptafluoropropane

   (c) $CH_3C\ (p\text{-}ClC_6H_4)_2CH(Br)CH_3$: 2-Bromo-3, 3-bis (4- chlorophenyl) butane

   (d) o-$BrC_6H_4CH\ (CH_3)\ CH_2CH_3$: 2-Bromo-l- methylpropyl benzene

4. Which of the following compounds has the highest boiling point?

(a)$CH_3CH_2CH_2Cl$

(b) $CH_3CH_2CH_2CH_2Cl$

(c) $CH_3CH(CH_3)CH_2Cl$

(d) $(CH_3)_3CCl$

In Q5 to Q8, a statement of assertion (A) is given followed by a corresponding statement of reason (R) just below it. Of the statements mark the correct answer as:

(i)Assertion and reason both are correct statements and reason is correct explanation for assertion.
(ii)Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(iii)Assertion is correct statement but reason is wrong statement.
(iv)Assertion and reason both are incorrect statements.
(v)Assertion is wrong statement but reason is a correct statement.

5 **Assertion**: Alkyl iodide can be prepared by treating RCl/RBr with NaI in acetone.
Reason: NaCl/NaBr are soluble in acetone while NaI is not.

6 **Assertion**: S_N2 reactions proceed with inversion of configuration.

Reason: S_N2 reactions occur in one step.

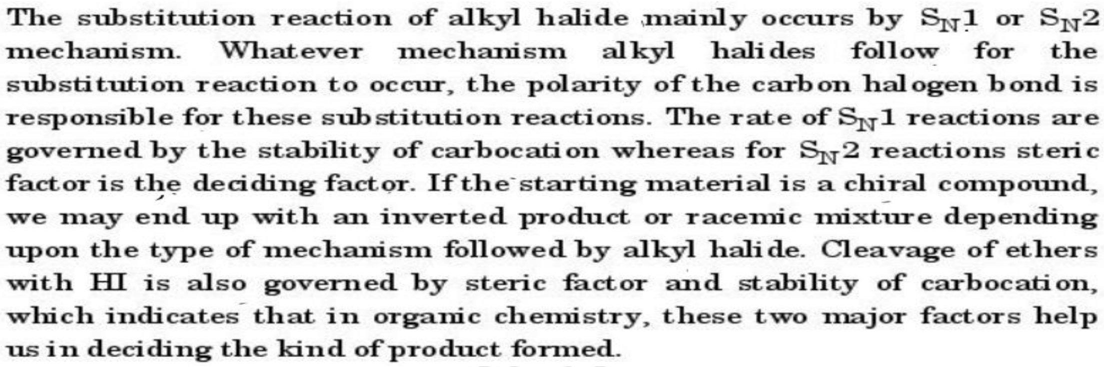
7 **Assertion**: Treatment of chloroethane with a saturated solution of AgCN gives ethyl isocyanide as a major product.

Reason: Cyanide ion (CN^-) is an ambident nucleophile

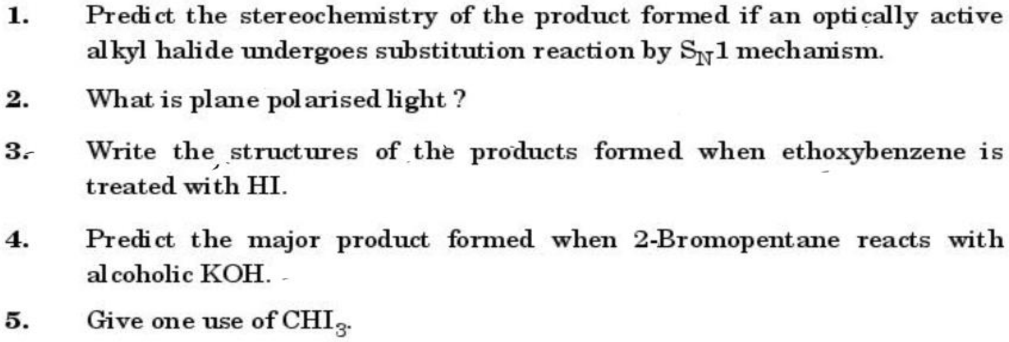
8. **Assertion**: Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.

Reason: Nitro group, being an electron-withdrawing group decreases the electron density over the benzene ring.

9. **Read the passage below and answer the questions 1-5 that follow:**



The substitution reaction of alkyl halide mainly occurs by S_N1 or S_N2 mechanism. Whatever mechanism alkyl halides follow for the substitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of S_N1 reactions are governed by the stability of carbocation whereas for S_N2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.



1. Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by S_N1 mechanism.

2. What is plane polarised light ?

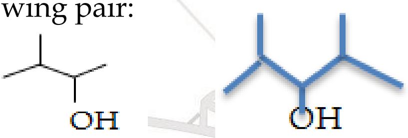
3. Write the structures of the products formed when ethoxybenzene is treated with HI.

4. Predict the major product formed when 2-Bromopentane reacts with alcoholic KOH.

5. Give one use of CHI_3.

10. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why?

11. (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.

12. Write the structure of 1-Bromo-4-chlorobut-2-ene.

13. 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.

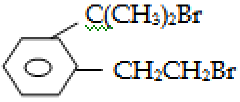
(ii) Write the compound which is optically active.

(iii)Write the compound which is most reactive towards β-elimination reaction.

14. Name the following halides according to IUPAC system:

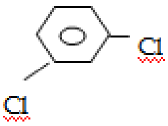
(a) $CH_3CH(Br)CH{=}C(CH_3)CH_2Cl$

(b)

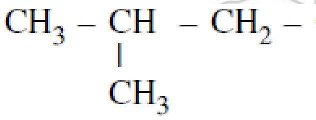
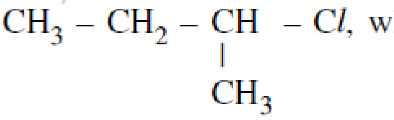


(c) $CH_3CH(CH_3)CH(Br)CH_3$ (d) $ClCH_2CH{=}CHCH_2Br$

(e)



(f) $CH_3CH \equiv C\text{-}I$

15. Out of $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-Cl$ and $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-Cl$, which is more reactive towards S_N1 reaction and why ?

16. What happens when bromine attacks $CH_2{=}CH\text{-}CH_2\text{-}C \equiv CH$?

17. 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

18. 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?

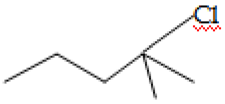
$CH_3CH(Cl)CH_2CH_3$ or $CH_3CH_2CH_2Cl$

(iii) Which one undergoes S_N2 faster and why?

or

19. Which one of the following reacts faster in an S_N1 reaction and why?

or



20. State one use of DDT and iodoform. Why is chloroform kept in dark coloured bottles completely filled?

21. What are ambident nucleophiles? Explain with the help of an example.

22. Write short notes on:

    (a) Fittig reaction (b) Swartz reaction

23. 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 immiscible with water.

    d) Chlorobenzene is extremely less reactive towards nucleophilic substitution reaction.

    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.

24. Carry out the following conversions:

    i) 1-Chlorobutane to n-octane

    ii) Toluene to benzyl alcohol

    iii) Benzyl chloride to benzyl alcohol

25. What will be the mechanism for the substitution of -Br by –OH in $(CH_3)_2C(Br)CH_2CH_3$?

26. Identify the following compounds from A to K:

(a) $CH_3CH_2CH_2Cl + NaI \xrightarrow{\text{Acetone, heat}} A$

(b) $(CH_3)_3CBr + KOH \xrightarrow{\text{Ethanol}} B$

(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) $CH_3CH_2Cl + SbF_5 \xrightarrow{\text{Heat}} F$

(g) $CH_2{=}CHCH_2Br + H_2O \xrightarrow{H^+} G$

(h) $C_6H_5CH_2Cl + C_2H_5ONa \longrightarrow H$

More Practice
Chapter 10: 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. Arrange the following compounds in increasing order of reactivity towards nucleophilic substitution reaction:

   1,4-Dichlorobenzene , 4-Methoxy chlorobenzene, benzene , 2,4,6- Trinitro chlorobenzene

4. Account for the following:

   a) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

   b) Vinyl chloride is unreactive towards nucleophilic substitution reactions.

   c) Grignard reagent should be prepared under anhydrous conditions.

   d) Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions.

5. Carry out the following conversions:

   (i) Propene to propyne

   (ii) Ethanol to but-1-yne

6. 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) $CH_2=CHCH_2Br + CH_3C\equiv CNa \xrightarrow{\text{liq NH3}} C$

(iv) $C_6H_4CH_2Cl + C_2H_5ONa \xrightarrow{\qquad} D$

(v) $CH_3CH_2CH_2OH + SOCl_2 \xrightarrow{\qquad} E$

(vi) $CH_3CH{=}C(CH_3)_2 + HBr \xrightarrow{\qquad} F$

(vii) $CH(CH_3)_2 + Br_2 \xrightarrow{\text{heat}} K$

(viii) $CH_3CH_2CH_2OH + SOCl_2 \xrightarrow{\qquad} L$

(ix) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{Peroxide}} M$

(x) $CH_3CH{=}C(CH_3)_2 + HBr \xrightarrow{\qquad} N$

Assignment

Chapter 11: Alcohols, Phenols and Ethers

1. IUPAC name of m-cresol is….

   (a)3-Methyl phenol (b) 3-Chlorophenol (c) 3-Methoxyphenol (d) Benzene-1,3-diol

2. 1-Phenylethanol can be prepared by the reaction of benzaldehyde with

   (a) methyl bromide

   (b) ethyl iodide and magnesium

   (c) methyl iodide and magnesium (Grignard reagent)

   (d) methyl bromide and aluminium bromide

3. Which of the following reagents can not be used to oxidise primary alcohols to aldehydes?

   (a) CrO_3 in anhydrous medium

   (b) $KMnO_4$ in acidic medium

   (c) Pyridinium chlorochromate

   (d) Heat in the presence of Cu at 573 K

4. An unknown alcohol is treated with "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism?

   (a) Tertiary alcohol by S_N2

   (b) Secondary alcohol by S_N1

   (c) Tertiary alcohol by S_N1

   (d) Secondary alcohol by S_N2

In Q5 and Q8, a statement of assertion (A) is given followed by a corresponding statement of reason (R) just below it. Of the statements mark the correct answer as:

(i)Assertion and reason both are correct statements and reason is correct explanation for assertion.

(ii)Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(iii)Assertion is correct statement but reason is wrong statement.

(iv)Assertion and reason both are incorrect statements.

(v)Assertion is wrong statement but reason is correct statement.

5. **Assertion**: Bond angle in ethers is slightly less than the tetrahedral angle.

   Reason: There is repulsion between two bulky (-R) groups.

6. **Assertion**: p-Nitrophenol is more acidic than phenol.

   Reason: Nitro group helps in the stabilization of the phenoxide ion by dispersal of negative charge due to resonance.

7. **Assertion:** Phenol is more acidic than ethanol.

   Reason: Phenoxide ion is resonance stabilized.

8. **Assertion:** Alcohols have higher boiling point than ethers of comparable molecular masses.

   Reason: Alcohols and ethers are isomeric in nature.

9. Out of t-butyl alcohol and n-butanol, which one will undergo acid catalysed dehydration faster and why?

10. Carry out the following conversions:

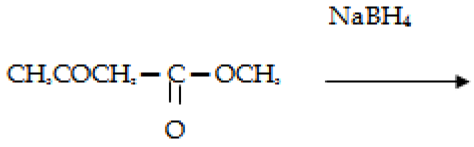
    (i) Phenol to salicylaldehyde

    (ii) t-butyl chloride to t-butyl ethyl ether

11. Give the mechanism of formation of ethanol from ethene.

12. Write the structures of the main products in the following reactions:

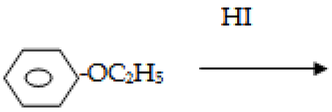
i.



$$CH_3COCH_2-\underset{\underset{O}{\|}}{C}-OCH_3 \xrightarrow{NaBH_4}$$

ii. $CH_3CH_2\,CH=CH_2 + H_2O \xrightarrow{H^+}$

iii.



13. Predict the reagent for carrying out the following conversions:

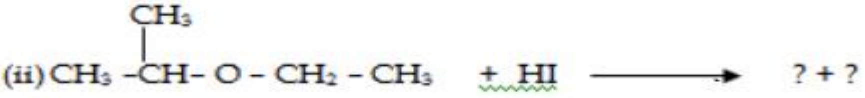
    (i) Phenol to benzoquinone

    (ii) Anisole to p-bromoanisole

    (iii) Phenol to 2,4,6- tribromophenol

14. (a) Write the product(s) in the following reactions :

(i)



$$\text{(ii)}\ CH_3-\overset{CH_3}{\overset{|}{C}H}-O-CH_2-CH_3 + HI \longrightarrow ?+?$$

$$\text{(iii)}\ CH_3-CH=CH-CH_2-OH \xrightarrow{PCC} ?$$

(b) Give simple chemical tests to distinguish between the following pairs of compounds :

(i) Ethanol and Phenol

(ii) Propanol and 2-methylpropan-2-ol

15. (a) Write the formula of reagents used in the following reactions :

(i) Bromination of phenol to 2,4,6-tribromophenol

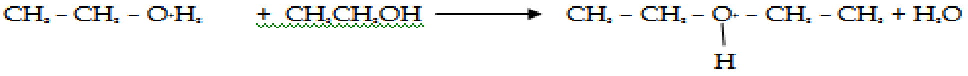
(ii) Hydroboration of propene and then oxidation to propanol.

(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 :



$$CH_3-CH_2-O^{+}H_2 + CH_3CH_2OH \longrightarrow CH_3-CH_2-\underset{H}{\underset{|}{O^{+}}}-CH_2-CH_3 + H_2O$$

16. Give the I.U.P.A.C. name of the following:

(i) $CH_3CH_2\text{-}CH=CH\text{-}CH_2OH$

(ii) $CH_3-CH_2\text{-}CH_2\text{-}OCH_2\text{-}CH(CH_3)\text{-}CH_2\text{-}CH_2CH_3$

(iii) $C_6H_5OCH_2CH_2CH_2CH_2CH-CH_2CH_3$

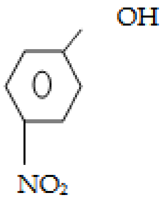
17. **Arrange the following as**

(i) Decreasing order of boiling points:

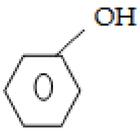
2-methyl-2-propanol, 1-butanol,2-methyl –1-propanol and 2-butanol.

(ii) Decreasing order of their acidic character:

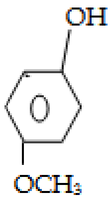
(a)



(b)



(c)



(iii) Increasing reactivity towards Lucas reagent:

1-butanol , 2-methyl-2- propanol , 2-butanol.

18. 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 $KMnO_4$

19. How does phenol react with the following?

(i) Acetyl chloride.

(ii) Bromine in water.

(iii) Chloroform in presence of NaOH

20. 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

21. Explain giving reasons:-

(i) Alcohols are generally soluble in water but alkyl halides are not.

(ii) Phenols exhibit an acidic character.

(iii) Phenol has a smaller dipole moment than methanol.

(iv) 2,3- dimethylbutanol has a lower boiling point than hexanol .

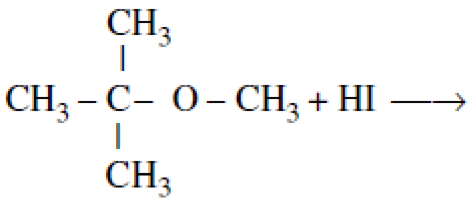
(v) 2-Nitrophenol is more volatile than 4-Nitrophenol.

22. Write the mechanism of the following reaction :

$$2CH_3CH_2OH \xrightarrow[413\ K]{Conc.\ H_2SO_4} CH_3CH_2-O-CH_2-CH_3$$

23. Write the main product(s) in each of the following reactions :

(i)



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3 + HI \longrightarrow$$

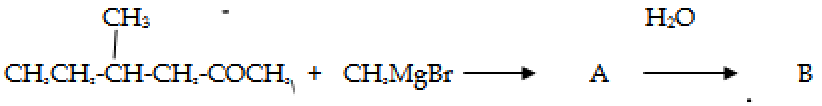
(ii) $CH_3-CH=CH_2 \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6}$

(iii) $C_6H_5-OH \xrightarrow[(ii)\ CO_2,\ H^+]{(i)\ aq.\ NaOH}$

More Practice

Chapter 11: Alcohols, Phenols and Ethers

1. Complete the following reactions

(a) 

$CH_3CH_2\text{-}\overset{CH_3}{\overset{|}{C}H}\text{-}CH_2\text{-}COCH_3 + CH_3MgBr \longrightarrow A \xrightarrow{H_2O} B$

(b) 

$CH_3\text{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{-}OH \xrightarrow{Cu\,/\,573\,K}$

(c) $C_2H_5Br + NaO\text{-}C\text{-}(CH_3)_3 \longrightarrow$

(d) $CH_3\text{-}C\,(CH_3)_2Br + NaOC_3H_7 \longrightarrow$

2 Convert:

(i) Chlorobenzene to Phenol

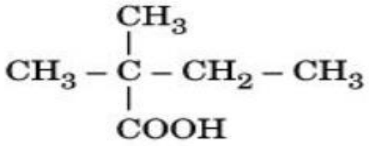
(ii) Aniline to phenol

(iii) Propanone to Propene

Assignment

Chapter 12: Aldehydes, Ketones and Carboxylic Acids

What is the correct IUPAC name of the given compound ?



$$CH_3-\underset{\displaystyle COOH}{\overset{\displaystyle CH_3}{C}}-CH_2-CH_3$$

(A) 2,2-Dimethylbutanoic acid

(B) 2-Carboxyl-2-methylbutane

(C) 2-Ethyl-2-methylpropanoic acid

(D) 3-Methylbutane carboxylic acid

2. The correct order of increasing acidic strength is _____________.

(i) Phenol < Ethanol < Chloroacetic acid < Acetic acid

(ii) Ethanol < Phenol < Chloroacetic acid < Acetic acid

(iii) Ethanol < Phenol < Acetic acid < Chloroacetic acid

(iv) Chloroacetic acid < Acetic acid < Phenol < Ethanol

3. In Clemmensen Reduction carbonyl compound is treated with _____________.

(i) Zinc amalgam + HCl

(ii) Sodium amalgam + HCl

(iii) Zinc amalgam + nitric acid

(iv) Sodium amalgam + HNO_3

4. **The formation of cyanohydrin from a ketone is an example of**

(i)electrophilic addition

(ii)nucleophilic addition

(iii)nucleophilic substitution

(iv)electrophilic substitution

5. **Heating a mixture of sodium benzoate and soda lime gives**

(i) calcium benzoate

(ii) benzene

(iii) sodium benzoate

(iv) methane

6. Iodoform test is given by:

(i) Pentan-2-one

(ii) Pentan-3-one

(iii)Ethanoic acid

(iv)Methoxymethane

In the following questions 7 to 10, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(i) Assertion and reason both are correct and reason is correct explanation of assertion.

(ii)Assertion and reason both are correct statements but reason is not correct explanation of assertion.

(iii) Assertion is correct statement but reason is wrong statement.

(iv) Assertion is wrong statement but reason is correct statement.

(v)Assertion and reason both are wrong statements.

7. **Assertion** : Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.

Reason : Both aldehydes and ketones contain a carbonyl group.

8 **Assertion** : Aromatic aldehydes and formaldehyde undergo Cannizaro reaction.

Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

9. **Assertion:** Isobutanal doesn't undergo iodoform test.

Reason: It doesn't contain alpha hydrogen.

10. **Assertion:**Mixture of benzaldehyde and acetaldehyde in hot alkaline solution results in the formation of cinnamaldehyde.

Reason: Benzaldehyde is a strong electrophile than acetaldehyde**.**

11. What happens when:

(a) acetone is treated with Zn(Hg) / conc HCl.

(b) Ethanal is treated with Methylmagnesium bromide and then hydrolysed.

12. (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?

13. 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

14. Account for the following:

(a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.

(b) pKa value of 4-nitrobenzoic acid is lower than that of benzoic acid.

15. Write structures of compounds A, B and C in each of the following reactions :

(i) $C_6H_5Br \xrightarrow{Mg/\text{dry ether}} A \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } CO_2(g)} B \xrightarrow{PCl_5} C$

(ii) $CH_3CN \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } SnCl_2/HCl} A \xrightarrow{\text{dil. } NaOH} B \xrightarrow{\Delta} C$

16. Write IUPAC names for the following :

(a) $C_6H_5CH_2CHO$

(b) $CH_2=CHCH_2CHO$

(c) $(CH_3)_2C=CHCOCH_2CH_3$

17. Arrange the following compounds as directed:

a) Acetaldehyde, acetone, Methyl tert-butyl ketone (reactivity towards HCN)

b) Benzoic acid, 3,4-Dinitrobenzoic acid, 4-methoxybenzoic acid

c) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$ (acid strength)

d) a) CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$(increasing order of their boiling point)

e) b) Ethanal, propanal, propanone , butanone (increasing order of their reactivity towards nucleophilic addition).

18. Give brief description with suitable example:

a) Cannizzaro Reaction

b) Hell-Volhard Zelinsky Reaction.Clemmensen Reduction

c) Wolff-Kishner Reduction.

d) Cross aldol condensation

e) Etard reaction

19. 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.

20. 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

21. 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

g) Propanal and Propanone

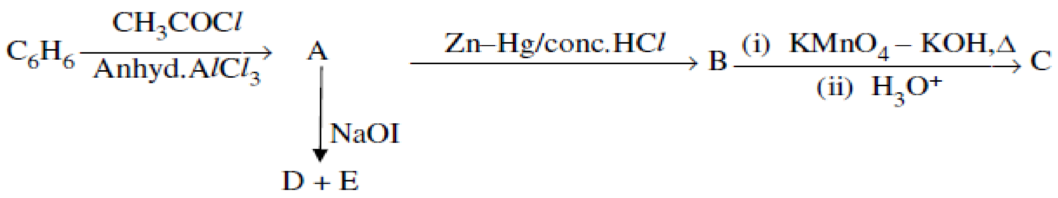
22. Complete the following reactions:

(a) $CH_3CO\ CH_3 + NH_2NH_2 \xrightarrow{KOH/glycol}$

(b) $C_6H_5COCH_3 + C_6H_5OH \xrightarrow{NaOH/\ I2}$

(c) $C_6H_5NH_2 \xrightarrow{NaOH/CaO}$

23. (a) Write the structures of A, B, C, D and E in the following reactions :



24. (i)Write a chemical equation for the reaction involved in the Cannizaro reaction.

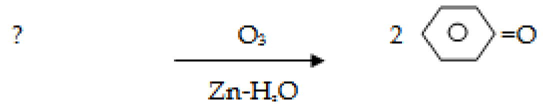
(ii)Draw structure of Semicarbazone of Ethanal.

(iii)Why is the pk$_a$ value of F-CH_2-COOH lower than *Cl*-CH_2-COOH?

(iv)Write product for the reaction:

$$CH_3\text{-}CH\text{=}CH\text{-}CH_2\text{-}CN \xrightarrow[\text{(ii)}H2O]{\text{(i) DIBAL-H}}$$

25. Complete the following reaction statements by giving the missing starting material, reagent or product as required:

(i)


(ii)


(iii)


More Practice

Chapter 12: 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 and 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

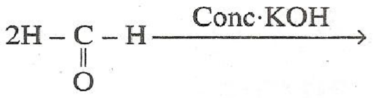
xii) propane to Propane

xiii) Benzoyl chloride to Benzaldehyde

xiv) Ethanol to But-2-enal

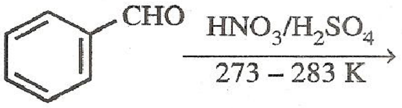
3 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Give two reasons.

4 (a) Complete the following reactions :

(i) 

$$2H-\overset{\displaystyle O}{\underset{}{C}}-H \xrightarrow{Conc\cdot KOH}$$

(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 13: Organic Compounds containing Nitrogen

1. Out the following, the strongest base in aqueous solution is:

   (i) Methylamine

   (ii)Dimethylamine

   (iii) Trimethylamine

   (iv)Aniline

2. Reduction of aromatic nitro compounds using Fe and HCl gives __________.

   (i) aromatic oxime

   (ii) aromatic hydrocarbon

   (iii) aromatic primary amine

   (iv) aromatic amide

3. Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is

   (i) Hoffmann Bromamide reaction

   (ii) Gabriel phthalimide synthesis

   (iii) Sandmeyer reaction

   (iv) Reaction with NH_3

4. **In this reaction acetamide is converted to methanamine**

   (i) Gabriel phthalimide synthesis

   (ii) Carbylamine reaction

   (iii) Stephen's reaction

   (iv) Hoffmann bromamide reaction

In the following questions 5 to 8, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(i) Both assertion and reason are wrong.

(ii) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

(iii) Assertion is correct statement but reason is wrong statement.

(iv) Both assertion and reason are correct statements and reason is correct explanation of assertion.

(v) Assertion is wrong statement but reason is correct statement

5. **Assertion** : N-Ethylbenzene sulphonamide is soluble in alkali.

   Reason : Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

6. **Assertion** : Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.

   Reason : Acyl group sterically hinders the approach of further acyl groups.

7. **Assertion:** Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.

   Reason: $FeCl_2$ formed gets hydrolyzed to release HCl during the reaction.

8. **Assertion:** Acetanilide is less basic than aniline.

   Reason: Acetylation of aniline results in a decrease of electron density on nitrogen.

9. (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.

10. **Give the structures of A and B in the following sequence of reactions :**

(a) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B$

(b) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[0^\circ - 5^\circ C]{NaNO_2 + HCl} B$

(c) $C_6H_5N_2^+Cl^- \xrightarrow[\Delta]{CuCN} A \xrightarrow{H_2O/H^+} B$

11. (a)Write the structures of the main products of the following reactions:

1. $C_6H_5NH_2 \xrightarrow{(CH_3CO)_2O,\ Pyridine}$

2. $C_6H_5SO_2Cl \xrightarrow{(CH_3)_2NH}$

3. $C_6H_5N_2^+Cl^- \xrightarrow{CH_3CH_2OH\ /\ Heat}$

(b)Give a simple chemical test to distinguish between

(i) Aniline and N- methylaniline.

(ii) Aniline and ethanamine

(a) Arrange the following in the increasing order of their pK_b values:

$C_6H_5NH_2$, $C_2H_5NH_2$, $C_6H_5NHCH_3$

12. Write IUPAC name of the following compound : $(CH_3CH_2)_2NCH_3$

13. 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.

14. Write IUPAC names of the following:

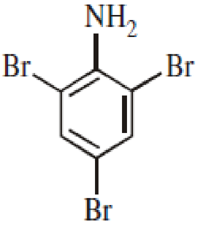
a) $CH_3-CH(NH_2)-CH(CH_3)-CONH_2$

b) $BrCH_2N(CH_3)_2$

c) $O_2N-CH_2-CH_2-CH=CH-CHO$

d) $(CH_3)_3CCN$

e)



15. For an amine RNH_2, write the expression for K_b to indicate its basic strength.

16. Describe the following processes giving suitable examples of each:

i) Diazotization

ii) Coupling reaction

iii) Carbylamine reaction

iv) Hofmann's bromamide reaction

17. 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

18. Write structures of the following:

i) P- Toluidine

ii) Picric acid

iii) Sulphanilic acid

19. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.

20. 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.

21. (i)Arrange in increasing order of boiling point: $C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$

(ii) Arrange the following in decreasing order of boiling point:

Butanol, butanamine,butane

22. Complete the following reaction equations:

i) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

ii) $C_6H_5NH_2 + Br_2(aq) \longrightarrow$

23. 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 13: 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. scribe 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. w 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 14: Biomolecules

Learning Outcomes - The learners

- applies scientific concepts in daily life with the knowledge of importance of carbohydrates , proteins and vitamins.
- draw conclusion, such as features inherited with the knowledge on nucleic acids, such as, protein synthesis
- explain processes taking place in the human body through the biomolecules.
- Distinguish between the primary, secondary, tertiary and quaternary structure of proteins, different types of carbohydrates or amino acids.
- Explain the structures of different carbohydrates and also hemiacetal form of it.
- explain denaturation of proteins, selectivity of enzyme action.
- Classify vitamins and also list the different vitamins with their uses and deficiency diseases

1. On oxidation with a mild oxidising agent like Br2/H20, the glucose is oxidized to

   (a) saccharic acid

   (b) glucaric acid

   (c) gluconic acid

   (d) valeric acid

2. Globular proteins are present in

   (a)Keratin (b) Muscles (c) Eggs (d) nucleoside

3. Invert sugar is

   (a) a type of cane sugar

   (b) optically inactive form of sugar

   (c) mixture of glucose and galactose

   (d) mixture of glucose and fructose in equimolar quantities

4. Purine and Pyrimidine bases present in both DNA and RNA are

   (a)Uracil (b) Thymine (c) Cytosine (d) Adenine

In Q5 to Q8, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(i) Both assertion and reason are wrong.

(ii) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

(iii) Assertion is correct statement but reason is wrong statement.

(iv) Both assertion and reason are correct statements and reason is correct explanation of assertion.

(v) Assertion is wrong statement but reason is correct statement

5. **Assertion:** Sucrose is a non-reducing sugar.

   Reason: Reducing groups of glucose and fructose are involved in glycosidic bond formation.

6. **Assertion: The amino acid Glycine comes under the category of non-essential amino acids.**

   Reason: This is due to the fact that it cannot be synthesised in our body.

7. **Assertion:** Cellulose is not digested by human beings.

   Reason: Cellulose is a polymer of β-D-glucose.

8. **Assertion:** Alpha amino acids exist as internal salt in solution as they have amino acid and carboxylic acid groups in near vicinity.

   Reason:H^+ ion given by carboxyl group(-COOH) is captured by amino group($-NH_2$) having lone pair of electrons.

9. Give the plausible explanation for the following:

   (a) Glucose doesn't give 2,4-DNP test.

   (b) The two strands in DNA are not identical but are complementary.

   (c) Starch and cellulose both contain glucose unit as monomer, yet they are structurally different.

10. Define the following with an example of each;

    (i) Polysaccharides

    (ii) Denatured proteins

    (iii) Essential aminoacids

11. (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.

12. State two main differences between globular proteins and fibrous proteins. Give one example of each.

13. 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?

14. Write chemical equations for the reactions of glucose with

    (i)Acetic Anhydride (ii) NH_2OH (iii) HNO_3 (iv) HI

15. 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 .

16. (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.

17. Define enzymes .State the activity of enzyme. How do enzymes differ from ordinary chemical catalysis? Comment on the specificity of enzyme action.

18. In what way is a nucleotide different from a nucleoside? Illustrate with examples?

19. What is essentially the difference between alpha-glucose and beta-glucose? What is meant by pyranose structure of glucose?

20. Name some biological functions of nucleic acids.

    What is the name given to the linkage which holds together two nucleotides

21. Explain what is meant by

    (i) a peptide linkage

    (ii) a glycosidic linkage

22. 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 ?

23. What is glycogen? How is it different from starch? How is starch structurally different from cellulose?

24. How do you explain amphoteric behaviour of amino acids?

25. Define denaturation in proteins.

26. 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 15: Polymers

Learning Outcomes: The learner

- differentiates between different types of polymers, based on properties or characteristics,
- makes efforts to conserve environment realising the inter-dependency and inter-relationship in the biotic and abiotic factors of environment and discover more biodegradable polymers
- classifies between different polymers based on their source, polymerization, structure and nature of intermolecular forces
- applies concepts of polymers in day-today life while making decisions and solving problems

1. **Nylon threads are made of**

   (i)polyester polymer

   (ii)polyamide polymer

   (iii)polyethylene polymer

   (iv)polyvinyl polymer

2. **Which of the following is a branched polymer?**

   (i)low density polymer

   (ii)polyester

   (iii)high density polymer

   (iv)nylon

3. The commercial name of polyacrylonitrile is _______________.

   (i) Dacron

   (ii) Orlon (acrilan)

   (iii) PVC

   (iii) Bakelite

4. Which of the following is not a semisynthetic polymer?
   (i) cis-polyisoprene
   (ii) Cellulose nitrate
   (iii) Cellulose acetate
   (iv) Vulcanised rubber

In the following question no. 5 to 8, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
(i) Assertion and reason both are correct statement but reason does not explain assertion.
(ii) Assertion and reason both are correct statements and reason explains the assertion.

(iii) Both assertion and reason are wrong statement.
(iv) Assertion is correct statement and reason is wrong statement.
(v) Assertion is wrong statement and reason is correct statement.

5. Assertion : Olefinic monomers undergo addition polymerisation.
Reason : Polymerisation of vinyl chloride is initiated by peroxides/ persulphates.

6. Assertion : For making rubber synthetically, isoprene molecules are polymerised.
Reason : Neoprene (a polymer of chloroprene) is a synthetic rubber.

7. Assertion: Natural rubber is a polymer of isoprene.
Reason: Isoprene is a pentene.

8. Assertion: Fibres are stronger than elastomers.
Reason: Fibres have strong H-bonds.

9. Write a difference between LDPE and HDPE.

10. What are biodegradable polymers? Give an example.

11. Write the structures of the monomers used for getting the following polymers :
(i) Dacron
(ii) Melamine – formaldehyde polymer
(iii)Buna-N
(iv)Teflon

12. 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 (ix) Buna-N

13. (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 :

$$[\mathrm{NH} - (\mathrm{CH_2})_6 - \mathrm{NH} - \mathrm{CO} - (\mathrm{CH2})_4 - \mathrm{CO} -]\mathrm{n}$$

(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.

14. (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

15. (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 ?

16. What are the uses of Teflon?

17. 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)

18. 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).

19. How is melamine polymer prepared? Give its two uses. What type of polymer is it?

20. Name the monomers of Nylon2-nylon-6 polymer.

21. PHBV (Poly-β-Hydroxybutyrate-co-β-hydroxy valerate) is a biodegradable polymer. It is a copolymer of 3-hydroxy valerate acid and 3-hydroxypentanoic acid.

    (a) How PHBV has found utility in medicines as Capsule?

    (b) Write the name of a polymer used in an 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

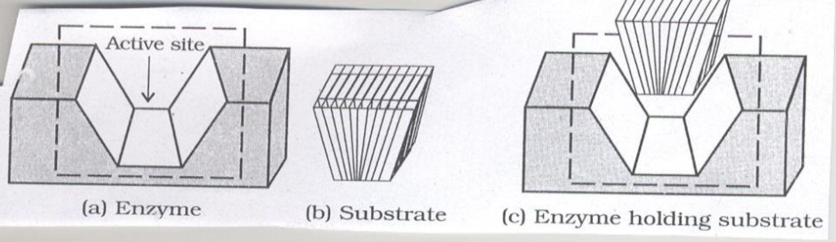
Macromolecules of biological origin perform various functions in the body. For eg- Proteins which perform role of biological catalyst in the body are called ENZYMES & those which are crucial to communication system are called RECEPTORS.

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.

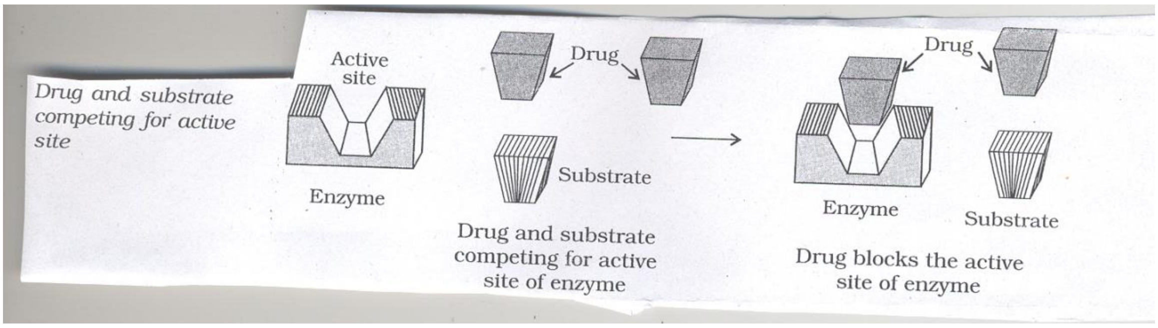
Enzymes hold the substrate for a chemical reaction. Active sites of enzymes hold substrate molecule in a suitable position, so that it can be attacked by the reagent effectively. Substrate binds themselves to the active sites by ionic bonding, hydrogen or by vanderwaals interaction.



(a) Enzyme (b) Substrate (c) Enzyme holding substrate

(a) Active site of an enzyme (b) Substrate (c) Substrate held in active site of the enzyme

Drug and substrate competing for active site



Drug and substrate competing for active site of enzyme

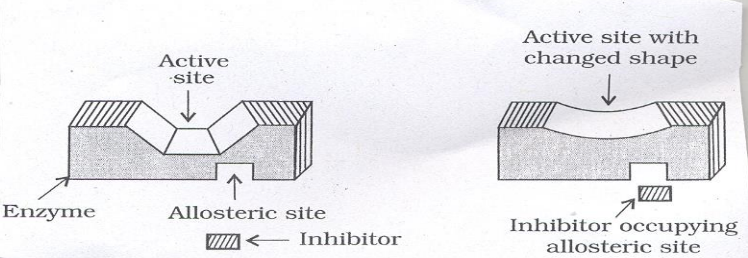
Drug blocks the active site of enzyme

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.

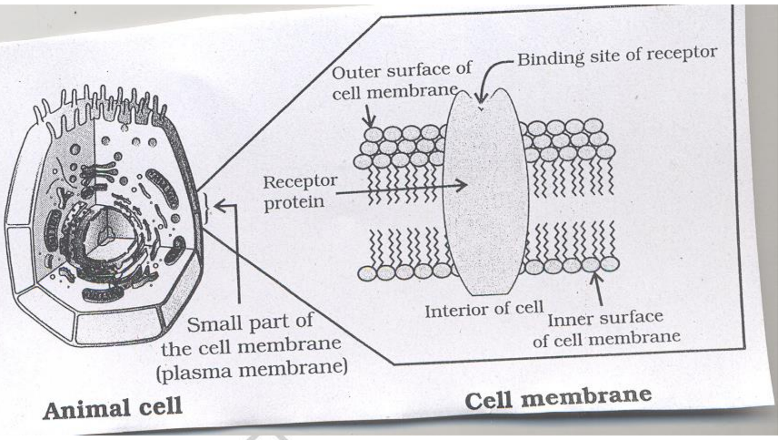
If the bond between an enzyme and inhibitor is a strong covalent bond and it cannot be easily broken, then the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesizes the new enzyme.



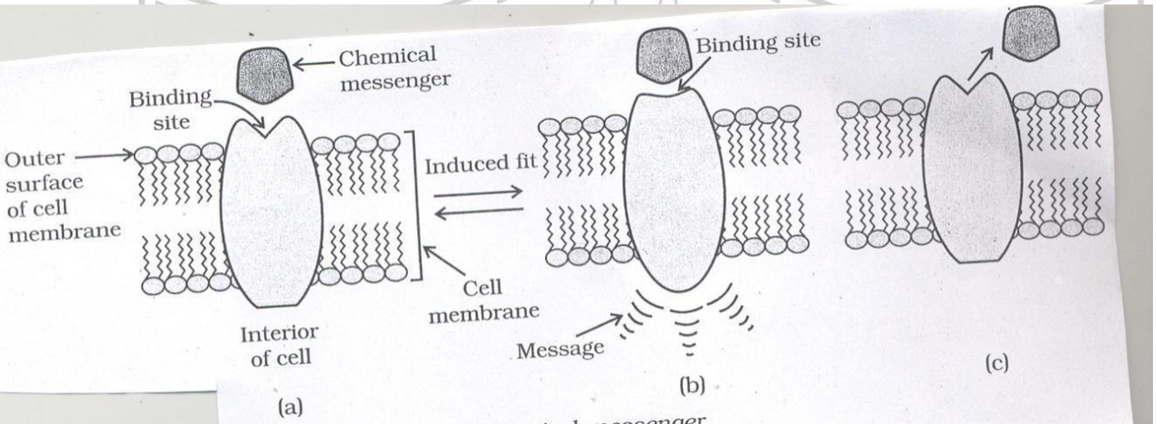
: Non-competitive inhibitor changes the active site of enzyme after binding at allosteric site.

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 <u>antagonists</u>. Drugs that mimic the natural messenger by switching on the receptors are called <u>agonists</u>. 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. Therefore these are for curing a variety of diseases. Eg- thetracycline, chloromycetin and chloramphenicol. Eg-

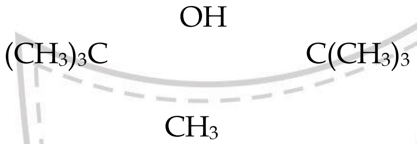
Chloramphenicol is a broad spectrum antibiotic which is used for curing typhoid, acute fever, dysentery, whooping cough, pneumonia, eye infections, certain urine infections etc. Sulphadrugs are used against pneumonia, tuberculosis, diphtheria etc. Some examples are sulphadiazine, sulphathiazole, sulphaacetamide 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

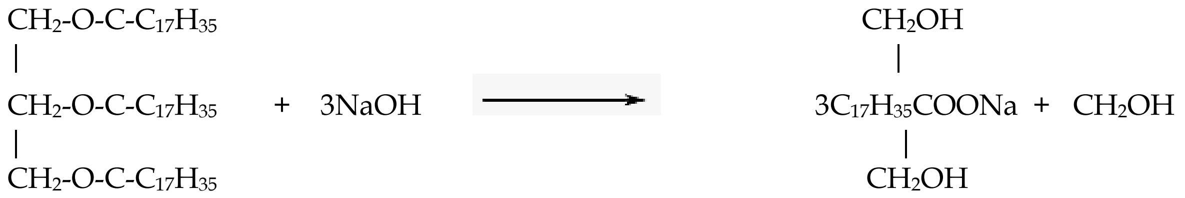
BHA

   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.



$$\begin{array}{l} CH_2\text{-}O\text{-}C\text{-}C_{17}H_{35} \\ | \\ CH_2\text{-}O\text{-}C\text{-}C_{17}H_{35} \\ | \\ CH_2\text{-}O\text{-}C\text{-}C_{17}H_{35} \end{array} + 3NaOH \longrightarrow 3C_{17}H_{35}COONa + \begin{array}{c} CH_2OH \\ | \\ CH_2OH \\ | \\ CH_2OH \end{array}$$

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 a large part of the molecule is anion. The anionic detergent is largest in use as household detergents. E.g.- Alkyl Benzene Sulphonate . 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 detergents 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.

$CH_3(CH_2)_{16}COOH+HO(CH_2CH_2O)_nCH_2CH_2OH$

$CH_3(CH_2)_{16}COO(CH_2CH_2O)nCH_2CH_2OH$

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 presentation with animations.

Assignment

Chapter 16: Chemistry in Everyday Life

Learning Outcomes: The learner

- relates the action of different medicines with causes and effects,
- exhibits values of objectivity, rational thinking in consumption and use of drugs
- applies scientific concepts of drug action on enzymes and receptors in daily life and solving problems,
- draws conclusion about the use of food additives, or medicines in our day to day life.
- exhibits creativity in designing eco-friendly resources ,such as, soaps and detergents.
- Explains cleansing action of soaps and detergents, advantages and disadvantages of soaps/ detergent
- list the names of artificial sweetening agents and explain its effect and potency

1. Which one of the following is antihistamine?
   (a) Chloramphenicol
   (b) Diphenyl hydramine
   (c) Norethindrone
   (d) Omeprazole

2. Bithional added to soap acts as
   (a) buffering agent
   (b) antiseptic
   (c) softener
   (d) drying

3. Cetyltrimethyl ammonium bromide is a popular
   (a)anionic detergent (b) cationic detergent (c) non-ionic detergent (d) antioxidant

4. The artificial sweetner containing chlorine that has the appearance and taste as that of sugar and is stable at cooking temperature is
   (a)Aspartame (b) Saccharin (c) Sucrolose (d) alitame

In Q5 to Q8, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
(i) Both assertion and reason are wrong.
(ii) Both assertion and reason are correct statements but reason is not correct explanation of assertion.
(iii) Assertion is correct statement but reason is wrong statement.
(iv) Both assertion and reason are correct statements and reason is correct explanation of assertion.
(v) Assertion is wrong statement but reason is correct statement

5. **Assertion**: Transparent soaps are made by dissolving soap in ethanol.
   Reason: Ethanol makes things invisible.

6. **Assertion**: Chemical messenger gives message to the cell without entering the cell.
   Reason: Chemical messenger is received at the binding site of receptor proteins.

7. **Assertion :** Penicillin (G) is an antihistamine
   Reason : Penicillin (G) is effective against gram positive as well as gram negative bacteria.

8. **Assertion :** Sulpha drug contain sulphonamide group.
   Reason : Salvarsan is a sulpha drug.

9. (i) What is tincture of iodine? Write its one use.
   (ii) Among the following, which one acts as a food preservative?
   Aspartame, Aspirin, Sodium Benzoate, Paracetamol

10. Define the following and give one example :
    (i) Anionic detergents
    (ii) Antimicrobials
    (iii) Antioxidants
    (iv) Broad spectrum antibiotics
    (v) Artificial sweetening agents
    (vi) Food Preservatives

11. What type of medicines are omeprazole and lansoprazole?

12. Give an example of a drug used in case of mental depression. Define that drug.

13. For which disease chloramphenicol is used?

14. (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?

15. Name a broad spectrum antibiotic and diseases for which it is prescribed.

16. (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.

17. Name the action of the following on the human body:
    (i) Equanil (ii) Morphine (iii) Norethindrone (iv) Aspirin (v) Penicillin
    (vi) Luminal (vii) Seconal

18. What are the essential components of dettol?

19. What are detergents? Give their scheme of classification. Why are detergents preferred over soaps?

20. What are biodegradable and non-biodegradable detergents? What are the consequences of using the latter kind? Give one example of each kind.

21. Why soaps do not act on hard water?

22. Explain the term ‘chemotherapy’.

23. Describe the function of the following with one example for each
 a. Antifertility drugs b. Antihistamines
 c. Analgesics d. Antioxidants e. Antacids

24. Explain the cleansing action of soaps. Why is ethanol added to soaps?

25. 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.

26. Except for vitamin B_{12}, all other vitamins of group B, should be supplied regularly in diet. Why?

27. 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

(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 18 carrying 35 marks.
(iv) Part B is practical related questions numbering 19 to 23 carrying 15 marks.
(v) Use log tables if necessary, use of calculators is not permitted.

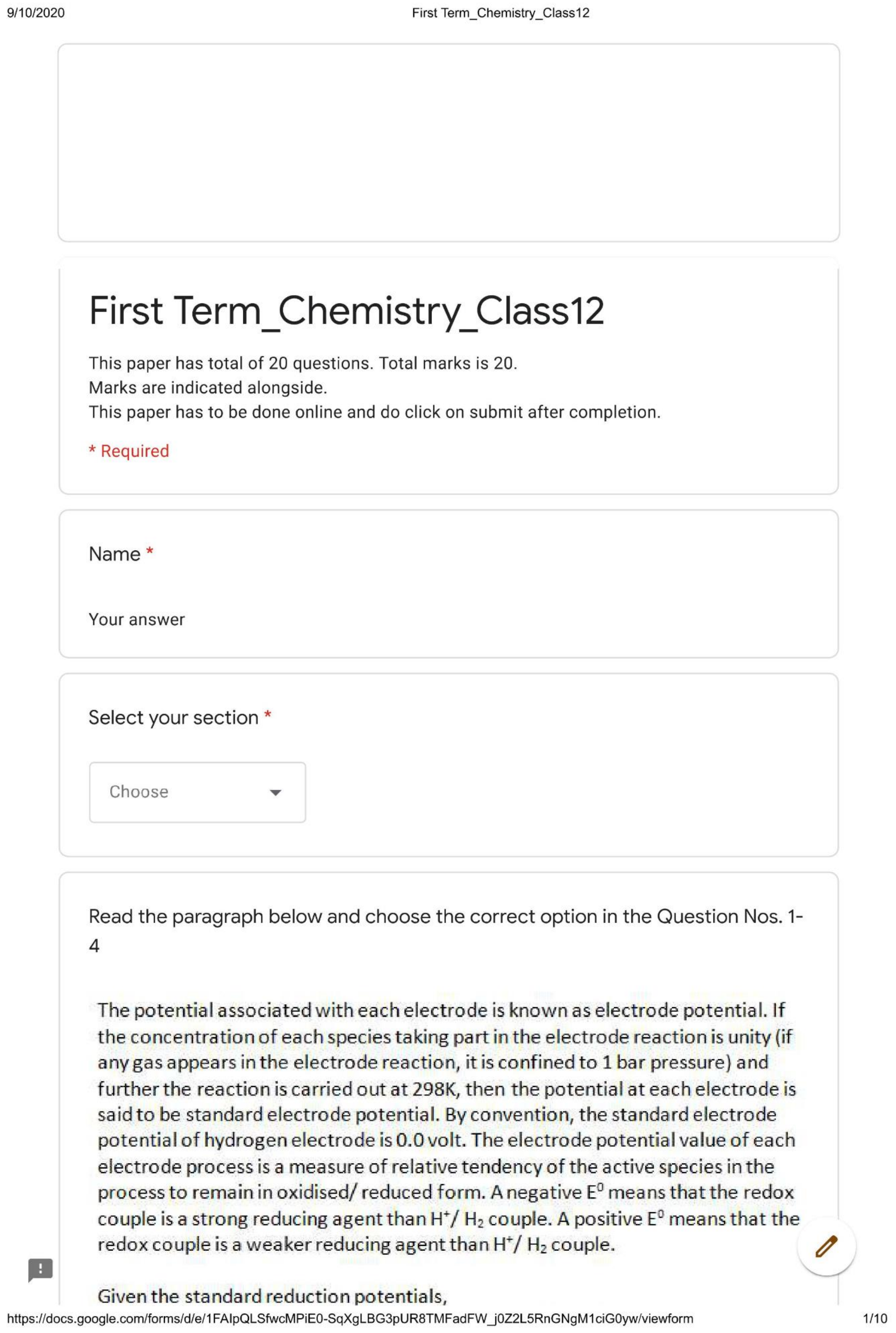
PART A

	There are two types of cells; Primary and Secondary. Primary cells once used cannot be recharged where as secondary cells once used can be recharged. Electrolysis may be defined as a process of decomposition of an electrolyte by the passage of electricity through its aqueous solution or molten state.	
1.	What type of cell is mercury cell? Write its overall reaction?	1
2.	Write the anodic and cathodic reaction for lead storage battery while discharging.	1
3.	Write the products of electrolysis of $CuSO_4$(aq) using Pt electrodes.	1
4.	How many Faradays of electricity is required to obtain 1 mol of Mn2+ from $KMnO_4$?	1
5.	Which of the following has maximum number of lone pairs associated with Xe? (a)XeO_3 (b) XeF_4 (c) XeF_6 (d) XeF_2	1
	In Q6 and Q7, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (i) Both assertion and reason are wrong. (ii) Both assertion and reason are correct statements but reason is not correct explanation of assertion. (iii) Assertion is correct statement but reason is wrong statement. (iv) Both assertion and reason are correct statements and reason is correct explanation of assertion. (v) Assertion is wrong statement but reason is correct statement	
6.	**Assertion:** Higher the molal depression constant of the solvent used, higher the freezing point of the solution. **Reason:** Depression in freezing point doennot depend on the nature of the solvent.	1
7.	**Assertion:** All collisions of reactant molecules lead to product formation.	1

	Reason: Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.	
8.	For a reaction, A+ B → P, the reaction is of first order in reactant A and second order in reactant B. How is the rate of this reaction affected when the concentration of B doubled. (i) What is the overall order of rection if A is present in large excess.	1
9.	How many grams of chlorine can be produced by the electrolysis of molten NaCl with a current of 1A for 15 minutes? (given atomic mass of Cl=35.5u, 1F=96500 C/mol)	2
10.	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
11.	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
12.	(i) Why is the freezing point depression of 0.1M sodium chloride solution nearly twice that of 0.1M glucose solution? (ii) A solution containing 8g of a substance in 100g of diethyl ether boils at 36.86^0C , whereas pure ether boils at 35.6^0C. Determine molecular mass of solute. [For ether, $K_b = 2.02$ K Kg mol^{-1}]	3
13.	The decomposition of phosphine, PH_3, proceeds according to the following equation: $4PH_3\ (g) \rightarrow 3P_4\ (g) + 6H_2(g)$ 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 $3/4^{th}$ of PH_3 to decompose? [log2=0.3010]	2
14.	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? b) What type of collisions is known to be effective?	2
15.	Write the Nernst equation and calculate the e.m.f of the following cell at 298K $Zn(s)\|Zn^{2+}(0.1\ M)\ \|\|\ Cd^{+2}(0.01M)\|Cd(s)$ ($E^0_{Zn^{2+}/Zn}$= -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 $Zn^{+2}/2Zn$.	3

	(iii) Which electrode is negatively charged? (iv) Individual reactions at each electrode.	
16.	A first order decomposition reaction takes 40 min for 30% decomposition. Calculate its $t_{1/2}$ value. (log10=1, log7=0.8451)	2
17.	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? 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.	3
18.	a) Complete the following chemical reaction equations: i. XeF_4 (s) + H_2O (l) ii. ClF + H_2O 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.	5
	PART B	
19.	Why is it that tests for Barium, Strontium and Calcium to be done in order?	2
20.	Explain one confirmatory test for Ni^{2+}.	2
21.	(a) Give the formula of reddish yellow vapours evolved during chromyl chloride test? (b) Explain the Cl_2 water test for iodide with equation.	1,2
22.	Explain the indicatory and confirmatory tests for sulphide.	3
23.	(a) How can one distinguish between sulphite and sulphate using $BaCl_2$ test. (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?	5

Academic session 2020-21 (Google Form)



9/10/2020 First Term_Chemistry_Class12

First Term_Chemistry_Class12

This paper has total of 20 questions. Total marks is 20.
Marks are indicated alongside.
This paper has to be done online and do click on submit after completion.

* Required

Name *

Your answer

Select your section *

Choose ▾

Read the paragraph below and choose the correct option in the Question Nos. 1-4

The potential associated with each electrode is known as electrode potential. If the concentration of each species taking part in the electrode reaction is unity (if any gas appears in the electrode reaction, it is confined to 1 bar pressure) and further the reaction is carried out at 298K, then the potential at each electrode is said to be standard electrode potential. By convention, the standard electrode potential of hydrogen electrode is 0.0 volt. The electrode potential value of each electrode process is a measure of relative tendency of the active species in the process to remain in oxidised/ reduced form. A negative E^0 means that the redox couple is a strong reducing agent than H^+/H_2 couple. A positive E^0 means that the redox couple is a weaker reducing agent than H^+/H_2 couple.

Given the standard reduction potentials,

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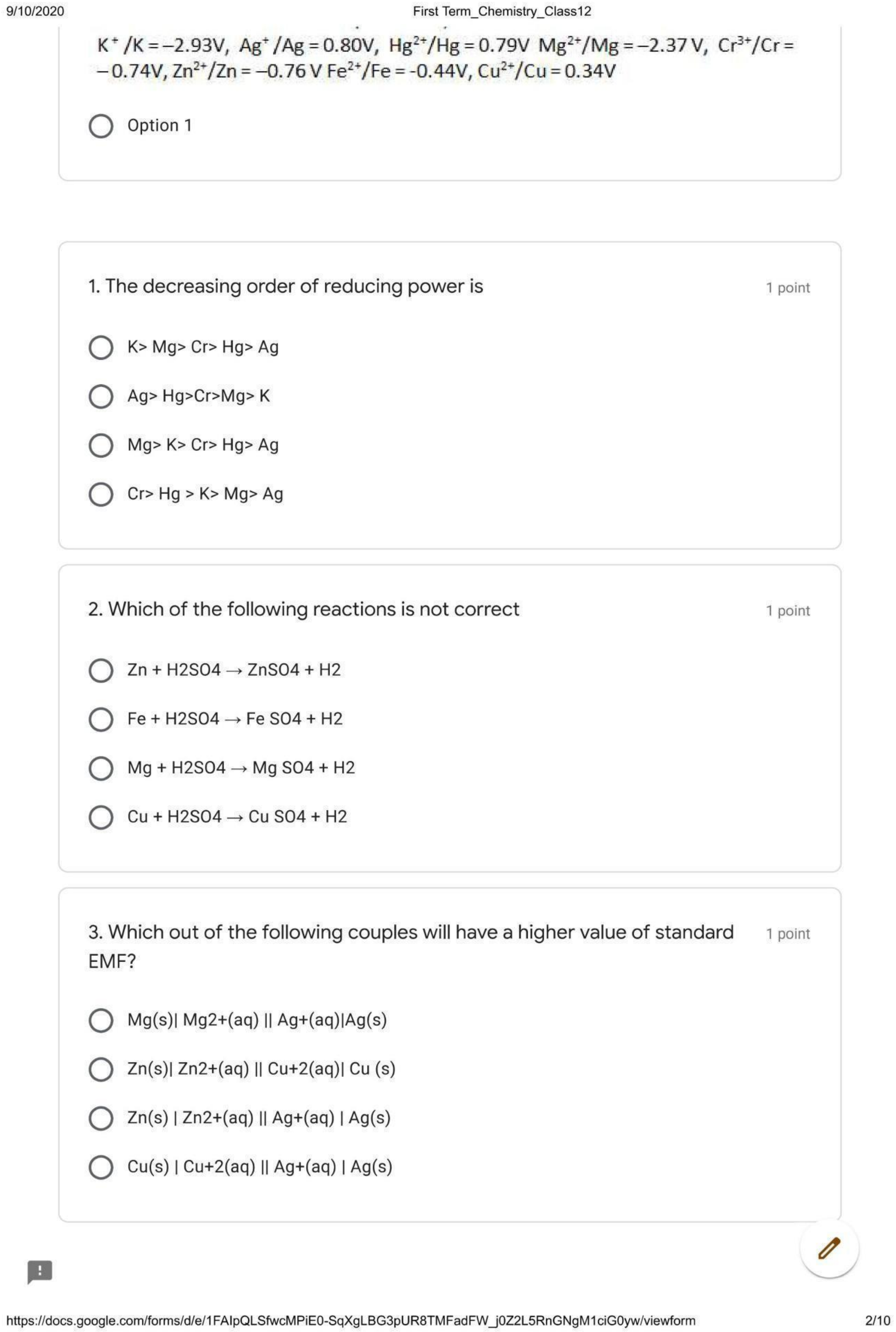


$K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$, $Hg^{2+}/Hg = 0.79V$ $Mg^{2+}/Mg = -2.37\,V$, $Cr^{3+}/Cr = -0.74V$, $Zn^{2+}/Zn = -0.76\,V$ $Fe^{2+}/Fe = -0.44V$, $Cu^{2+}/Cu = 0.34V$

○ Option 1

1. The decreasing order of reducing power is 1 point

○ K> Mg> Cr> Hg> Ag

○ Ag> Hg>Cr>Mg> K

○ Mg> K> Cr> Hg> Ag

○ Cr> Hg > K> Mg> Ag

2. Which of the following reactions is not correct 1 point

○ Zn + H2SO4 → ZnSO4 + H2

○ Fe + H2SO4 → Fe SO4 + H2

○ Mg + H2SO4 → Mg SO4 + H2

○ Cu + H2SO4 → Cu SO4 + H2

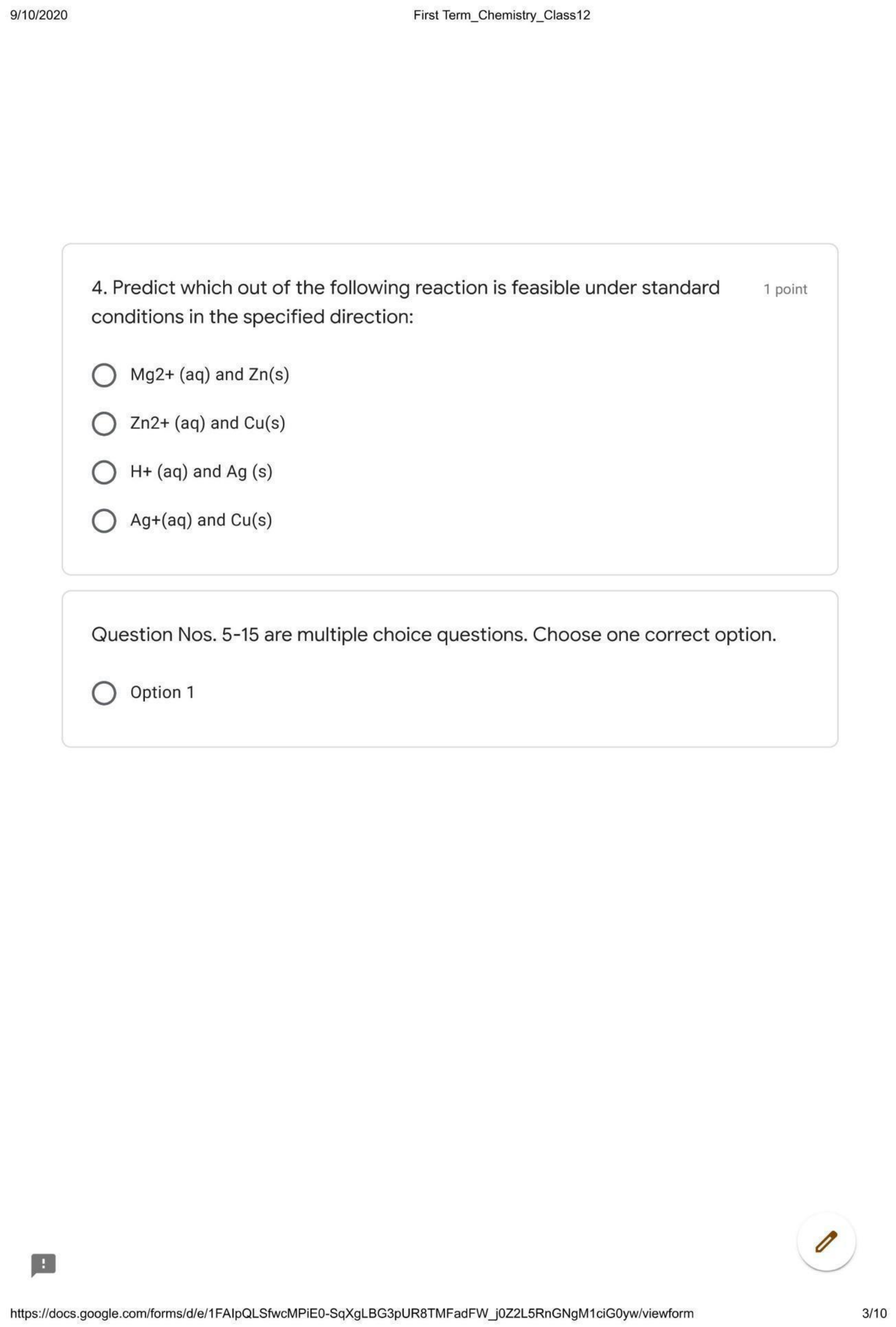
3. Which out of the following couples will have a higher value of standard EMF? 1 point

○ Mg(s)| Mg2+(aq) || Ag+(aq)|Ag(s)

○ Zn(s)| Zn2+(aq) || Cu+2(aq)| Cu (s)

○ Zn(s) | Zn2+(aq) || Ag+(aq) | Ag(s)

○ Cu(s) | Cu+2(aq) || Ag+(aq) | Ag(s)



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4. Predict which out of the following reaction is feasible under standard conditions in the specified direction: 1 point

○ Mg2+ (aq) and Zn(s)

○ Zn2+ (aq) and Cu(s)

○ H+ (aq) and Ag (s)

○ Ag+(aq) and Cu(s)

Question Nos. 5-15 are multiple choice questions. Choose one correct option.

○ Option 1

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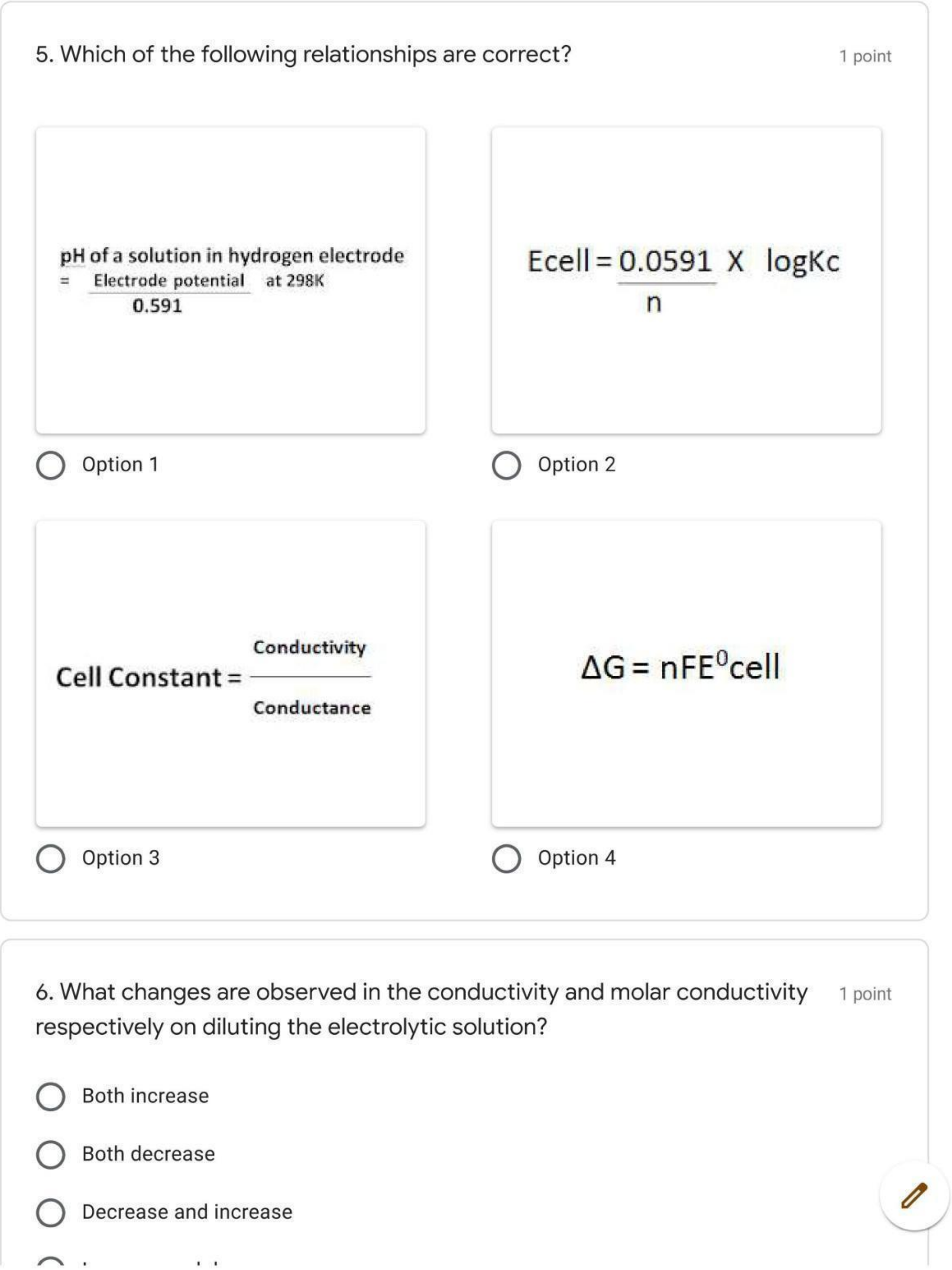


5. Which of the following relationships are correct? 1 point

pH of a solution in hydrogen electrode $= \frac{\text{Electrode potential}}{0.591}$ at 298K

○ Option 1

$E_{cell} = \frac{0.0591}{n} \times \log K_c$

○ Option 2

$\text{Cell Constant} = \frac{\text{Conductivity}}{\text{Conductance}}$

○ Option 3

$\Delta G = nFE^0_{cell}$

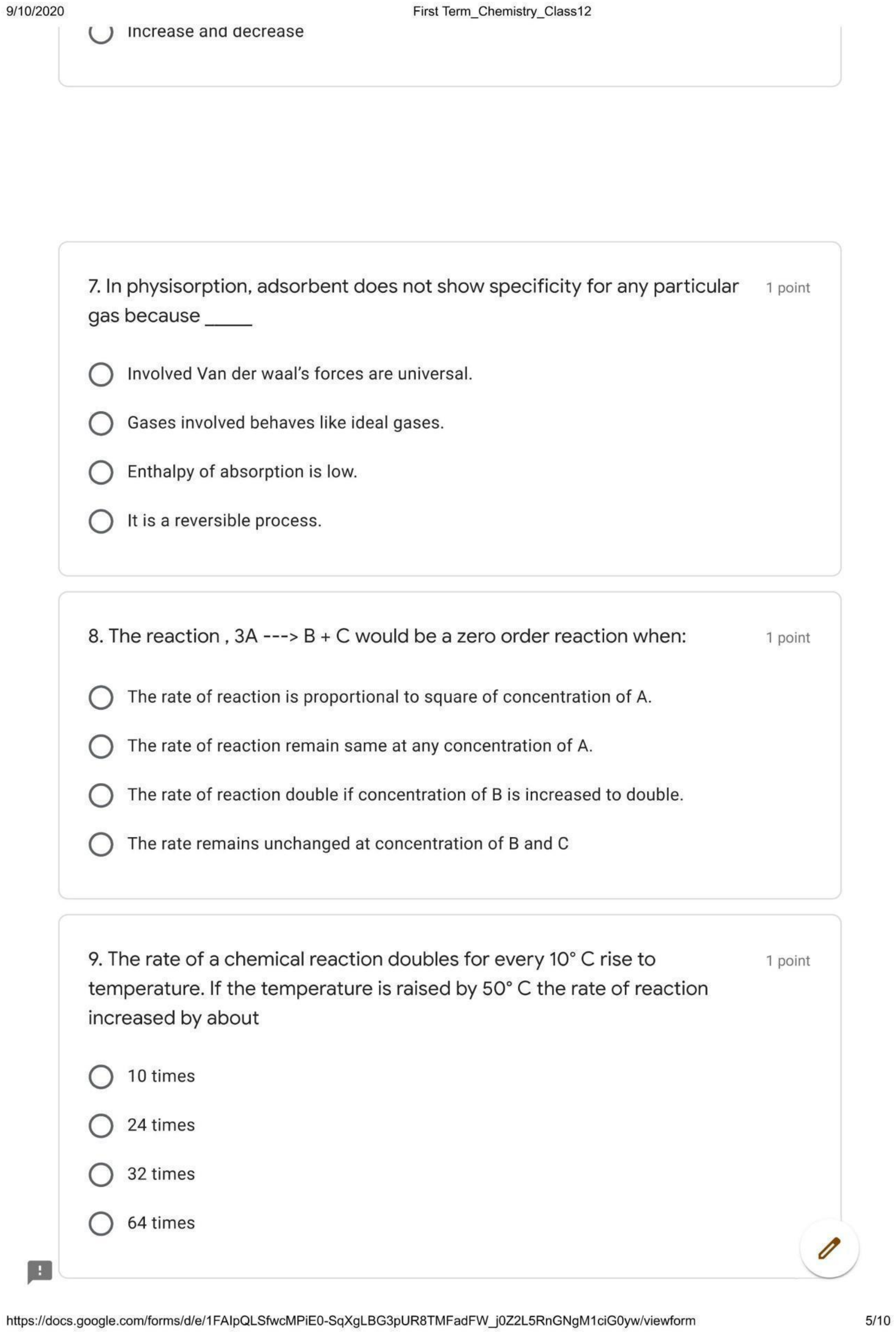
○ Option 4

6. What changes are observed in the conductivity and molar conductivity respectively on diluting the electrolytic solution? 1 point

○ Both increase

○ Both decrease

○ Decrease and increase



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○ Increase and decrease

7. In physisorption, adsorbent does not show specificity for any particular gas because _____ 1 point

○ Involved Van der waal's forces are universal.

○ Gases involved behaves like ideal gases.

○ Enthalpy of absorption is low.

○ It is a reversible process.

8. The reaction , 3A ---> B + C would be a zero order reaction when: 1 point

○ The rate of reaction is proportional to square of concentration of A.

○ The rate of reaction remain same at any concentration of A.

○ The rate of reaction double if concentration of B is increased to double.

○ The rate remains unchanged at concentration of B and C

9. The rate of a chemical reaction doubles for every 10° C rise to temperature. If the temperature is raised by 50° C the rate of reaction increased by about 1 point

○ 10 times

○ 24 times

○ 32 times

○ 64 times

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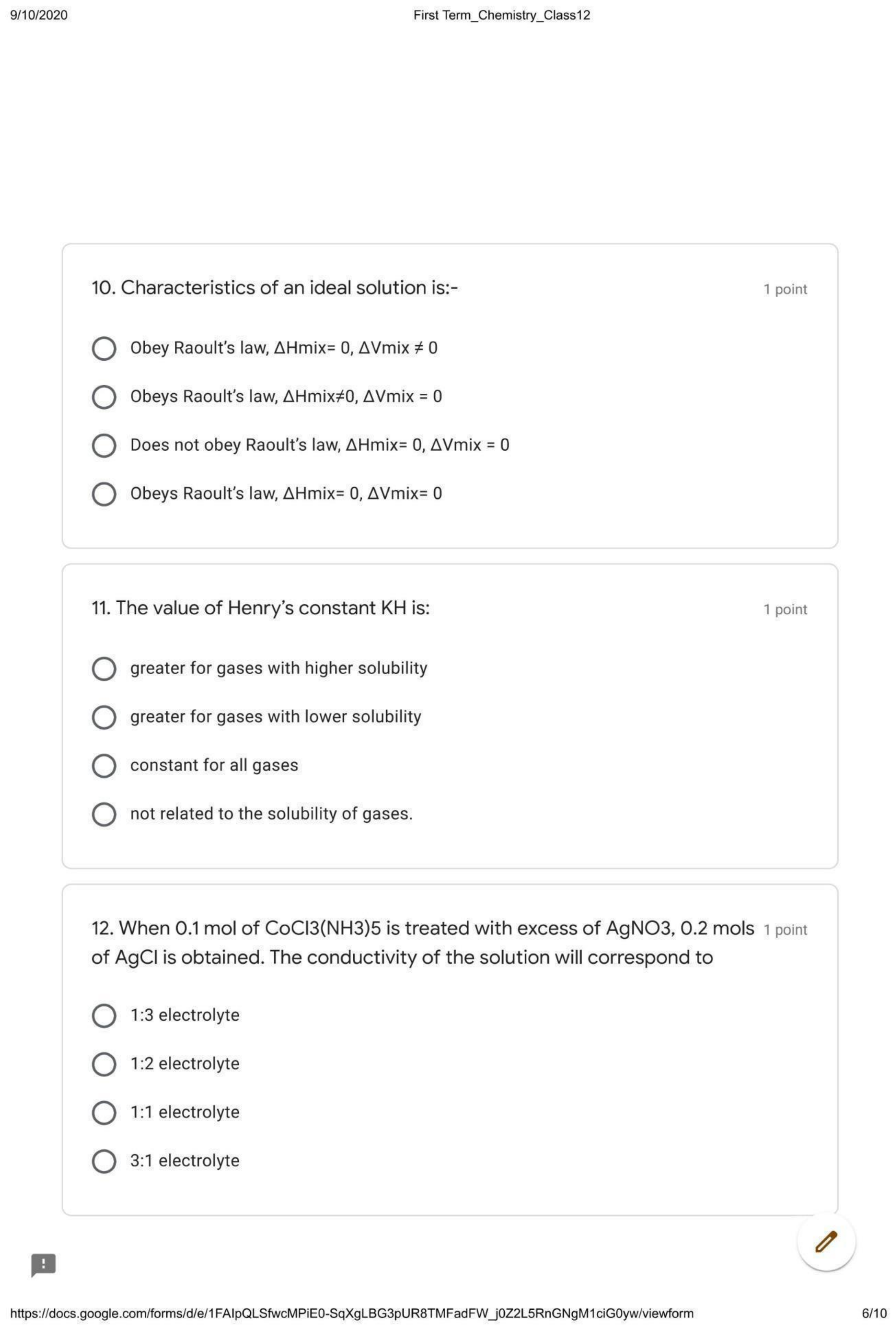

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10. Characteristics of an ideal solution is:- 1 point

○ Obey Raoult’s law, ΔHmix= 0, ΔVmix ≠ 0

○ Obeys Raoult’s law, ΔHmix≠0, ΔVmix = 0

○ Does not obey Raoult’s law, ΔHmix= 0, ΔVmix = 0

○ Obeys Raoult’s law, ΔHmix= 0, ΔVmix= 0

11. The value of Henry’s constant KH is: 1 point

○ greater for gases with higher solubility

○ greater for gases with lower solubility

○ constant for all gases

○ not related to the solubility of gases.

12. When 0.1 mol of CoCl3(NH3)5 is treated with excess of AgNO3, 0.2 mols of AgCl is obtained. The conductivity of the solution will correspond to 1 point

○ 1:3 electrolyte

○ 1:2 electrolyte

○ 1:1 electrolyte

○ 3:1 electrolyte

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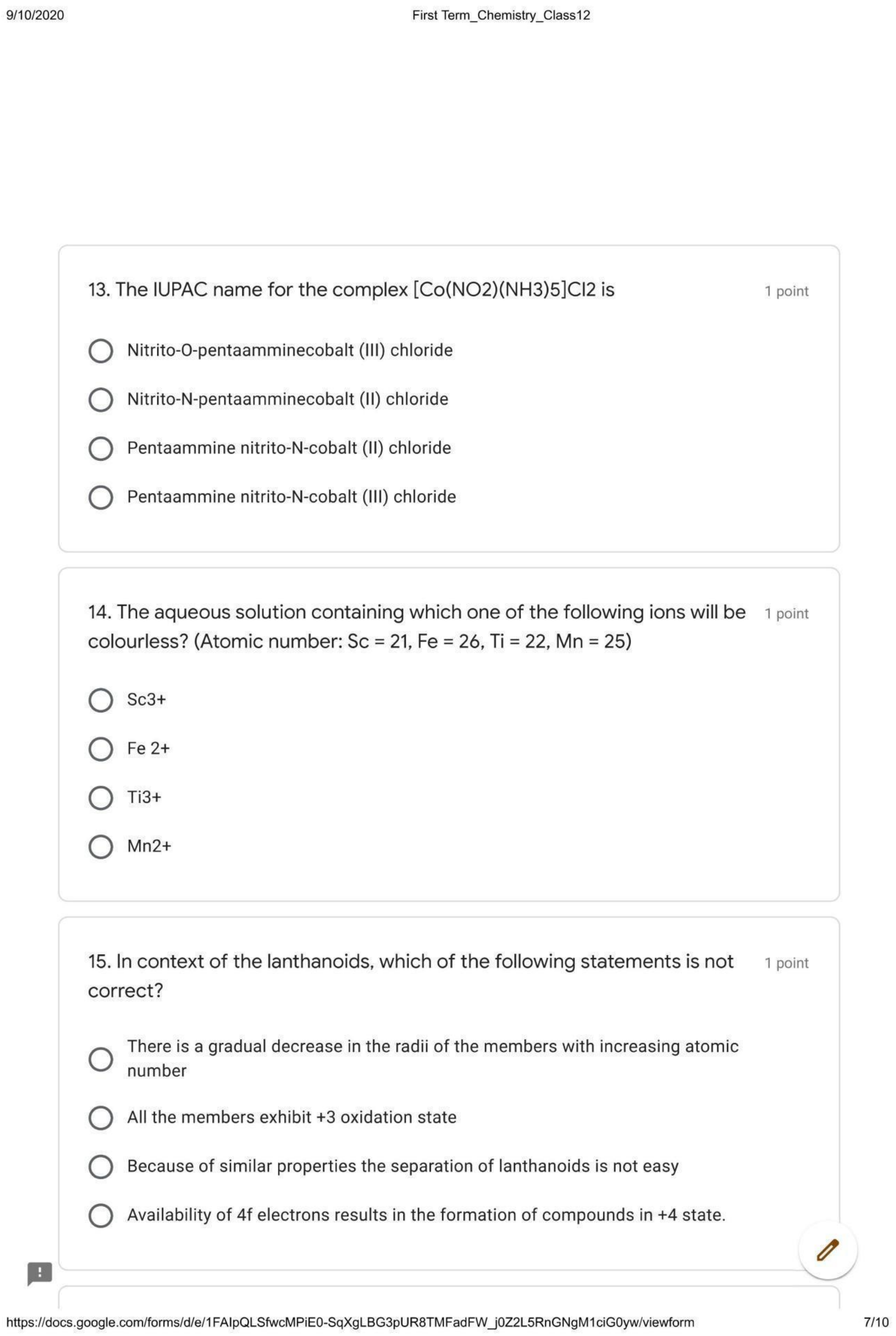


13. The IUPAC name for the complex [Co(NO2)(NH3)5]Cl2 is 1 point

○ Nitrito-O-pentaamminecobalt (III) chloride

○ Nitrito-N-pentaamminecobalt (II) chloride

○ Pentaammine nitrito-N-cobalt (II) chloride

○ Pentaammine nitrito-N-cobalt (III) chloride

14. The aqueous solution containing which one of the following ions will be colourless? (Atomic number: Sc = 21, Fe = 26, Ti = 22, Mn = 25) 1 point

○ Sc3+

○ Fe 2+

○ Ti3+

○ Mn2+

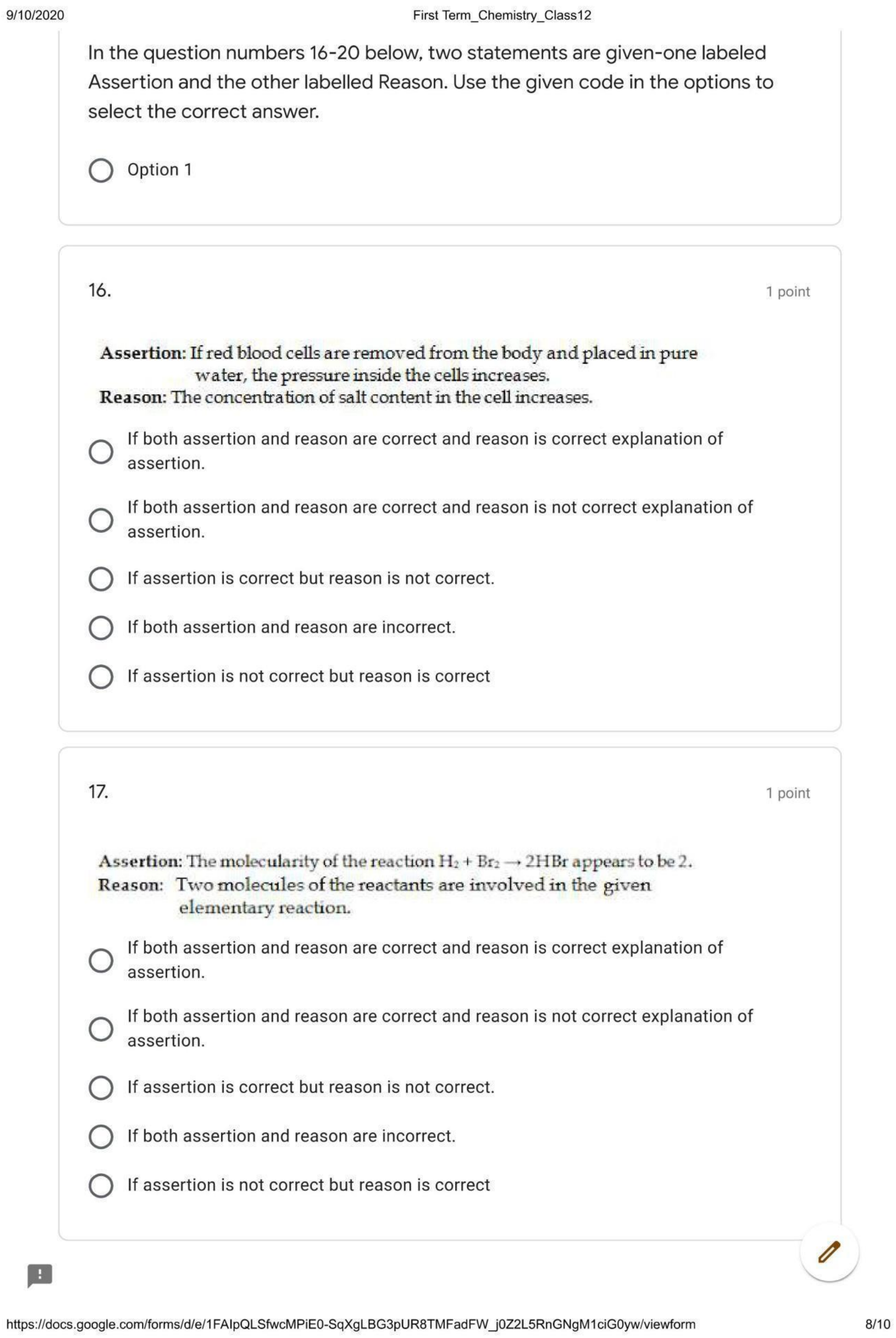
15. In context of the lanthanoids, which of the following statements is not correct? 1 point

○ There is a gradual decrease in the radii of the members with increasing atomic number

○ All the members exhibit +3 oxidation state

○ Because of similar properties the separation of lanthanoids is not easy

○ Availability of 4f electrons results in the formation of compounds in +4 state.



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In the question numbers 16-20 below, two statements are given-one labeled Assertion and the other labelled Reason. Use the given code in the options to select the correct answer.

○ Option 1

16. 1 point

Assertion: If red blood cells are removed from the body and placed in pure water, the pressure inside the cells increases.
Reason: The concentration of salt content in the cell increases.

○ If both assertion and reason are correct and reason is correct explanation of assertion.

○ If both assertion and reason are correct and reason is not correct explanation of assertion.

○ If assertion is correct but reason is not correct.

○ If both assertion and reason are incorrect.

○ If assertion is not correct but reason is correct

17. 1 point

Assertion: The molecularity of the reaction $H_2 + Br_2 \rightarrow 2HBr$ appears to be 2.
Reason: Two molecules of the reactants are involved in the given elementary reaction.

○ If both assertion and reason are correct and reason is correct explanation of assertion.

○ If both assertion and reason are correct and reason is not correct explanation of assertion.

○ If assertion is correct but reason is not correct.

○ If both assertion and reason are incorrect.

○ If assertion is not correct but reason is correct

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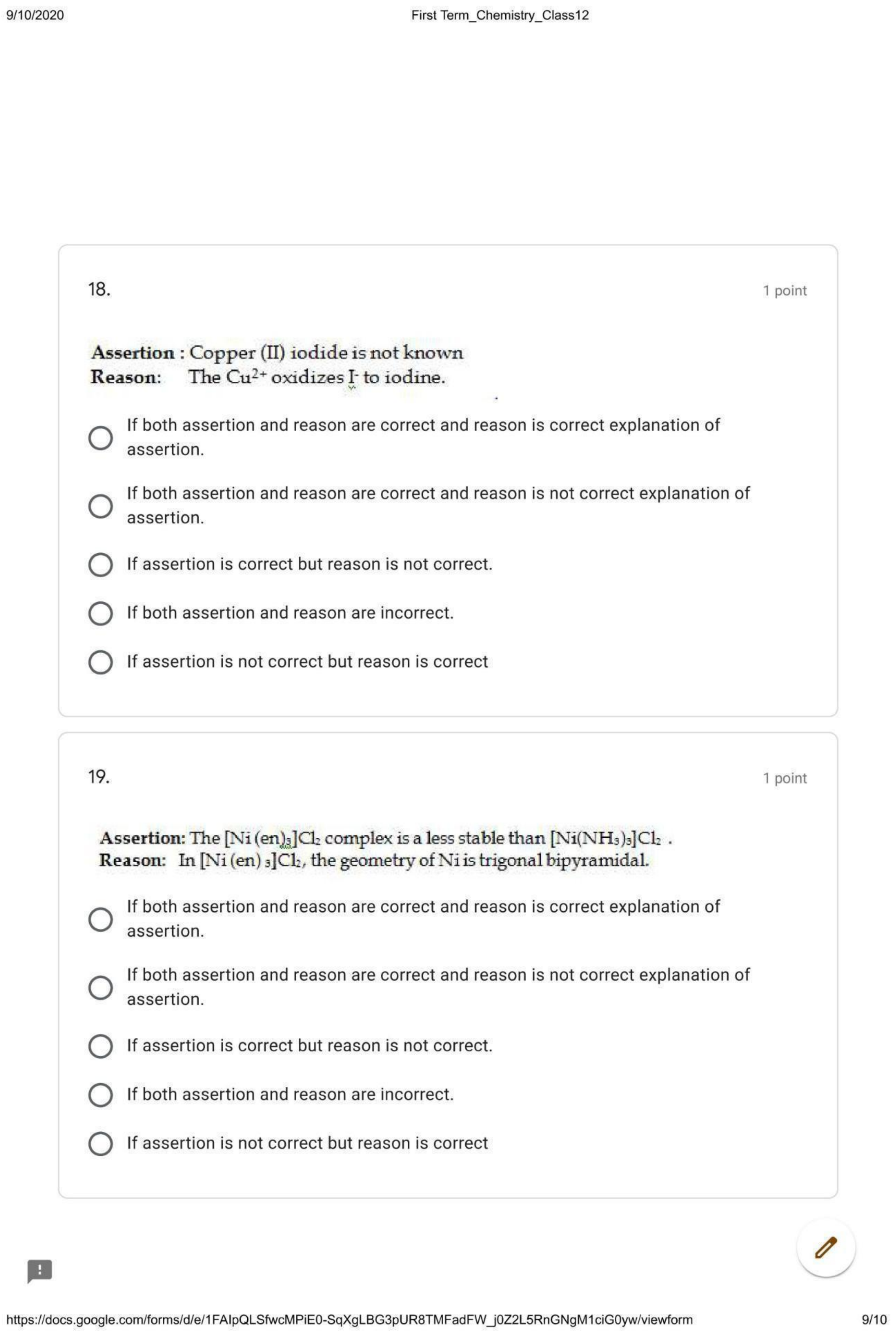


18. 1 point

Assertion : Copper (II) iodide is not known
Reason: The Cu^{2+} oxidizes I^- to iodine.

○ If both assertion and reason are correct and reason is correct explanation of assertion.

○ If both assertion and reason are correct and reason is not correct explanation of assertion.

○ If assertion is correct but reason is not correct.

○ If both assertion and reason are incorrect.

○ If assertion is not correct but reason is correct

19. 1 point

Assertion: The $[Ni(en)_3]Cl_2$ complex is a less stable than $[Ni(NH_3)_3]Cl_2$.
Reason: In $[Ni(en)_3]Cl_2$, the geometry of Ni is trigonal bipyramidal.

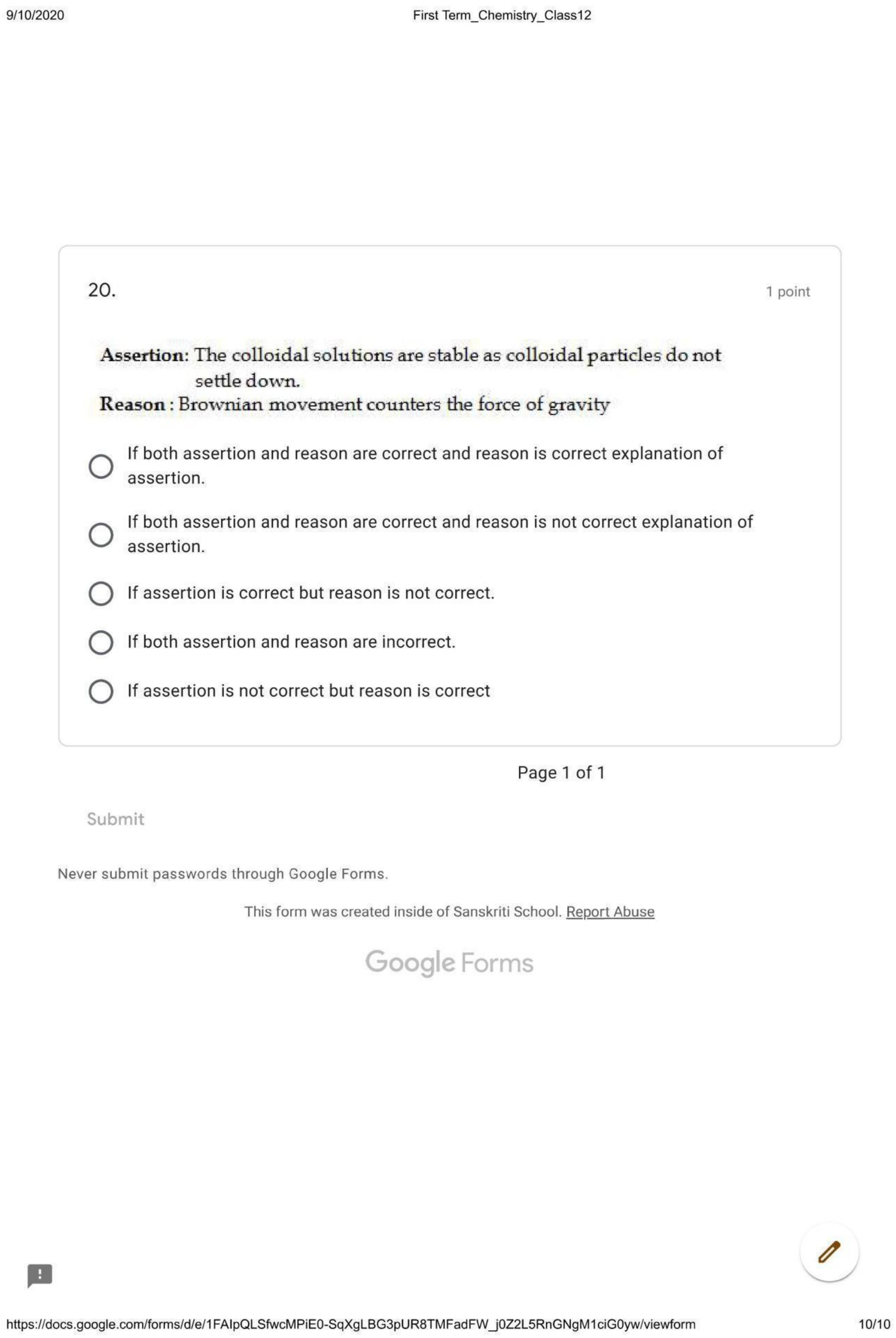
○ If both assertion and reason are correct and reason is correct explanation of assertion.

○ If both assertion and reason are correct and reason is not correct explanation of assertion.

○ If assertion is correct but reason is not correct.

○ If both assertion and reason are incorrect.

○ If assertion is not correct but reason is correct



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20. 1 point

Assertion: The colloidal solutions are stable as colloidal particles do not settle down.
Reason : Brownian movement counters the force of gravity

○ If both assertion and reason are correct and reason is correct explanation of assertion.

○ If both assertion and reason are correct and reason is not correct explanation of assertion.

○ If assertion is correct but reason is not correct.

○ If both assertion and reason are incorrect.

○ If assertion is not correct but reason is correct

Page 1 of 1

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SANSKRITI SCHOOL
Dr. S. Radhakrishnan Marg,
New Delhi

Academic Session: 2020-21
First term exam
Subject: Chemistry
Class- XII

Time: 2 hours

Max marks: 60
Google form – 20 marks
Subjective paper – 40 marks

General Instructions:.

- The reading time is from 7:45 am to 8:00 am.
- The writing time is from 8:00 am to 10:00 am.
- By 10:15am, the pdf file of the answer sheets needs to be created, attached and submitted. Once submitted, it can't be resubmitted.
- Children who avail extra time, may submit the answer sheets by 11:00 am.
- All questions are compulsory.
- Question nos. 1- 20 Objective Type questions of 1 mark each to be attempted Online through Google form.
- Question nos. 21-30 in Section A are very short answer questions and carry 1 mark each.
- Question nos. 31-35 in Section B are short answer questions and carry 2 marks each.
- Question nos.36-40 in Section C care short answer questions and carry 3 marks each.
- Question no. 41 in Section D is a long answer question and carries 5 marks.
- Please write your name class section and page number used on right top corner
- The Answer sheets need to be scanned and uploaded as a pdf file in portrait mode.
- Make sure that you turn in the work in the time frame assigned.
- No image to be uploaded.
- This paper has 3 printed sides.

SECTION A

Question number 21-30 are one word or one line answers

21. Why do transition metals form alloys with other transition metals easily? Give an example of an alloy of transition metal. (1)

22. In the ions Mn^{3+},V^{3+}, Cr^{3+}, Ti^{4+} (Atomic numbers of Mn=25, V=23, Cr=24, Ti=22) (1)
    a) Which ion is most stable in aqueous solution?
    b) Which ion will have the maximum number of unpaired electrons?

23. Using Crystal Field Theory, write the electronic configuration of the central atom in $[Co(CN)_6]^{3-}$. (Atomic number of Co=27) (1)

24. What is the significance of synergic bonding in Metal Carbonyls. (1)

35. Calculate ΔG^0 and log Kc for the reaction: (2)
$Zn (s) + Cu^{2+} (aq) \rightarrow Zn^{2+} (aq) + Cu (s)$.
Given : E^0 for $Zn^{2+}/Zn = - 0.76V$ and E^0 for $Cu^{2+}/Cu = + 0.34$ V at 298K.
$R = 8.314\ JK^{-1}\ mol^{-1}$, $F = 96500\ C\ mol^{-1}$.

SECTION C

36. Using valence bond theory, predict the hybridization, geometry and magnetic behavior of $[FeF_6]^{3-}$ and $[Ni(CN)_4]^{2-}$. (3)

37. (i) Which of the following electrolytes is most effective for coagulation of Hydrated ferric oxide sol and why? NaCl, Na_2SO_4 , Na_3PO_4 (3)
(ii) Give specific terms to show the effect of the following processes:
a) A beam of light is passed through arsenic oxide solution
b) Ferric chloride solution is mixed with freshly prepared precipitate of ferric oxide.
Also define the terms.

38. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume: $SO_2Cl_2(g) \rightarrow SO_2 (g) + Cl_2(g)$ (3)

Experiment	Time / s	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate constant.

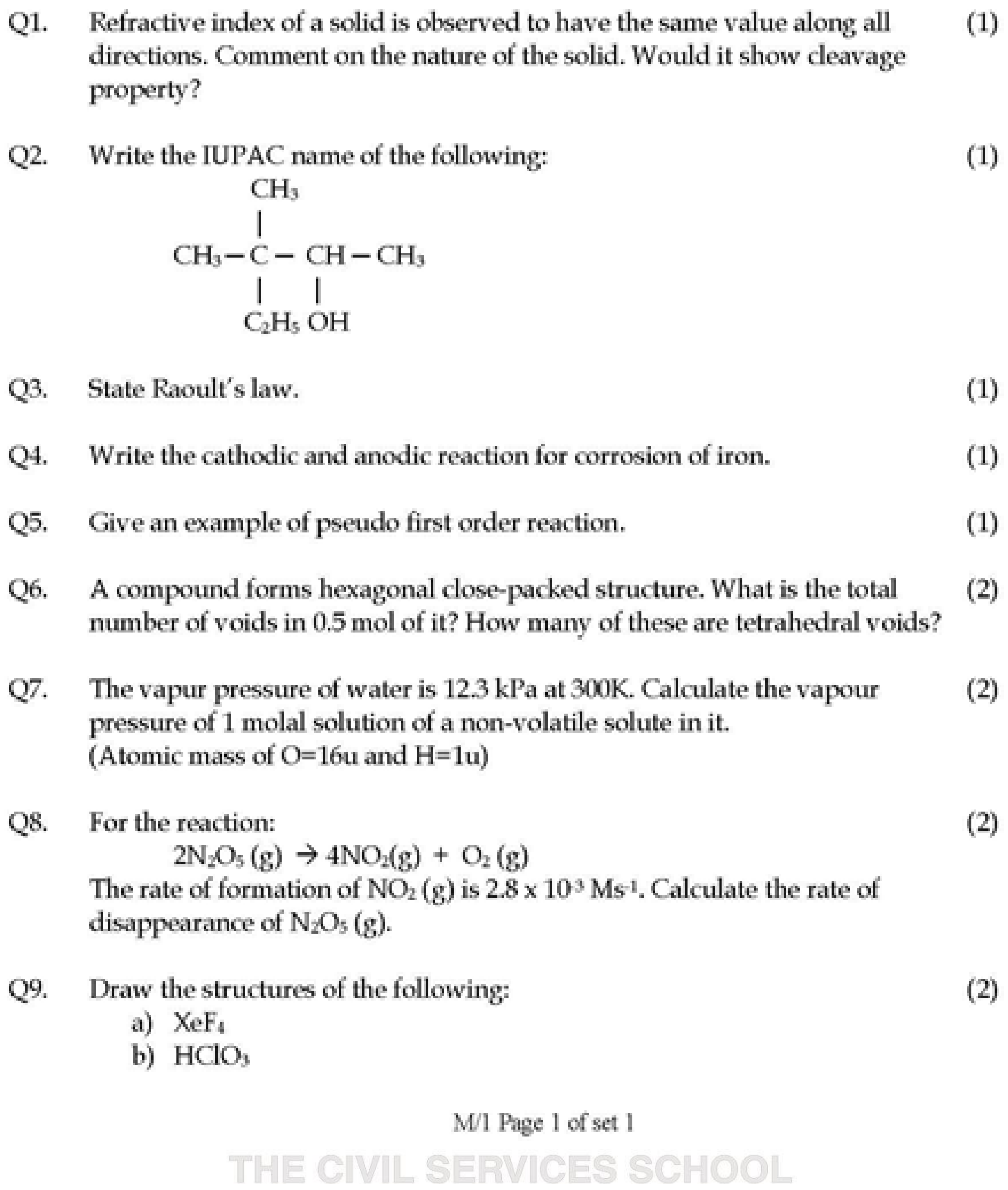
39. Boiling point of water at 750mmHg is 99.63^0C. Calculate the mass of sucrose (Molar mass = 342 g mol^{-1}) to be dissolved in 500g of water such that it boils at 100^0C. (K_b for water = 0.52 K kg mol^{-1}) (3)

40. Out of the following pairs, predict with reason which one will allow greater conduction of electricity : (3)
(i) Silver wire at 30^0C or silver wire at 60^0C.
(ii) 0.1 M CH_3COOH solution or 1 M CH_3COOH solution.
(iii) KCl solution at 20^0C or KCl solution at 50^0C.

SECTION D

41. (i) Explain giving reason: (5)
a) Of the d^4 species Cr^{2+} is strongly reducing while Manganese (III) is strongly oxidizing.
b) The E^0 (M^{2+}/M) value of copper is positive (0.34V).
c) Transition metals and their many compounds act as good catalysts.
(ii) Give reason and select one atom/ion which will exhibit asked property :
a) Sc^{3+} or Cr^{3+} (Exhibit diamagnetic behaviour)
b) Cr or Cu (High melting and boiling point)

Question Bank (short and long questions)



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)

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_2H_5}{|}}{C}}-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$$

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. (2)
(Atomic mass of O=16u and H=1u)

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 2.8×10^{-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) $HClO_3$

M/1 Page 1 of set 1

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.

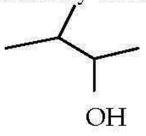
Q12. a) Write the equation involved in Reimer–Tiemann reaction. (2)
b) Ortho-nitrophenol is more acidic than ortho-methoxyphenol. Why?

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' ($N_a = 6.023 \times 10^{23}$ 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?

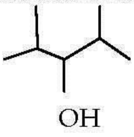
Q15. a) Calculate the freezing point of a solution containing 60g of glucose in 250g of water. (3)
(Molar mass of glucose = 180 g/mol, k_f of water = 1.8k $KKgmol^{-1}$)
b) What are hypertonic solutions?

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.

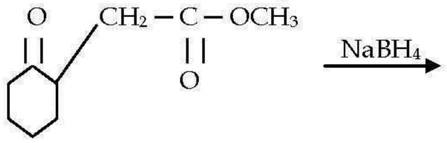
Q17. Give reasons for the following: (3)
a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macro molecules such as proteins and polymers.
b) Aquatic animals are more comfortable in cold water than in warm water.
c) Elevation of boiling point of 1M KCl solution is nearly double than that of 1M sugar solution.

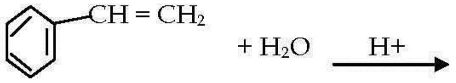
Q18. A first order reaction is 50% completed in 40 minutes at 300K and in 20 minutes at 320K. Calculate the activation energy of the reaction. (3)
[Given log 2 = 0.3010, log 4 = 0.6020, R = 8.314 $JK^{-1}mol^{-1}$]

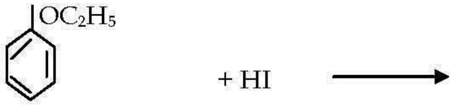
Q19. For the reaction: (3)
$2AgCl\,(s) + H_2\,(g)\,(1atm) \rightarrow 2Ag\,(s) + 2H^+\,(0.1M) + 2Cl^-\,(0.1M)$
Calculate the e.m.f of the cell.
[Given $\Delta G^\circ = -43600$ J at 25°C , $\log 10^{-n} = -n$]

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.


ii.


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	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-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) | Sn^{2+} (0.004M) | | H^+ (0.20M) | H_2 (g) (1bar) | 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?

M/1 Page 4 of set 1

28. Write the products and give balanced equations for the following: (2)

(a) $3MnO_4^{2-} + 4H^+$ □

(b) $Cr_2O_7^{2-} + 8H^+ + 3H_2S$ □.

29. (a) Why is adsorption always exothermic? (2)

(b) Give the expression of Freundlich adsorption isotherm.

30 (a) Give the IUPAC name of $CH_3CH_2COCH_2CH(CH_3)CH_2CHO$ (2)

(b) Give chemical test to distinguish between acetaldehyde and benzaldehyde.

SECTION : C

31 (a) A compound 'X'(C_2H_4O) on oxidation gives 'Y' ($C_2H_4O_2$). 'X' undergoes haloform reaction. On treatment with HCN, 'X' forms a product 'Z' which on hydrolysis gives 2- Hydroxy propanoic acid. (3)

(i) Write down the products of 'X', 'Y' and 'Z'.

(ii) Write the name of the product when 'X' reacts with dil NaOH.

(b) Convert benzoic acid to benzaldehyde.

Q32. (a) What is coagulation value? (3)

(b) Define peptization.

(c) Why does leather get hardened after tanning?

Q33. (a) Write a short note on Clemmensen reduction. (3)

(b) Give the mechanism of nucleophillic addition of OH^- in RCHO.

SECTION : D

34. (a) Which site of enzyme is called allosteric site? (5)

(b) What is the chemical composition of cationic detergents?

(c) Which class of drugs is used in sleeping pills? Write a short note on them.

(d) Account for the following:

(i) Aspirin is pain relieving antipyretic drug but can be used to prevent heart attack.

(ii) Diabetic patients are advised to take artificial sweeteners instead of natural sweeteners.

35. (a) An ore sample of galena (PbS) is contaminated with zinc blende (ZnS). Name one chemical which can be used to concentrate galena selectively by froth floatation method. (5)

(b) Describe the role of :

(i) SiO_2 in the extraction of copper from copper matte.

(ii) Iodine in the refining of zirconium.

Write chemical equations for the involved. reactions.

(c) The extraction of Au by leaching involves both oxidation and reduction. Justify giving equations

36. (a) Give reasons for the following: (5)

(i) 4d and 5d series have higher enthalpies of atomization than 3d series.

(ii) Transition metals and their many compounds act as good catalysts.

(iii) Of the d^4 species, Cr^{2+} is strongly reducing while manganese (III) is strongly oxidisiing.

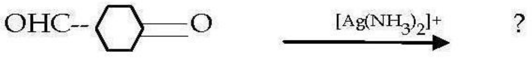
(iv) The highest oxidation state is exhibited in oxo-anions of a metal.

Out of Cu_2Cl_2 and $CuCl_2$, which is more stable in water and why?

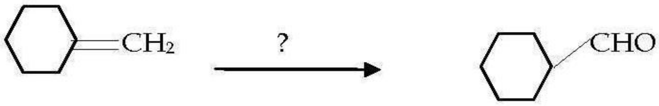
OR

Complete each synthesis by giving missing reagents or products:

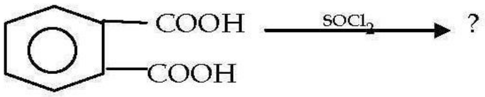
(i)



(ii)



(iii)



(iv) $C_6H_5CHO + CH_3CH_2CH_2CHO \xrightarrow{\text{Dil. NaOH}}$

(v) $CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii) H+}]{\text{(i) NaBH}_4}$

QUESTION BANK (Objective: VSA, MCQ, A/R based questions)

Q1. Draw the structure of Buna-S. Is it a homopolymer or a co-polymer? (1)

Q2. Name the monomer of Nylon 6. Does it polymerize by chain growth or step growth polymerization? (1)

Q3. Give an example of biodegradable synthetic polymer. (1)

Q4. Melamine is a condensation polymer. Draw the structure of the polymer. (1)

Q5. What are thermoplastics? Give an example. (1)

Questions 6 to 8 are Multiple Choice Questions:

Q6. The correct order of increasing acid strength is (1)

(a) Phenol $<$ Ethanol $<$ Chloroacetic acid $<$ acetic acid

(b) Ethanol $<$ Phenol $<$ Chloroacetic acid $<$ acetic acid

(c) Ethanol $<$ Phenol $<$ acetic acid $<$ Chloroacetic acid

(d) Chloroacetic acid $<$ acetic acid $<$ Phenol $<$ Ethanol

Q7. Compound Ph-OCO-Ph can be prepared by the reaction of: (1)

(a) Phenol and benzoic acid in presence of NaOH.

(b) Phenol and benzoyl chloride in the presence of pyridine.

(c) Phenol and benzoyl chloride in the presence of $ZnCl_2$.

(d) Phenol and benzaldehyde in the presence of palladium.

Q8. Colloidion is a colloidal solution of : (1)

(a) cellulose in ethyl alcohol (b) cellulose nitrate in water and ether

(c) sucrose in water (d) cellulose nitrate in ethyl alcohol and ether

Questions 9 to 12 are one word questions:

Q9. Which product is formed when MnO_2 is fused with KOH? (1)

Q10. Out of the following ions, which one is colourless? (1)

V^{3+}, Cr^{3+}, Sc^{3+}, Ni^{3+}

Q11. Based on the type of particles of the dispersed phase, Sulphur sol is what type of colloid? (1)

Q12. Name the polymer formed from ethylene glycol and terephthalic acid. (1)

The questions 13 to 15 consist of Assertion (A) and Reason (R). Use the following key to select the correct answer.

(a) If both assertion and reason are correct and reason is correct explanation for assertion.

(b) If both assertion and reason are correct but reason is not correct explanation for assertion.

(c) If assertion is correct but reason is incorrect.

(d) If assertion and reason both are incorrect.

Q13. Assertion : Lyophilic sols are more stable than lyophobic sols. (1)

Reason : Lyophilic sols are more readily hydrated than lyophobic sols.

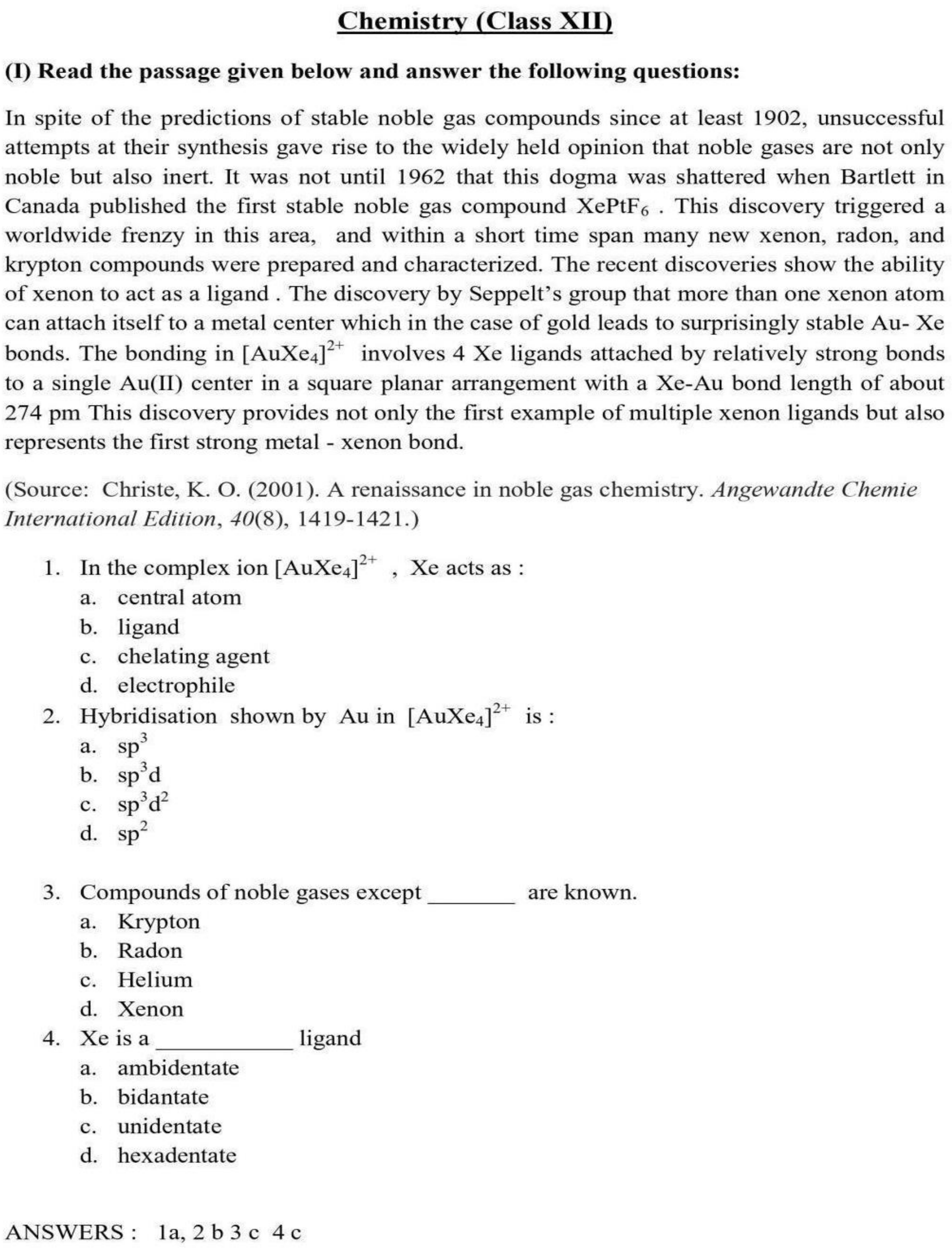
Q14. Assertion : $\Delta_f G^0$ for the formation of Al_2O_3 and Cr_2O_3 involving one mole of oxygen are -827kJ/mol and -540kJ/mol respectively. (1)

Reason : Al can reduce Cr_2O_3 since more energy is liberated when Al_2O_3 is formed.

Q15. Assertion : Ce^{4+} is used as oxidizing agent in volumetric analysis. (1)

Reason: Ce^{4+} has the tendency to acquire +3 oxidation state.

QUESTION BANK (SOURCE BASED/ CASE BASED)



Chemistry (Class XII)

(I) Read the passage given below and answer the following questions:

In spite of the predictions of stable noble gas compounds since at least 1902, unsuccessful attempts at their synthesis gave rise to the widely held opinion that noble gases are not only noble but also inert. It was not until 1962 that this dogma was shattered when Bartlett in Canada published the first stable noble gas compound $XePtF_6$. This discovery triggered a worldwide frenzy in this area, and within a short time span many new xenon, radon, and krypton compounds were prepared and characterized. The recent discoveries show the ability of xenon to act as a ligand . The discovery by Seppelt's group that more than one xenon atom can attach itself to a metal center which in the case of gold leads to surprisingly stable Au- Xe bonds. The bonding in $[AuXe_4]^{2+}$ involves 4 Xe ligands attached by relatively strong bonds to a single Au(II) center in a square planar arrangement with a Xe-Au bond length of about 274 pm This discovery provides not only the first example of multiple xenon ligands but also represents the first strong metal - xenon bond.

(Source: Christe, K. O. (2001). A renaissance in noble gas chemistry. *Angewandte Chemie International Edition*, *40*(8), 1419-1421.)

1. In the complex ion $[AuXe_4]^{2+}$, Xe acts as :
   a. central atom
   b. ligand
   c. chelating agent
   d. electrophile
2. Hybridisation shown by Au in $[AuXe_4]^{2+}$ is :
   a. sp^3
   b. sp^3d
   c. sp^3d^2
   d. sp^2

3. Compounds of noble gases except _______ are known.
   a. Krypton
   b. Radon
   c. Helium
   d. Xenon
4. Xe is a ___________ ligand
   a. ambidentate
   b. bidantate
   c. unidentate
   d. hexadentate

ANSWERS : 1a, 2 b 3 c 4 c

(II) Read the passage given below and answer the following questions:

Boiling point or freezing point of liquid solution would be affected by the dissolved solids in the liquid phase. A soluble solid in solution has the effect of raising its boiling point and depressing its freezing point. The addition of non-volatile substances to a solvent decreases the vapor pressure and the added solute particles affect the formation of pure solvent crystals. According to many researches the decrease in freezing point directly correlated to the concentration of solutes dissolved in the solvent. This phenomenon is expressed as freezing point depression and it is useful for several applications such as freeze concentration of liquid food and to find the molar mass of an unknown solute in the solution. Freeze concentration is a high quality liquid food concentration method where water is removed by forming ice crystals. This is done by cooling the liquid food below the freezing point of the solution. The freezing point depression is referred as a colligative property and it is proportional to the molar concentration of the solution (m), along with vapor pressure lowering, boiling point elevation, and osmotic pressure. These are physical characteristics of solutions that depend only on the identity of the solvent and the concentration of the solute. The characters are not depending on the solute's identity. (Jayawardena, J. A. E. C., Vanniarachchi, M. P. G., & Wansapala, M. A. J. (2017). Freezing point depression of different Sucrose solutions and coconut water.)

1. When a non volatile solid is added to pure water it will:
   a. boil above $100^{o}C$ and freeze above $0^{o}C$
   b. boil below $100^{o}C$ and freeze above $0^{o}C$
   c. boil above $100^{o}C$ and freeze below $0^{o}C$
   d. boil below $100^{o}C$ and freeze below $0^{o}C$

2. Colligative properties are:

a. dependent only on the concentration of the solute and independent of the solvent's and solute's identity.

b. dependent only on the identity of the solute and the concentration of the solute and independent of the solvent's identity.

c. dependent on the identity of the solvent and solute and thus on the concentration of the solute.

d. dependent only on the identity of the solvent and the concentration of the solute and independent of the solute's identity.

3. Assume three samples of juices A, B and C have glucose as the only sugar present in them. The concentration of sample A, B and C are 0.1M, .5M and 0.2 M respectively. Freezing point will be highest for the fruit juice:

a. A
b. B
c. C
d. All have same freezing point

4. Identify which of the following is a colligative property :

a. freezing point
b. boiling point
c. osmotic pressure
d. all of the above

Ans 1 (b) 2 (d) 3 (a) 4(c)

(III) Read the passage given below and answer the following questions:

The rate of a reaction, which may also be called its velocity or speed, can be defined with relation to the concentration of any of the reacting substances, or to that of any product of the reaction. If the species chosen is a reactant which has a concentration c at time t the rate is -dc/dt, while the rate with reference to a product having a concentration x at time t is dx/dt. Any concentration units may be used for expressing the rate; thus, if moles per liter are employed for concentration and seconds for the time, the units for the rate are moles liter^{-1}sec^{-1}. For gas reactions pressure units are sometimes used in place of concentrations, so that legitimate units for the rate would be (mm. Hg) sec^{-1} and atm. sec^{-1}

The order of a reaction concerns the dependence of the rate upon the concentrations of reacting substances; thus, if the rate is found experimentally to be proportional to the α^{th} power of the concentration of one of the reactants A, to the β^{th} power of the concentration of a second reactant B, and so forth, via.,

rate = $k\, C_A^{\alpha} C_B^{\beta}$ (1)

the over-all order of the reaction is simply

$n = \alpha + \beta +$ ----- (2)

Such a reaction is said to be of the α^{th} order with respect to the substance A, the β^{th} order with respect to B and so on...

(Laidler, K. J., & Glasstone, S. (1948). Rate, order and molecularity in chemical kinetics. *Journal of Chemical Education*, *25*(7), 383.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

A. Assertion and reason both are correct statements and reason is correct explanation for assertion.
B. Assertion and reason both are correct statements but reason is not correct explanation for assertion.
C. Assertion is correct statement but reason is wrong statement.
D. Assertion is wrong statement but reason is correct statement.

1. **Assertion:** Rate of reaction is a measure of change in concentration of reactant with respect to time.

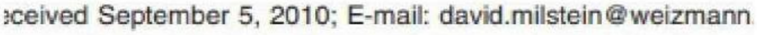
   Reason: Rate of reaction is a measure of change in concentration of product with respect to time.

2. **Assertion:** For a reaction: P +2Q → Products, Rate = k $[P]^{1/2}[Q]^1$ so the order of reaction is 1.5
   Reason: Order of reaction is the sum of stoichiometric coefficients of the reactants.
3. **Assertion:** The unit of k is independent of order of reaction.
   Reason: The unit of k is moles $L^{-1}s^{-1}$.
4. **Assertion:** Reactions can occur at different speeds.
   Reason: Rate of reaction is also called speed of reaction.

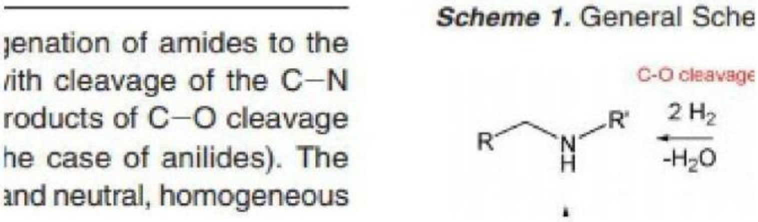
Ans: 1B 2C 3D 4B

(IV) Read the passage given below and answer the following questions:

Reduction of carboxylic acids and their derivatives plays an important role in organic synthesis, in both laboratory and industrial processes. Traditionally, the reduction is performed using stochiometric amounts of hydride reagents, generating stochiometric amounts of waste. A much more attractive, atom-economical approach is a catalytic reaction using H2; however, hydrogenation of carboxylic acid derivatives under mild conditions is a very challenging task, with amides presenting the highest challenge among all classes of carbonyl compounds. Very few examples of the important hydrogenation of amides to amines, in which the C-O bond is cleaved with the liberation of water (Scheme 1), were reported. C-O cleavage of amides can also be affected with silanes as reducing agents.



eceived September 5, 2010; E-mail: david.milstein@weizmann.



jenation of amides to the
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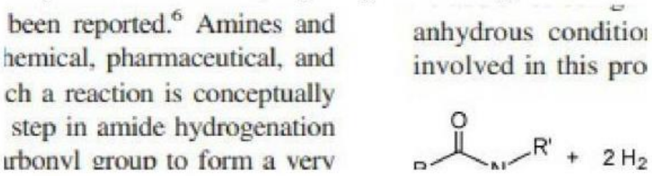
Scheme 1. General Sche

We have now prepared the new, dearomatized, bipyridine-based pincer complex 3, catalyst 3(Here refered as Cat. 3). Remarkably, it efficiently catalyzes the selective hydrogenation of amides to form amines and alcohols (eq 1). The reaction proceeds under mild pressure and neutral conditions, with no additives being required. Since the reaction proceeds well under anhydrous conditions, hydrolytic cleavage of the amide is not involved in this process.



been reported.[6] Amines and
hemical, pharmaceutical, and
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step in amide hydrogenation
rbonyl group to form a very

anhydrous conditio
involved in this pro

(Balaraman, E., Gnanaprakasam, B., Shimon, L. J., & Milstein, D. (2010). Direct hydrogenation of amides to alcohols and amines under mild conditions. *Journal of the American Chemical Society*, *132*(47), 16756-16758.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

A. Assertion and reason both are correct statements and reason is correct explanation for assertion.
B. Assertion and reason both are correct statements but reason is not correct explanation for assertion.
C. Assertion is correct statement but reason is wrong statement.
D. Assertion is wrong statement but reason is correct statement.

1. **Assertion:** The use of catalyst 3 is an efficient method of preparation of primary amines
   Reason: Use of catalyst 3 is a step down reaction.
2. **Assertion:** Use of hydride catalyst or hydrogen brings about cleavage of C-O bond in amides.
   Reason: Hydride catalyst or hydrogen cause to reduction of amides.
3. **Assertion:** N-methyl ethanamide on reaction with catalyst 3 will yield ethanol and methanamine**.**
   Reason: Use of Catalyst 3 brings about cleavage of C-N bond of amides
4. **Assertion:** Aniline can be prepared from suitable amide using catalyst 3
   Reason: The use of catalyst 3 is limited to aliphatic amides only.

Ans: 1B 2B 3 A 4C

(V) Read the passage given below and answer the following questions:

Nucleophilic substitution reaction of haloalkane can be conducted according to both S_N^1 and S_N^2 mechanisms. However, which mechanism it is based on is related to such factors as the structure of haloalkane, and properties of leaving group, nucleophilic reagent and solvent.

Influences of halogen : No matter which mechanism the nucleophilic substitution reaction is based on, the leaving group always leave the central carbon atom with electron pair. This is just the opposite of the situation that nucleophilic reagent attacks the central carbon atom with electron pair. Therefore, the weaker the alkalinity of leaving group is , the more stable the anion formed is and it will be more easier for the leaving group to leave the central carbon atom; that is to say, the reactant is more easier to be substituted. The alkalinity order of halogen ion is $I^- < Br^- < Cl^- < F^-$ and the order of their leaving tendency should be $I^- > Br^- > Cl^- > F^-$. Therefore, in four halides with the same alkyl and different halogens, the order of substitution reaction rate is RI> RBr > RCl > RF . In addition, if the leaving group is very easy to leave, many carbocation intermediates are generated in the reaction and the reaction is based on S_N^1 mechanism. If the leaving group is not easy to leave, the reaction is based on S_N^2 mechanism.

Influences of solvent polarity: In S_N^1 reaction, the polarity of the system increases from the reactant to the transition state, because polar solvent has a greater stabilizing effect on the transition state than the reactant, thereby reduce activation energy and accelerate the reaction. In S_N^2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. For example, the decomposition rate (S_N^1) of tertiary chlorobutane in 25℃ water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (S_N^2) of 2-bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. In a word, the level of solvent polarity has influence on both S_N^1 and S_N^2reactions, but with different results. Generally speaking, weak polar solvent is favorable for S_N^2 reaction, while strong polar solvent is favorable for S_N^1 reaction, because only under the action of polar solvent can halogenated hydrocarbon dissociate into carbocation and halogen ion and solvents with a strong polarity is favorable for solvation of carbocation, increasing its stability. Generally speaking, the substitution reaction of tertiary haloalkane is based on S_N^1 mechanism in solvents with a strong polarity (for example, ethanol containing water).

(Ding, Y. (2013). A Brief Discussion on Nucleophilic Substitution Reaction on Saturated Carbon Atom. In *Applied Mechanics and Materials* (Vol. 312, pp. 433-437). Trans Tech Publications Ltd.)

1. S_N^1 mechanism is favoured in which of the following solvents:
    a. benzene
    b. carbon tetrachloride
    c. acetic acid
    d. carbon disulphide
2. Nucleophilic substitution will be fastest in case of:
    a. 1-Chloro-2,2-dimethyl propane

b. 1-Iodo-2,2-dimethyl propane
c. 1-Bromo-2,2-dimethyl propane
d. 1-Fluoro-2,2-dimethyl propane

3. S_N^1 reaction will be fastest in which of the following solvents?
   a. Acetone (dielectric constant 21)
   b. Ethanol (dielectric constant 24)
   c. Methanol (dielectric constant 32)
   d. Chloroform (dielectric constant 5)
4. Polar solvents make the reaction faster as they:
   a. destabilize transition state and decrease the activation energy
   b. destabilize transition state and increase the activation energy
   c. stabilize transition state and increase the activation energy
   d. stabilize transition state and decrease the activation energy
5. S_N^1 reaction will be fastest in case of:
   a. 1-Chloro-2-methyl propane
   b. 1-Iodo-2-methyl propane
   c. 1-Chlorobutane
   d. 1-Iodobutane

Ans: 1 c, 2b, 3 c, 4c, 5 b

(VI) Read the passage given below and answer the following questions:

Within the 3d series, manganese exhibits oxidation states in aqueous solution from +2 to +7, ranging from Mn^{2+}(aq) to $MnO^{-}{}_{4}$ (aq). Likewise, iron forms both Fe^{2+}(aq) and Fe^{3+}(aq) as well as the $FeO^{2-}{}_{4}$ ion. Cr and Mn form oxyions $CrO^{2-}{}_{4}$, $MnO^{-}{}_{4}$, owing to their willingness to form multiple bonds . The pattern with the early transition metals—in the 3d series up to Mn, and for the 4d, 5d metals up to Ru and Os—is that the maximum oxidation state corresponds to the number of ''outer shell'' electrons. The highest oxidation states of the 3d metals may depend upon complex formation (e.g., the stabilization of Co^{3+} by ammonia) or upon the pH (thus MnO_4^{2-} (aq) is prone to disproportionation in acidic solution). Within the 3d series, there is considerable variation in relative stability of oxidation states, sometimes on moving from one metal to a neighbor; thus, for iron, Fe^{3+} is more stable than Fe^{2+}, especially in alkaline conditions, while the reverse is true for cobalt. The ability of transition metals to exhibit a wide range of oxidation states is marked with metals such as vanadium, where the standard potentials can be rather small, making a switch between states relatively easy.

(Cotton, S. A. (2011). Lanthanides: Comparison to 3d metals. *Encyclopedia of inorganic and Bioinorganic Chemistry*.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

A. Assertion and reason both are correct statements and reason is correct explanation for assertion.
B. Assertion and reason both are correct statements but reason is not correct explanation for assertion.
C. Assertion is correct statement but reason is wrong statement.
D. Assertion is wrong statement but reason is correct statement.

1.Assertion: Highest oxidation state is exhibited by transition metal lying in the middle of the series.

Reason: The highest oxidation state exhibited corresponds to number of (n-1)d electrons.

2. Assertion: Fe^{3+} is more stable than Fe^{2+}

Reason: Fe^{3+} has $3d^5$ configuration while Fe^{2+} has $3d^6$ configuration.

3. Assertion: Vanadium had the ability to exhibit a wide range of oxidation states.

Reason: The standard potentials Vanadium are rather small, making a switch between oxidation states relatively easy.

4. Assertion: Transition metals like Fe, Cr and Mn form oxyions

Reason: Oxygen is highly electronegative and has a tendency to form multiple bonds.

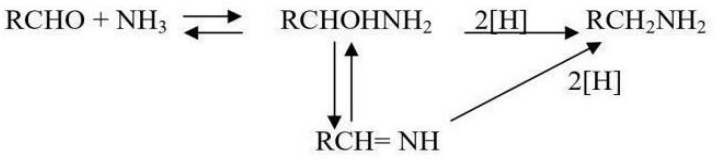
5.Assertion: The highest oxidation states of the 3d metals depends only on electronic configuration of the metal.

Reason: The number of electrons in the (n-1)d and ns subshells determine the oxidation states exhibited by the metal.

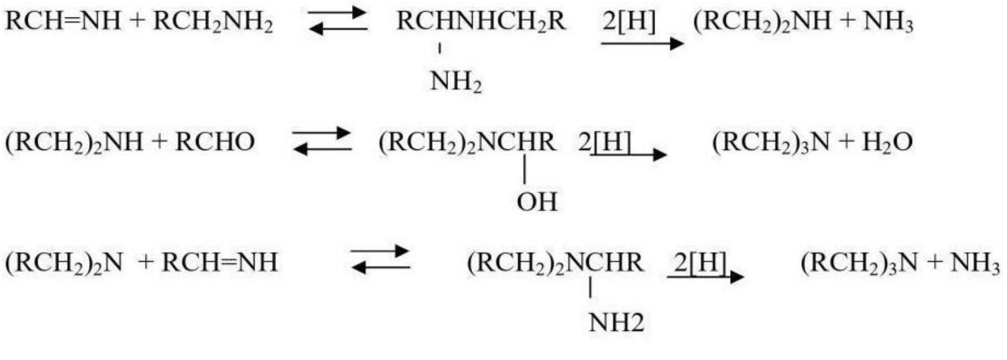
Ans: 1.c 2 a 3 a 4 b 5d

(VII) Read the passage given below and answer the following questions:

Reductive alkylation is the term applied to the process of introducing alkyl groups into ammonia or a primary or secondary amine by means of an aldehyde or ketone in the presence of a reducing agent. The present discussion is limited to those reductive alkylations in which the reducing agent is hydrogen and a catalyst or "nascent" hydrogen, usually from a metal-acid combination; most of these reductive alkylations have been carried out with hydrogen and a catalyst. The principal variation excluded is that in which the reducing agent is formic acid or one of its derivatives; this modification is known as the Leuckart reaction. The process of reductive alkylation of ammonia consists in the addition of ammonia to a carbonyl compound and reduction of the addition compound or its dehydration product. The reaction usually is carried out in ethanol solution when the reduction is to be effected catalytically



Since the primary amine is formed in the presence of the aldehyde it may react in the same way as ammonia, yielding an addition compound, a Schiff's base (RCH= NCH_2R) and finally, a secondary amine. Similarly, the primary amine may react with the imine, forming an addition product which also is reduced to a secondary amine Finally, the secondary amine may react with either the aldehyde or the imine to give products which are reduced to tertiary amines.



$$RCH{=}NH + RCH_2NH_2 \rightleftharpoons \underset{NH_2}{RCHNHCH_2R} \xrightarrow{2[H]} (RCH_2)_2NH + NH_3$$

$$(RCH_2)_2NH + RCHO \rightleftharpoons (RCH_2)_2N\underset{OH}{CHR} \xrightarrow{2[H]} (RCH_2)_3N + H_2O$$

$$(RCH_2)_2N + RCH{=}NH \rightleftharpoons (RCH_2)_2N\underset{NH2}{CHR} \xrightarrow{2[H]} (RCH_2)_3N + NH_3$$

Similar reactions may occur when the carbonyl compound employed is a ketone.

(source: Emerson, W. S. (2011). *The Preparation of Amines by Reductive Alkylation. Organic Reactions, 174–255.* doi:10.1002/0471264180.or004.03)

Q1. Ethanal on reaction with ammonia forms an imine (X) which on reaction with nascent hydrogen gives (Y). Identify 'X' and 'Y'.

A. X is $CH_3CH{=}NH$ and Y is CH_3NH_2
B. X is $CH_3CHOHNH_2$ and Y is $CH_3CH_2NH_2$
C. X is $CH_3CHOHNH_2$ and Y is CH_3NH_2
D. X is $CH_3CH{=}NH$ and Y is $CH_3CH_2NH_2$

Q2. Acetaldehyde is reacted with ammonia followed by reduction in presence of hydrogen as a catalyst. The primary amine so formed further reacts with acetaldehyde. The Schiff's base formed during the reaction is:

A. $CH_3CH{=}NHCH_3$
B. $CH_3CH{=}NHCH_2CH_3$
C. $CH_3{=}NHCH_2CH_3$
D. $CH_3CH_2CH{=}NHCH_3$

Q3. The reaction of ammonia and its derivatives with aldehydes is called:

A. Nucleophilic substitution reaction
B. Electrophilic substitution reaction
C. Nucleophilic addition reaction
D. Electrophilic addition reaction

Q4. $(CH_3CH_2CH_2)_2NH + CH_3CH_2CHO \longrightarrow P \xrightarrow{2[H]} Q$

The compound Q is:

A. $(CH_3CH_2CH_2)_3N$
B. $(CH_3CH_2CH_2)_2N(CH_2CH_3)$
C. $(CH_3CH_2)_3N$
D. $(CH_3CH_2)_2NH$

Q5. Reductive alkylation of ammonia by means of an aldehyde in presence of hydrogen as reducing agents results in formation of:

A. Primary amines
B. Secondary amines
C. Tertiary amines
D. Mixture of all three amines

(Ans: 1D,2B,3C,4 A,5D)

(VIII) Read the passage given below and answer the following questions:

Some colloids are stable by their nature, i.e., gels, alloys, and solid foams. Gelatin and jellies are two common examples of a gel. The solid and liquid phases in a gel are interdispersed with both phases being continuous. In most systems, the major factor influencing the stability is the charge on the colloidal particles. If a particular ion is preferentially adsorbed on the surface of the particles, the particles in suspension will repel each other, thereby preventing the formation of aggregates that are larger than colloidal dimensions. The ion can be either positive or negative depending on the particular colloidal system, i.e., air bubbles accumulate negative ions, sulphur particles have a net negative charge in a sulphur sol, and the particles in a metal hydroxide sol are positively charged. Accumulation of charge on a surface is not an unusual phenomenon-dust is attracted to furniture surfaces by electrostatic forces. When salts are added to lyophobic colloidal systems the colloidal particles begin to form larger aggregates and a sediment forms as they settle. This phenomenon is called flocculation, and the suspension can be referred to as flocculated, or colloidally unstable. If the salt is removed, the suspension can usually be restored to its original state; this process is called deflocculation or peptization. The original and restored colloidal systems are called deflocculated, peptized, or stable sols.

Why does a small amount of salt have such a dramatic effect on the stability of a lyophobic colloidal system? The answer lies in an understanding of the attractive and repulsive forces that exist between colloidal particles. Van der Waals forces are responsible for the attractions, while the repulsive forces are due to the surface charge on the particles. In a stable colloid, the repulsive forces are of greater magnitude than the attractive forces. The magnitude of the electrical repulsion is diminished by addition of ionized salt, which allows the dispersed particles to aggregate and flocculate. River deltas provide an example of this behaviour. A delta is formed at the mouth of a river because the colloidal clay particles are flocculated when the freshwater mixes with the salt water of the ocean

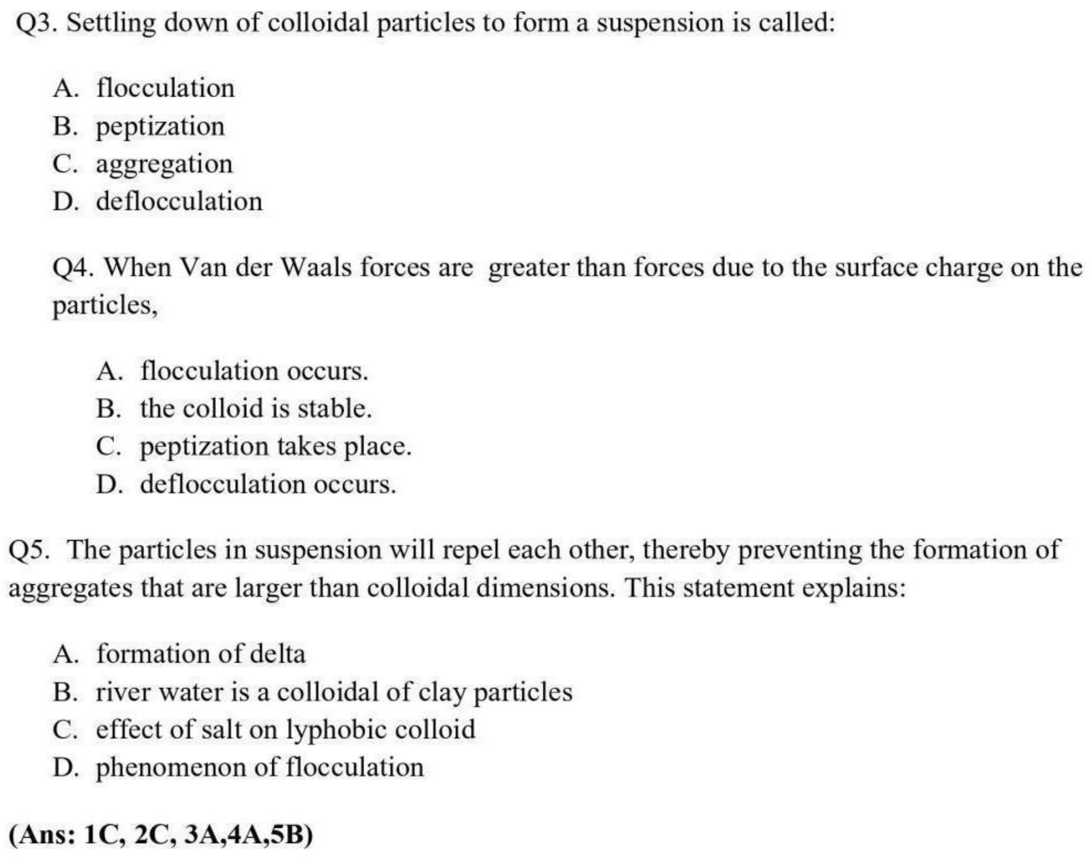
(source: Sarquis, J. (1980). *Colloidal systems. Journal of Chemical Education, 57(8), 602.* doi:10.1021/ed057p602)

Q1. Gelatin is a ________________ colloidal system.

A. Solid in solid
B. Solid in gas
C. Liquid in solid
D. Liquid in gas

Q2.Colloidal solutions are stable due to:

A. presence of charges on the colloidal particles
B. formation of aggregates by colloidal particles
C. preferential adsorption on the surface
D. preferential absorption on the surface



Q3. Settling down of colloidal particles to form a suspension is called:

A. flocculation
B. peptization
C. aggregation
D. deflocculation

Q4. When Van der Waals forces are greater than forces due to the surface charge on the particles,

A. flocculation occurs.
B. the colloid is stable.
C. peptization takes place.
D. deflocculation occurs.

Q5. The particles in suspension will repel each other, thereby preventing the formation of aggregates that are larger than colloidal dimensions. This statement explains:

A. formation of delta
B. river water is a colloidal of clay particles
C. effect of salt on lyphobic colloid
D. phenomenon of flocculation

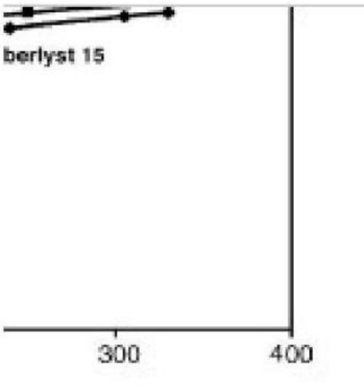
(Ans: 1C, 2C, 3A,4A,5B)

(IX) Read the passage given below and answer the following questions:

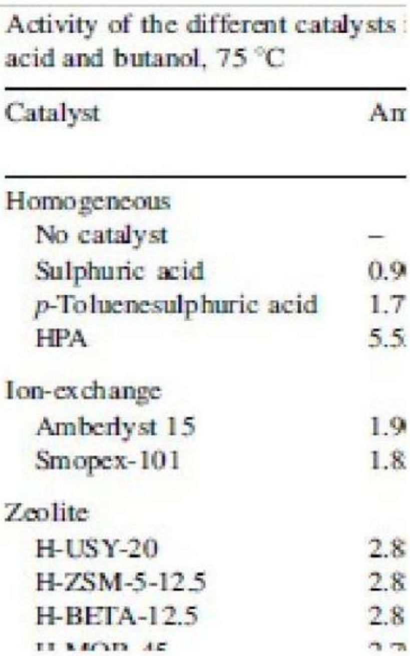
Industrially widely applied esterification reactions are commonly catalysed using mineral liquid acids, such as sulphuric acid and p-toluenesulphonic acid. The catalytic activity of homogeneous catalysts is high. They suffer, however, from several drawbacks, such as their corrosive nature, the existence of side reactions, and the fact that the catalyst cannot be easily separated from the reaction mixture. The use of solid acid catalysts offers an alternative and has received a lot of attention in the past years. Solid acid catalysts are not corrosive and, coated onto a support, they can be easily reused. Examples of solid acid catalysts used in esterification reactions include ion-exchange resins , zeolites and superacids like sulphated zirconia and niobium acid. Ion-exchange resins are the most common heterogeneous catalysts used and have proven to be effective in liquid phase esterification and etherification reactions. Because of their selective adsorption of reactants and swelling nature, these resins not only catalyse the esterification reaction but also affect the equilibrium conversion. Shortcomings include insufficient thermal resistance, which limits the reaction temperature to 120 ^{o}C, preventing widespread use in industry. Zeolites, like Y, X, BEA, ZSM-5 and MCM-41 offer an interesting alternative and have proven to be efficient catalysts for esterification reactions. Zeolites have found wide application in oil refining, petrochemistry and in the production of fine chemicals. Their success is based on the possibility to prepare zeolites with strong Brønsted acidity that can be controlled within a certain range, combined with a good resistance to high reaction temperatures.

In this study, the activity of various commercial available solid acid catalysts is assessed with respect to the esterification of acetic acid with butanol. The ion-exchange resins Amberlyst 15 and Smopex-101, the acid zeolites H-ZSM-5, H-MOR, H-BETA and H-USY, and the solid superacids sulphated zirconia and niobium acid are selected. Comparative esterification experiments have been carried out using the homogeneous catalysts sulphuric acid, p-toluenesulphuric acid and a heteropolyacid (HPA).

The weight-based activity of the heterogeneous catalysts tested is maximum for Smopex101. The following table gives the activity of different catalysts in the esterification reaction between acetic acid and butanol at 75^{0}C.



of process time in the ester-
-exchange resins as catalyst,



Activity of the different catalysts
acid and butanol, 75 °C

Catalyst	Am
Homogeneous	
No catalyst	–
Sulphuric acid	0.9
p-Toluenesulphuric acid	1.7
HPA	5.5
Ion-exchange	
Amberlyst 15	1.9
Smopex-101	1.8
Zeolite	
H-USY-20	2.8
H-ZSM-5-12.5	2.8
H-BETA-12.5	2.8

Here: k_{obs}: observed reaction rate constant ($m^3mol^{-1}s^{-1}$)
kc catalysed reaction rate constant ($m^3mol^{-1}g_{cat}^{-1}s^{-1}$)
Please note: k c = k obs/ amount (in g)

(source: PETERS, T., BENES, N., HOLMEN, A., & KEURENTJES, J. (2006). *Comparison of commercial solid acid catalysts for the esterification of acetic acid with butanol. Applied Catalysis A: General, 297(2), 182–188.* doi:10.1016/j.apcata.2005.09.00)

Q1. Which of the following are heterogeneous catalysts for esterifctaion reaction:

A. sulphuric acid and p-toluenesulphonic acid
B. sulphuric acid and niobium acid
C. p-toluenesulphonic acid and niobium acid
D. niobium acid and sulphated zirconia

Q2. Unit for observed rate constant for esterification reaction is $m^3mol^{-1}s^{-1}$, so the reaction is:

A. zero order
B. first order
C. second order
D. third order

Q3. The catalytic activity of homogeneous catalysts is high. The weight based activity of HPA is less than which of the following heterogenous catalysts?

A. Smopex-101
B. Amberlyst 15
C. sulphated ZrO2

D. H-USY-20

Q4. The weight-based activity of the heterogeneous catalysts tested decreases in the following order:

A. Smopex-101 > Amberlyst 15 > sulphated ZrO2 > H-USY-20 >H-BETA-12.5 > H-MOR-45 > Nb2O5 > H-ZSM-5-12
B. Smopex-101 > Amberlyst 15 > sulphated ZrO2 > H-USY-20 >H-BETA-12.5 > H-MOR-45 > H-ZSM-5-12> Nb2O5
C. Smopex-101 > Amberlyst 15 > sulphated ZrO2 > H-USY-20 >H-BETA-12.5 > Nb2O5> H-MOR-45 > H-ZSM-5-12
D. Smopex-101 > sulphated ZrO2 > Amberlyst 15 > H-USY-20 >H-BETA-12.5 > H-MOR-45 > H-ZSM-5-12> Nb2O5

Q5. Catalysts used in oil refining industry are:

A. ion exchange resins
B. superacids
C. zeolites
D. mineral liquid acids

(ANS: 1D, 2C, 3A, 4A, 5C)

(X) Read the passage given below and answer the following questions:

Biopolymers are polymers that are generated from renewable natural sources, are often biodegradable and nontoxic. They can be produced by biological systems (i.e. microorganisms, plants and animals), or chemically synthesized from biological materials (e.g., sugars, starch, natural fats or oils, etc.). Two strategies are applied in converting these raw materials into biodegradable polymers: extraction of the native polymer from a plant or animal tissue, and a chemical or biotechnological route of monomer polymerization. Biodegradable biopolymers (BDP) are an alternative to petroleum-based polymers (traditional plastics). Some BDP degrade in only a few weeks, while the degradation of others takes several months. In principle the properties relevant for application as well as biodegradability are determined by the molecular structure. According to the American Society for Testing and Materials, biopolymers are degradable polymers in which degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae .

Polylactic acid (PLA) is an example of biopolymer. It is a thermoplastic polyester. Generally, there are two major routes to produce polylactic acid from the lactic acid ($CH_3CH(OH)$-$COOH$)monomer. The first route involves condensation–water removal by the use of solvent under high vacuum and temperature. This approach produces a low to intermediate molar mass polymer. An alternative method is to remove water under milder conditions, without solvent, to produce a cyclic intermediate dimer, referred to as lactide. This intermediate is readily purified by vacuum distillation. Ring opening polymerization of the dimer is accomplished under heat, again without the need for solvent. By controlling the purity of the dimer it is possible to produce a wide range of molar masses .PLA is a good material for production of clothing, carpet tiles, interior and outdoor furnishing, geotextiles, bags, filtration systems, etc.

The primary biodegradability of PLA was tested using hydrolysis tests at various composting temperatures and pH. It was demonstrated that composting is a useful method for PLA biodegradation. The degradation rate is very slow in ambient temperatures. A 2017 study found that at 25 °C in sea water, PLA showed no degradation over a year. As a result, it is poorly degraded in landfills and household composts, but is effectively digested in hotter industrial composts.

(source: Flieger, M., Kantorová, M., Prell, A., Řezanka, T., & Votruba, J.
(2003). *Biodegradable plastics from renewable sources. Folia Microbiologica, 48(1), 27–*
44. doi:10.1007/bf02931273)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

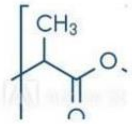
A. Assertion and reason both are correct statements and reason is correct explanation for assertion.
B. Assertion and reason both are correct statements but reason is not correct explanation for assertion.

C. Assertion is correct statement but reason is wrong statement.
D. Assertion is wrong statement but reason is correct statement.

Q1.Assertion: Biodegradable polymers degrade in few weeks.

Reason: Microorganisms bring about degradation of biopolymers.

Q2. Assertion: Lactic acid on polymerisation forms



Reason: PLA is used in producing geotextiles.

Q3. Assertion: Lactic acid undergoes condensation polymerisation

Reason: Lactic acid is a bifunctional monomeric unit.

Q4. Assertion: . The degradation of PLA is very slow in ambient temperature.

Reason: PLA is a thermoplastic.

Q5.Assertion: PLA is poorly degraded in landfills.

Reason: The degradation rate of PLA is very slow in ambient temperatures.

(ANS: 1D, 2B, 3A,4B,5A)

(XI) Read the passage given below and answer the following questions:

In the last 10 years much has been learned about the molecular structure of elemental sulfur. It is now known that many different types of rings are sufficiently metastable to exist at room temperature for several days. It is known that at high temperature, the equilibrium composition allows for a variety of rings and chains to exist in comparable concentration, and it is known that at the boiling point and above, the vapor as well as the liquid contains small species with three, four, and five atoms.

The sulfur atom has the same number of valence electrons as oxygen. Thus, sulfur atoms S_2 and S_3 have physical and chemical properties analogous to those of oxygen and ozone. S_2 has a ground state of 38 $\sigma 3s^2 \sigma^* 3s^2 \sigma 3pz^2 \pi 3px^2 = \pi 3py^2 \pi^* 3px^1 = \pi^* 3py^1$. S3 , thiozone has a well-known uv spectrum, and has a bent structure, analogous to its isovalent molecules 0_3, SO_2, and S_20. The chemistry of the two elements, sulphur and oxygen, differs because sulfur has a pronounced tendency for catenation. The most frequently quoted explanation is based on the electron structure of the atom. Sulfur has low-lying unoccupied 3d orbitals, and it is widely believed that the 4s and 3d orbitals of sulfur participate in bonding in a manner similar to the participation of 2s and 2p orbitals in carbon.

(source: Meyer, B. (1976). *Elemental sulfur. Chemical Reviews, 76(3), 367–388.* doi:10.1021/cr60301a003)

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A. Assertion and reason both are correct statements and reason is correct explanation for assertion.
B. Assertion and reason both are correct statements but reason is not correct explanation for assertion.
C. Assertion is correct statement but reason is wrong statement.
D. Assertion is wrong statement but reason is correct statement.

Q1 Assertion: Sulphur belongs to same group in the periodic table as oxygen.

Reason: S2 has properties analogous to O2.

Q2. Assertion: Thiozone has bent structure like ozone.

Reason: Ozone has a lone pair which makes the molecule bent.

Q3. Assertion: S2 is paramagnetic in nature

Reason: The electrons in π^*3px and π^*3py orbitals in S_2 are unpaired.

Q4. Assertion: Sulphur has a greater tendency for catenation than oxygen.

Reason: 3d and 4s orbitals of Sulphur have same energy.

(ANS: 1B,2B, 3A,4C)

(XII) Read the passage given below and answer the following questions:

Adenosine triphosphate (ATP) is the energy-carrying molecule found in the cells of all living things. ATP captures chemical energy obtained from the breakdown of food molecules and releases it to fuel other cellular processes. ATP is a nucleotide that consists of three main structures: the nitrogenous base, adenine; the sugar, ribose; and a chain of three phosphate groups bound to ribose. The phosphate tail of ATP is the actual power source which the cell taps. Available energy is contained in the bonds between the phosphates and is released when they are broken, which occurs through the addition of a water molecule (a process called hydrolysis). Usually only the outer phosphate is removed from ATP to yield energy; when this occurs ATP is converted to adenosine diphosphate (ADP), the form of the nucleotide having only two phosphates.

The importance of ATP (adenosine triphosphate) as the main source of chemical energy in living matter and its involvement in cellular processes has long been recognized. The primary mechanism whereby higher organisms, including humans, generate ATP is through mitochondrial oxidative phosphorylation. For the majority of organs, the main metabolic fuel is glucose, which in the presence of oxygen undergoes complete combustion to CO_2 and H_2O:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6O_2 + 6H_2O + \text{energy}$$

The free energy (ΔG) liberated in this exergonic (ΔG is negative) reaction is partially trapped as ATP in two consecutive processes: glycolysis (cytosol) and oxidative phosphorylation (mitochondria). The first produces 2 mol of ATP per mol of glucose, and the second 36 mol of ATP per mol of glucose. Thus, oxidative phosphorylation yields 17-18 times as much useful energy in the form of ATP as can be obtained from the same amount of glucose by glycolysis alone.

The efficiency of glucose metabolism is the ratio of amount of energy produced when 1 mol of glucose oxidised in cell to the enthalpy of combustion of glucose. The energy lost in the process is in the form of heat. This heat is responsible for keeping us warm.

(source: Erecińska, M., & Silver, I. A. (1989). ATP and Brain Function. *Journal of Cerebral Blood Flow & Metabolism*, *9*(1), 2–19. https://doi.org/10.1038/jcbfm.1989.2 and https://www.britannica.com/science/adenosine-triphosphate)

Q1. Cellular oxidation of glucose is a:

A. spontaneous and endothermic process
B. non spontaneous and exothermic process
C. non spontaneous and endothermic process
D. spontaneous and exothermic process

Q2. What is the efficiency of glucose metabolism if 1 mole of glucose gives 38ATP energy?(Given: The enthalpy of combustion of glucose is 686 kcal, 1ATP= 7.3kcal)

A. 100%
B. 38%
C. 62%
D. 80%

Q3.Which of the following statement is true?

A. ATP is a nucleoside made up of nitrogenous base adenine and ribose sugar .
B. ATP consists the nitrogenous base, adenine and the sugar, deoxyribose.
C. ATP is a nucleotide which contains a chain of three phosphate groups bound to ribose sugar.
D. The nitrogenous base of ATP is the actual power source.

Q4. Nearly 95% of the energy released during cellular respiration is due to:

A. glycolysis occurring in cytosol
B. oxidative phosphorylation occurring in cytosol
C. glycolysis in occurring mitochondria
D. oxidative phosphorylation occurring in mitochondria

Q5. Which of the following statements is correct:

A. ATP is a nucleotide which has three phosphate groups while ADP is a nucleoside which three phosphate groups.
B. ADP contains a nitrogenous bases adenine, ribose sugar and two phosphate groups bound to ribose.
C. ADP is the main source of chemical energy in living matter.
D. ATP and ADP are nucleosides which differ in number of phosphate groups.

(ANS: 1D,2B(Glucose catabolism yields a TOTAL of 38 ATP. 38 ATP x 7.3 kcal/mol ATP = 262 kcal. Glucose has 686 kcal. Thus the efficiency of glucose metabolism is 262/686 x 100 = 38%.) ,3C,4D,5B)

(XIII) Read the passage given below and answer the following questions:

The transition metals when exposed to oxygen at low and intermediate temperatures form thin, protective oxide films of up to some thousands of Angstroms in thickness. Transition metal oxides lie between the extremes of ionic and covalent binary compounds formed by elements from the left or right side of the periodic table. They range from metallic to semiconducting and deviate by both large and small degrees from stoichiometry. Since d-electron bonding levels are involved, the cations exist in various valence states and hence give rise to a large number of oxides. The crystal structures are often classified by considering a cubic or hexagonal close-packed lattice of one set of ions with the other set of ions filling the octahedral or tetrahedral interstices. The actual oxide structures, however, generally show departures from such regular arrays due in part to distortions caused by packing of ions of different size and to ligand field effects. These distortions depend not only on the number of d-electrons but also on the valence and the position of the transition metal in a period or group. (source: Smeltzer, W. W., & Young, D. J. (1975). Oxidation properties of transition metals. *Progress in Solid State Chemistry*, *10*, 17-54.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

A. Assertion and reason both are correct statements and reason is correct explanation for assertion.
B. Assertion and reason both are correct statements but reason is not correct explanation for assertion.
C. Assertion is correct statement but reason is wrong statement.
D. Assertion is wrong statement but reason is correct statement.

1.Assertion: Cations of transition elements occur in various valence states

Reason: Large number of oxides of transition elements are possible.

2.Assertion: Crystal structure of oxides of transition metals often show defects.

Reason: Ligand field effect cause distortions in crystal structures.

3.Assertion : Transition metals form protective oxide films.

Reason: Oxides of transition metals are always stoichiometric.

4.Assertion: CrO crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by chromium ions.

Reason: Transition metal oxide may be hexagonal close-packed lattice of oxide ions with metal ions filling the octahedral voids.

(ANS: 1 B , 2 A, 3C , 4D)

(XIV) Read the passage given below and answer the following questions:

The d block elements are the 40 elements contained in the four rows of ten columns (3-12) in the periodic table. As all the d block elements are metallic, the term d-block metals is synonymous. This set of d-block elements is also often identified as the transition metals, but sometimes the group 12 elements (zinc, cadmium, mercury) are excluded from the transition metals as the transition elements are defined as those with partly filled d or f shells in their compounds. Inclusion of the elements zinc, cadmium and mercury is necessary as some properties of the group 12 elements are appropriate logically to include with a discussion of transition metal chemistry.

The term transition element or transition metal appeared to derive from early studies of periodicity such as the Mendeleev periodic table of the elements. His horizontal table of the elements was an attempt to group the elements together so that the chemistry of elements might be explained and predicted. In this table there are eight groups labeled I-VIII with each subdivided into A and B subgroups. Mendeleev recognized that certain properties of elements in Group VIII are related to those of some of the elements in Group VII and those at the start of the next row Group I. In that sense, these elements might be described as possessing properties transitional from one row of the table to the next. (source: Winter, M. J. (2015). *D-block Chemistry* (Vol. 27). Oxford University Press, USA.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

A. Assertion and reason both are correct statements and reason is correct explanation for assertion.
B. Assertion and reason both are correct statements but reason is not correct explanation for assertion.
C. Assertion is correct statement but reason is wrong statement.
D. Assertion is wrong statement but reason is correct statement.

1.Assertion: Group 12 elements are not considered as transition metals.

Reason: Transition metals are those which have incompletely filled d shell in their compounds.

2.Assertion: All d block elements are metallic in nature.

Reason: The d –block elements belong to Group3 -12 of the periodic table.

3.Assertion : Group VII elements of Mendeleev periodic table are transition elements.

Reason: Group I –VIII in Mendleev periodic table is divided into two subgroups, A and B.

4.Assertion: Nickel is a transition element that belongs to group 10 and period 4 of the modern periodic table.

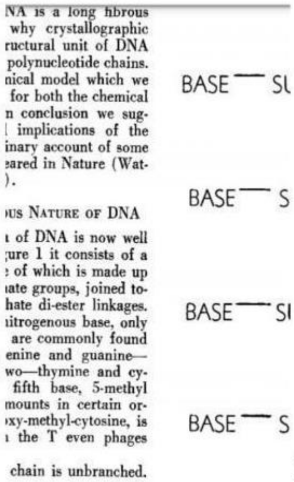
Reason: Electronic configuration of Nickel is $[Ar]_{18}3d^8 4s^2$

(ANS: 1A, 2B, 3D,4A)

(XV) Read the passage given below and answer the following questions:

EVIDENCE FOR THE FIBROUS NATURE OF DNA

The basic chemical formula of DNA is now well established. As shown in Figure 1 it consists of a very long chain, the backbone of which is made up of alternate sugar and phosphate groups, joined together in regular 3' 5' phosphate di-ester linkages. To each sugar is attached a nitrogenous base, only four different kinds of which are commonly found in DNA. Two of these---adenine and guanine--- are purines, and the other two thymine and cytosine-are pyrimidines. A fifth base, 5-methyl cytosine, occurs in smaller amounts in certain organisms, and a sixth, 5-hydroxy-methyl-cytosine, is found instead of cytosine in the T even phages. It should be noted that the chain is unbranched, a consequence of the regular internucleotide linkage. On the other hand the sequence of the different nucleotides is, as far as can be ascertained, completely irregular. Thus, DNA has some features which are regular, and some which are irregular. A similar conception of the DNA molecule as a long thin fiber is obtained from physicochemical analysis involving sedimentation, diffusion, light scattering, and viscosity measurements. These techniques indicate that DNA is a very asymmetrical structure approximately 20 A wide and many thousands of angstroms long. Estimates of its molecular weight currently center between 5 X 10^6 and 10^7 (approximately 3 x10^4 nucleotides). Surprisingly each of these measurements tend to suggest that the DNA is relatively rigid, a puzzling finding in view of the large number of single bonds (5 per nucleotide) in the phosphate-sugar back bone. Recently these indirect inferences have been confirmed by electron microscopy.


NA is a long fibrous
why crystallographic
ructural unit of DNA
polynucleotide chains.
nical model which we
for both the chemical
n conclusion we sug-
implications of the
inary account of some
eared in Nature (Wat-
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US NATURE OF DNA

of DNA is now well
ure 1 it consists of a
of which is made up
ate groups, joined to-
hate di-ester linkages.
itrogenous base, only
are commonly found
enine and guanine—
wo—thymine and cy-
fifth base, 5-methyl
mounts in certain or-
xy-methyl-cytosine, is
the T even phages

chain is unbranched.

Figure 1

(source: Watson, J. D., & Crick, F. H. (1953, January). The structure of DNA. In *Cold Spring Harbor symposia on quantitative biology* (Vol. 18, pp. 123-131). Cold Spring Harbor Laboratory Press.)

1.Purines present in DNA are:

A. adenine and thymine
B. guanine and thymine
C. cytosine and thymine
D. adenine and guanine

2. DNA molecule has ___________ internucleotide linkage and __________ sequence of the different nucleotides

A. regular , regular
B. regular , irregular
C. irregular , regular
D. irregular , irregular

3.DNA has a ___________ backbone

A. phosphate -purine
B. pyrimidines- sugar
C. phosphate- sugar
D. purine- pyrimidine

4. Out of the four different kinds of nitrogenous bases which are commonly found in DNA, ___________ has been replaced in some organisms.

A. adenine
B. guanine
C. cytosine
D. thymine

(ANS 1D, 2 B, 3 C, 4 C)

(XVI) Read the passage given below and answer the following questions:

Polysaccharides may be very large molecules. Starch, glycogen, cellulose, and chitin are examples of polysaccharides.

Starch is the stored form of sugars in plants and is made up of amylose and amylopectin (both polymers of glucose). Amylose is soluble in water and can be hydrolyzed into glucose units breaking glycocidic bonds, by the enzymes α- amylase and β-amylase. It is straight chain polymer. Amylopectin is a branched chain polymer of several D-glucose molecules. 80% of amylopectin is present in starch. Plants are able to synthesize glucose, and the excess glucose is stored as starch in different plant parts, including roots and seeds. The starch that is consumed by animals is broken down into smaller molecules, such as glucose. The cells can then absorb the glucose.

Glycogen is the storage form of glucose in humans and other vertebrates, and is made up of monomers of glucose. It is structurally quite similar to amylopectin . Glycogen is the animal equivalent of starch. It is stored in liver and skeletal muscles.

Cellulose is one of the most abundant natural biopolymers. The cell walls of plants are mostly made of cellulose, which provides structural support to the cell. Wood and paper are mostly cellulosic in nature.

Like amylose, cellulose is a linear polymer of glucose. Cellulose is made up of glucose monomers that are linked by bonds between particular carbon atoms in the glucose molecule.Every other glucose monomer in cellulose is flipped over and packed tightly as extended long chains. This gives cellulose its rigidity and high tensile strength—which is so important to plant cells. Cellulose passing through our digestive system is called dietary fiber. (Source: https://chem.libretexts.org)

1. In animals , Glycogen is stored in :

   A. Liver
   B. Spleen
   C. Lungs
   D. Small Intestine

2. Amylose is :

   A. straight chain , water insoluble component of starch ,which constitutes 20 % of it .
   B. straight chain , water soluble component of starch ,which constitutes 20 % of it.
   C. branched chain , water insoluble component of starch ,which constitutes 80 % of it .
   D. branched chain , water soluble component of starch ,which constitutes 80 % of it .

3. Which biopolymer breaks down to release glucose , whenever glucose levels drop in Our body :

   A.starch
   B. cellulose
   C. chitin

D. glycogen

4. The linkages which join monosaccharides to form long chain polysaccharides :

A. Peptide linkage

B. Disulphide bonds

C. Hydrogen bonds

D. Glycosidic linkage

5. Cellulose on complete hydrolysis yields:

A. amylose

B. amylopectin

C. glucose

D. amylose and amylopectin

(ANS 1 A,2B,3D, 4D,5C)

Academic Session: 2020-21
Preboard Examination I
Subject: Chemistry
Class: XII

Time : 3 Hrs **Max marks : 70**

General Instructions:

Read the following instructions carefully.
a) There are 33 questions in this question paper. All questions are compulsory.
b) Section A: Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
c) Section B: Q. No. 17 to 25 are short answer questions and carry 2 marks each.
d) Section C: Q. No. 26 to 30 are short answer questions and carry 3 marks each.
e) Section D: Q. No. 31 to 33 are long answer questions carrying 5 marks each.
f) There is no overall choice. However, internal choices have been provided.
g) Use of calculators and log tables is not permitted.
There are 277 printed pages.
Reading Time: 9.25 - 9.40 am
Writing Time: 9.40 am-12.40 pm
Scan & turn in: By 1.00 pm
Children who avail time can turn in by 2:00 pm

1 Read the given passage and answer the questions that follow: *(1X 4)*

Colloidal particles always carry an electric charge which may be either positive or negative. For example , when $AgNO_3$ solution is added to KI solution, a negatively charged colloidal sol is obtained. The presence of equal and similar charges on colloidal particles provide stability to the colloidal sol and if, somehow , charge is removed, coagulation of sol occurs. Lyophobic sols are readily coagulated as compared to lyophilic sols. Lyophobic sols are positively or negatively charged. These are coagulated by electrolytes. Oppositely charged ions are most effective for coagulation. For As_2S_3 sol, out of 0.1 M $AlCl_3$. 0.1M $MgCl_2$ and 0.1 M NaCl solution, 0.1 M $AlCl_3$ is most effective. The number of particles produced by electrolyte in aqueous solution depends upon degree of ionisation.

The potential difference between the fixed charged layer and the diffused layer having opposite charge is called
(a) Zeta potential
(b) Electrokinetic potential

(c) Both (a) and (b)
(d) Streaming potential

(i) Negatively charged sol is obtained when

(a) KI solution is added to $AgNO_3$ solution

(b) $AgNO_3$ solution is added to KI solution

(c)When AgI is dissolved in water

(d) all of these

(ii) Name the method by which coagulation of lyophobic sol can be carried out ?

(a) electrophoresis

(b) by adding oppositely charged sol

(c)boiling

(d)all of these

(iii) Identify the positively charged sol

(a) As_2S_3

(b) Haemoglobin

(c) clay

(d) gold sol

2 Alcohols are the hydroxy derivatives of aliphatic hydrocarbons whereas phenols are hydroxy derivatives of arenes in which the -OH group is directly linked with the benzene ring . These are used in daily life. Ordinary spirit is used as antiseptic for cleaning wounds as well as for polishing furniture. The sugar we eat, cotton (cellulose) we wear, the paper on which we write all are made up of alcohol. Alcohol is present in wine, cough syrups, and tonics. Phenol is used as antiseptic and disinfectant and preparation of medicines like Aspirin, Iodex etc. Aspirin is prepared by reacting salicylic acid with acetic anhydride in presence of H_2SO_4. It is used as an analgesic, antipyretic and prevents heart attack. Iodex , is methyl salicylate , used in muscle pain reliever. (1X4)

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct and reason is the correct explanation of assertion.

(b) Both assertion and reason are correct statements but reason is not the correct explanation of assertion.

(c) Assertion is the correct statement but reason is the wrong statement.

(d) Assertion is wrong statement but reason is correct statement..

(i) Assertion : Addition reaction of water to but-1-ene in acidic medium yields butan-1-ol

Reason : Addition of water in acidic medium proceeds through the formation of carbocation.

(ii) Assertion : p-nitrophenol is more acidic than phenol.

Reason : Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

(iii) Assertion : Bond angle in ethers is slightly less than the tetrahedral angle.

Reason : There is a repulsion between the two bulky (—R) groups.

(iv) Assertion : Boiling points of alcohols and ethers are higher than alkanes.

Reason : They can form intermolecular hydrogen-bonding.

3 Which cell will measure standard electrode potential of copper electrode? *1*

(a) Pt (s) H_2 (g, 0.1 bar) | H^+ (aq., 1 M) | | Cu^{2+}(aq., 1M) | Cu (s)

(b) Pt(s) H_2 (g, 1 bar) | H^+ (aq., 1 M) | | Cu^{2+} (aq., 2 M) | Cu (s)

(c) Pt(s) H_2 (g, 1 bar) | H^+ (aq., 1 M) | | Cu^{2+} (aq., 1 M) | Cu (s)

(d) Pt(s) H_2 (g, 1 bar) | H^+ (aq., 0.1 M) | | Cu^{2+} (aq., 1 M) | Cu (s)

4 Which of the following is a nonreducing sugar *1*

(a) glucose

(b) lactose

(c) maltose

(d) Sucrose

OR

Glucose does not react with

(a) NH_2OH

(b) conc. HNO_3

(c)($CH_3CO)_2O$

(d) $NaHSO_3$

5 Maximum amount of a solid solute that can be dissolved in a specified amount of a given liquid solvent does not depend upon *1*

(a) Temperature

(b) nature of solute

(c) pressure

(d) nature of solvent

6 Which of the following has magnetic moment value of 5.9? *1*
(a) Fe^{2+}
(b) Fe^{3+}
(c) Ni^{2+}
(d) Cu^{2+}

Or

Which of the following are d-block elements but not regarded as transition elements?
(a) Cu, Ag, Au
(b) Zn, Cd, Hg
(c) Fe, Co, Ni
(d) Ru, Rh, Pd

7 Aniline is less basic than ethylamine. This is due to *1*
(a) Conjugation of lone pair of nitrogen with the ring
(b) The insoluble nature of aniline

(c) More K_b value of aniline
(d) Hydrogen bonding

OR

Primary and secondary amines cannot be distinguished by
(a) Schiff's reagent
(b) Carbylamine reaction
(c) Reaction with Nitrous acid
(d) Hinsberg reagent and solubility in alkali

8 The stabilization of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species? 1

(a) $[Fe(CO)_5]$

(b) $[Fe(CN)_6]^{3-}$

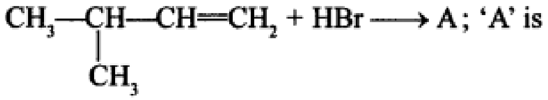
(c) $[Fe(C_2O_4)_3]^{3-}$

(d) $[Fe(H_2O)]^{3+}$

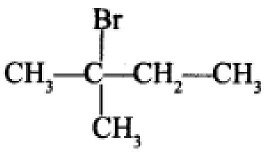
Or

Which of the following has square planar structure?
(a) $[NiCl_4]^{2-}$
(b) $[Ni(CO)_4]$
(c) $[Ni(CN)_4]^{2-}$
(d) None of these

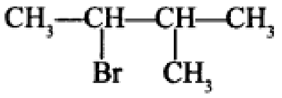
9 Which one of the following characteristics of the transition metals is associated with higher catalytic activity? 1
(a) High enthalpy of atomisation
(b) Paramagnetic behaviour
(c) Colour of hydrated ions
(d) Variable oxidation states

10  1

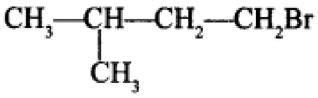
$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH=CH_2 + HBr \longrightarrow A$; 'A' is

(a) 

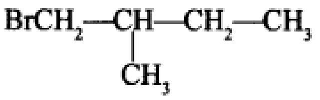
$CH_3-\underset{\substack{|\\ CH_3}}{\overset{\substack{Br\\ |}}{C}}-CH_2-CH_3$

(b) 

$CH_3-\underset{\substack{|\\ Br}}{CH}-\underset{\substack{|\\ CH_3}}{CH}-CH_3$

(c) 

$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-CH_2Br$

(d) 

$BrCH_2-\underset{\substack{|\\ CH_3}}{CH}-CH_2-CH_3$

11 Which of the following statements is not true about the hexagonal close packing? 1

(a) The coordination number is 12

(b) It has 74% packing efficiency

(c) Tetrahedral voids of the second layer are covered by the spheres of the third layer

(d) In this arrangement, spheres of the fourth layer are exactly aligned with those of the first layer.

In the following questions, 12-17, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(A) Assertion and reason both are correct and reason is correct explanation of assertion.
(B) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

(C) Assertion is correct statement but reason is wrong statement.
(D) Assertion is wrong statement but reason is correct statement.

12 **Assertion** : Valine must be taken through diet. *1*
Reason : It is a non essential amino acid.

OR

Assertion: The two strands of DNA are complementary to each other

Reason: The disulphide bonds are formed between specific pairs of bases

13 **Assertion :** When NaCl is added to water a depression in freezing point is observed. *1*
Reason : The lowering of the vapour pressure of a solution causes depression in the freezing point.

14 **Assertion :** SF_6 cannot be hydrolysed but SF_4 can be. *1*
Reason : Six F atoms in SF_6 prevent the attack of H_2O on sulphur atom of SF_6.

15 **Assertion** : o-Nitrophenol is less soluble in water than the m- and p-isomers. *1*
Reason : m- and p- Nitrophenols exist as associated molecules.

16 **Assertion :** p-nitrophenol is more acidic than phenol. *1*

Reason : Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

SECTION B

17 Convert 2

(i) 1-bromobutane to 2-bromobutane

(ii) aniline to chlorobenzene

18 18 g of glucose, $C_6H_{12}O_6$ (Molar mass – 180 g mol^{-1}) is dissolved in 1 kg of water in a saucepan. At what temperature will this solution boil? (K_b for water = 0.52 K kg mol^{-1}, boiling point of pure water = 373.15 K) 2

19 Name the following coordination compounds according to IUPAC system of nomenclature : 2
(i) $[Co(NH_3)_4(H_2O)Cl]Cl_2$
(ii) $[CrCl_2(en)_2]Cl$

Or

Describe the shape and magnetic behaviour of following complexes :
(i) $[Co(NH_3)_6]^{3+}$
(ii) $[Ni(CN)_4]^{2-}$ (At. No. Co = 27, Ni = 28)

20 A reaction is first order with respect to the reactant and A and second order w.r.t the reactant B in a reaction, A+ B → product. 2

(i) Write the differential rate equation

(ii) How is the rate of the reaction affected on increasing the concentration of B by 2 times?

21 Show that in case of a first order reaction, the time taken for completion of 99.9% reaction is ten times the time required for half life of the reaction. 2

Or

The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value? (log2 = 0.3010)

22 (i) Give a chemical test to distinguish between 2-Pentanol and 3-Pentanol 2

(ii) How will you bring about the conversion of methyl magnesium bromide to 2-Methylpropan-2-ol

Or

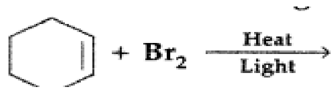
Write the equations involved in the following reactions:
(i) Reimer-Tiemann reaction
(ii) Williamson's Synthesis

23 Draw the shape of the following compounds *2*

(i) H_2SO_4 (ii) ClF_3

24 Complete the following equation *2*

(i)



(ii)

$$CH_3CH_2Cl \xrightarrow{KNO_2} ?$$

25 (i) In a compound, nitrogen atoms (N) make cubic close packed lattice and metal atoms (M) occupy one-third of the tetrahedral voids present. Determine the formula of the compound formed by M and N? *2*

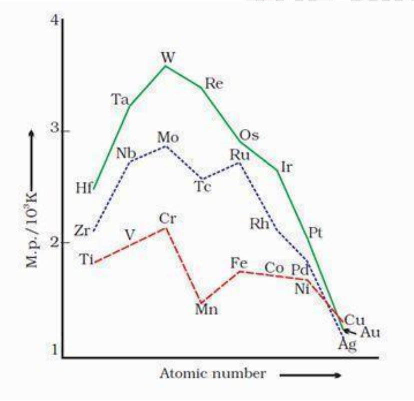
(ii) Which stoichiometric defect is seen when there is large variation in the size of cation and anion? Give an example.

SECTION C

26 Assign reasons for the following : *3*
(i) Transition metals form interstitial compounds
(ii) Transition metals generally form coloured compounds

(iii) Cr^{2+} is a strong reducing agent.

Or



(i) Why the melting point of transition elements are very high in comparison with alkali and alkaline earth metals

(ii) Why the melting point of 4d and 5d series higher than 3d elements.

(iii) Why silver, gold and copper have lower melting points though having maximum no. of d electrons

27 **(i)** Arrange the following in increasing order of their basic strength : *3*
$C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$, $(C_2H_5)_2NH$

(ii) In increasing order of boiling point:
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$
(iii) In increasing order of solubility in water:
$C_6H_5NH_2$,$(C_2H_5)_2NH$,$C_2H_5NH_2$

Or

(i) Give IUPAC name and classify as primary, secondary or tertiary amine:
$(CH_3)_3CNH_2$

(ii) Account for the following

Aniline does not undergo Friedel-Crafts reaction.

(iii) Write short note on the following:

Gabriel phthalimide synthesis

28 Silver crystallizes in face-centred cubic unit cell. Each side of the unit cell has a length of 400 pm. Calculate the radius of the silver atom. Also calculate the density of the unit cell. Take the atomic mass of Ag= 108 g/ mol, N= 6 x 10^{23} mol^{-1} *3*

29 (i) Where does the water present in the egg go after boiling the egg? *3*

(ii) What happens when D-glucose is treated with HI

(iii) Draw the □ - glucopyranose structure .

30 Explain the following observations: *3*
(i) H_2S is less acidic than H_2Te.
(ii) Fluorine is a stronger oxidising agent than chlorine

(iii) bond angle decreases from H_2O to H_2Te.

SECTION D

31 (a) Complete the following reactions: 5

(i) $Cl_2+H_2O\rightarrow$

(ii) Cu + HNO_3 (dilute) →

(iii) $SO_2 + H_2O + MnO_4^- \rightarrow$

(b)Account for the following observations:

(i) Acidity of oxo-acids of chlorine is $HOCl < HOClO < HOClO_2 < HOClO_3$.

(ii) Fluorine never acts as the central atom in polyatomic interhalogen compounds.

OR

(a) How would you account for the following:

(i) O_2 and F_2 both stabilize higher oxidation states of metals but O_2 exceeds F_2 in doing so .

(ii) The electron gain enthalpy with negative sign is less for oxygen than that for sulphur.

(b) A colourless and inert diatomic gas 'A' is prepared from thermal decomposition of an azide. This gas when treated with hydrogen at 773 K form another gas " B' which is highly basic in nature and has high solubility in water. This gas ' B' when treated with salt solution of metal 'C' forms a complex which dissolve in excess to give deep blue coloration. Identify A,B,C and write corresponding equations

32 a) An organic compound 'A' with molecular formula C_8H_8O forms an orange red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with I_2 and NaOH. It neither reduces Tollen's reagent nor Fehling's reagent nor does it decolourize bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid having molecular formula $C_7H_6O_2$. Identify the compounds 'A' and 'B' and explain the reactions involved. 5

(b)Show the mechanism of formation of acetaldehyde cyanohydrin.

Or

(a) An organic compound (A) has characteristic odour. On treatment with NaOH, it forms compounds (B) and (C). Compound (B) has molecular formula C_7H_8O which on oxidation gives back (A). The compound (C) is a sodium salt of an acid. When (C) is treated with soda-lime, it yields an aromatic compound (D). Deduce the structures of (A), (B), (C) and (D). Write the sequence of reactions involved.

(b) Write the reaction for cross aldol condensation of acetone and ethanal

33 (a) A strip of nickel metal is placed in a 1 molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed on a 1-molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter. It is observed that the conc. of nickel decreases, while that of silver ions increases. Predict which electrode acts as an anode ? Which electrode acts as a positive electrode? 5

(b) Why on dilution the Λ_m of CH_3COOH increases drastically while that of CH_3COONa increases gradually?

(c) Calculate $\Delta_rG°$ and log K. for the following reaction at 298 K

$$2Al_{(s)} + 3Cu^{2+}_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3Cu_{(s)}$$

$$(E^o_{Cell} = 2.02\ V),\ IF = 96500\ C\ mol^{-1}]$$

Or

(a) State Kohlrausch law of independent migration of ions.

(b) Why does the conductivity of a solution decrease with dilution?

(c) Calculate emf of the following cell at 25°C :

$Fe \mid Fe^{2+}\ (0.001\ M) \mid\mid H^+\ (0.01\ M) \mid H_2(g)\ (1\ bar) \mid Pt(s)$

$E^0(Fe^{2+} \mid Fe) = -0.44\ V$ $E^0(H^+ \mid H_2) = 0.00V$

Academic Session:2020-21

Pre Board II Examination
Subject : Chemistry
Class: XII

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

General Instructions:

Read the following instructions carefully.

1. There are 33 questions in this question paper. All questions are compulsory.
2. Section A: Q. No. 1 to 2 are case-based questions having four MCQs or Reason Assertion type based on given passage each carrying 1 mark.
3. Section A: Question 3 to 16 are MCQs and Reason Assertion type questions carrying 1 mark each
4. Section B: Q. No. 17 to 25 are short answer questions and carry 2 marks each.
5. Section C: Q. No. 26 to 30 are short answer questions and carry 3 marks each.
6. Section D: Q. No. 31 to 33 are long answer questions carrying 5 marks each.
7. There is no overall choice. However, internal choices have been provided.
8. Use of calculators and log tables is not permitted.
9. The paper has 9 printed sides.

1.	SECTION A (OBJECTIVE TYPE) Read the passage given below and answer the following questions:	(1x4=4)
	The properties of p-block elements are greatly influenced by atomic sizes, ionisation enthalpy, electron gain enthalpy and electronegativity. The absence of d orbital in second period and presence of d or d and f orbitals in heavier elements have significant effects on the properties of elements . As a consequence of anomalous behaviour some of them exhibit variable oxidation states, oxidising/reducing nature, formation of ∏ bonds, hydrogen bond formation etc. Their compounds also exhibit acidic/basic nature by virtue of these properties. **Following questions are multiple choice questions. Choose the most appropriate answer:** i).The correct order of acidic strength of hydrogen halides is a) HF > HCl> HBr > HI	

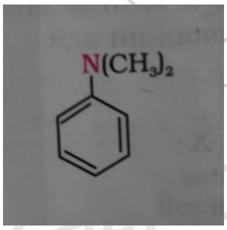
	b) $HCl > HBr > HI > HF$ c) $HF < HCl < HBr < HI$ d) $HCl < HBr < HI < HF$ ii) SO_2 , a reducing agent ,is estimated by reaction with a) $KMnO_4$ b) mohr salt c) oxalic acid d) Na_2SO_3 iii) N-N is weaker than P-P due to a) absence of d orbital in nitrogen b) inertness of N_2 c) high inter-electronic repulsion of non-bonding electrons in nitrogen d) none of the above iv) The bleaching action of Chlorine is due to a) liberation of nascent oxygen b) its oxidising property c) both are correct d) both are wrong	
2.	Read the passage given below and answer the following questions: The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. Hence , the carbonyl carbon is an electrophilic(Lewis acid) , and carbonyl oxygen, a nucleophilic (Lewis base) centre . Carbonyl compounds have substantial dipole moments and are polar than ethers. In carboxylic acid the carboxylic carbon is less electrophilic than carbonyl carbon because of possible resonance structures. **In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.** a) Assertion and reason both are correct statements and reason is correct explanation for assertion. b) Assertion and reason both are correct statements but reason is not correct explanation for assertion. c) Assertion is correct statement but reason is wrong statement. d) Assertion is wrong statement but reason is correct statement. i) Assertion : CH_3CH_2CHO readily reacts with HCN than CH_3COCH_3 Reason : Two $-CH_3$ reduce electrophilicity of carbonyl carbon in CH_3COCH_3 ii) Assertion : HCHO undergoes Cannizzaro reaction Reason : It contains alpha hydrogen iii) Assertion : C_6H_5COOH does not react with CH_3COCl in presence of anhy $AlCl_3$	(1x4=4)

	Reason : The carboxyl group gets bonded to $AlCl_3$ iv) Assertion : 2,2,6-Trimethylcyclohexanone doesn't form cyanohydrin Reason : Ketones do not form cyanohydrin **Following questions (No. 3 -11) are multiple choice questions carrying 1 mark each:**	
	3. A unit cell contains atoms at all corners as well as at the centre . It's packing efficiency is a) 74% b) 68% c) 52.4% d) 72.8%	
	4. Azeotropic mixtures a) are ideal solutions b) have high boiling point c) boil at constant temperature d) all of the above **OR** Henry's law is not applicable in following a) increasing solubility of CO_2 in soft drinks b) in dealing of problem of bends c) in increasing solubility of O_2 in hot water d) all of the above	
	5. Limiting molar conductivity of Al^{3+} and SO_4^{2-} are 125.2 and 160.0 S cm^2 /mol respectively. The limiting molar conductivity of Aluminium sulphate is : a) 285.2 S cm^2 /mol b) 695.6 S cm^2 /mol c) 34.8 S cm^2 /mol d) 730.4 S cm^2 /mol **OR** Electrode potential of any electrode depends on a) nature of metal b) temperature of solution c) molarity of solution d) all of these	
	6. Fog is a colloidal solution of a) solid in gas b) gas in gas c) liquid in gas d) gas in liquid **OR** Stability of lyophilic colloids is due to a) same charge on all the colloidal particles b) solvation of the colloidal particles	

	c) both a) and b) d) none of the above	
	7. The element in the first transition series which has maximum melting point is a) Cr b) Sc c) Mn d) Ni **OR** Which of the following does not exhibit paramagnetic behaviour a) $ZnCl_2$ b) $FeCl_3$ c) both a) and b) d) none of the above	
	8. $[NiCl_4]^{2-}$, according to VBT has a) dsp^2 hybridisation b) square planar structure c) paramagnetic behaviour d) none of the above	
	9. Out of 1-Chlorobutane and 1-Iodobutane , compound which undergo S_N2 reaction faster is a) 1-Chlorobutane as Cl is more electronegative b) 1-Chlorobutane as C-Cl bond is more polar c) 1-Iodobutane as I is better leaving group d) 1-Iodobutane as I is more electronegative **OR** C_2H_5Cl is converted into butane using the reagent a) aq NaOH b) $LiAlH_4$ c) Na in dry ether d) H_2O	
	10. Aldehydes having α-H atom undergo a) Aldol condensation b) electrophilic substitution c) Cannizzaro reaction d) Haloform reaction	
	11. Reagents used to convert ethanamine into ethanol are a) CH_3Cl and aq. NaOH b) $CHCl_3$ and aq. NaOH c) $NaNO_2$ + HCl and H_2O d) Br_2 + NaOH	

	In the following questions (Q. No. 12 - 16) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. a) Assertion and reason both are correct statements and reason is correct explanation for assertion. b) Assertion and reason both are correct statements but reason is not correct explanation for assertion. c) Assertion is correct statement but reason is wrong statement. d) Assertion is wrong statement but reason is correct statement	
	12. Assertion: The two strands in DNA are complementary to each other . Reason : The hydrogen bonds are formed between specific pairs of bases. 13. Assertion : The vapour pressure of a solution at a given temperature is higher than the vapour pressure of pure solvent. Reason : Due to the presence of solute molecules at the surface, escaping capacity of solvent decreases. 14. Assertion: Transition elements form coordination compounds. Reason: It is due to presence of unpaired electrons 15. Assertion: Sucrose is non-reducing sugar. Reason : It's aldehydic/ketonic groups are bonded 16. Assertion: Solubility of a gas increases with increase in pressure Reason : Raoult's law gives relation between pressure and solubility of a gas in solution	
	SECTION B	
	The following questions, Q. No 17 – 25 are short answer type and carry 2 marks each.	
17.	A solution of glucose (Molar mass=180 g mol^{-1}) in water has a boiling point of 100.20°C. Calculate the freezing point of same solution. Molal constants for water K_f and K_b are 1.86 K Kg mol^{-1} and 0.512 K Kg mol^{-1} respectively.	
18.	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 6.25= 0.7959) **OR** A first order reaction takes 30 minutes for 50% completion . Calculate the time required for 90% completion of this reaction . (log 2= 0.3010)	
19.	i) Draw the structure of XeF_6. ii) Write balanced chemical equation for thermal decomposition of ammonium dichromate.	
20.	i) On the basis of CFT, what is the electron distribution for d^6 if $\Delta_o < p$? ii) What is meant by ambidentate ligand?	

	OR i) Write name and formula of a ligand having denticity 6. ii) Calculate instability/dissociation constant for [$PtCl_4$], given that stability constant (β_4) for this complex as $5x10^4$.	
21.	Write mechanism for following reaction along with stereospecific aspect $(CH_3)_3Cl + OH^-$ (aq) $(CH_3)_3OH + Cl^-$ **OR** $CH_3CH_2Br + KCN$ $CH_3CH_2CN + KBr$	
22.	A hydrocarbon having formula C_3H_6 reacts with B_2H_6,H_2O_2 and NaOH and gives compound (A). [A] on oxidation with PCC is converted into compound [B] .[B] gives positive Tollen's test. Identify [A] and [B] and write the sequence of reactions.	
23.	i) Aniline is less basic than aliphatic amines. Why? ii) $C_6H_5NO_2$ $^{Sn/HCl}$ A $^{CHCl_3+KOH}$ B. Identify A and B. **OR** i) Write chemical reaction for distinction between primary and secondary amines. ii) Write the zwitter ionic form of sulphanilic acid.	
24.	i) Hydrolysis of esters is pseudo first order reaction . Comment. ii) Rate law for a given reaction is $R = k[A]^2[B]^3$. How is the reaction rate affected when the concentration of B is increased three times.	
25.	i) Why aryl halides do not undergo nucleophilic substitution reaction? ii) Write reaction for preparation of Fluoroethane from Chloroethane.	
	SECTION C	
	Q. No 26 -30 are Short Answer Type II carrying 3 mark each	
26.	i) Describe the type of point defects which are found in non-ionic solids. Which one of them increases density of the substance? ii) Refractive index of a solid gives different values along different directions. Mention the type of solid and the property shown by it. **OR** i) Chemical analysis shows the formula of Iron Oxide is $Fe_{0.96}O$. Why does this anomaly arises? What type of defect is this? ii) Name the type of solids which have coulombic forces of attraction between constituent particles and comment on their electrical conductivity.	

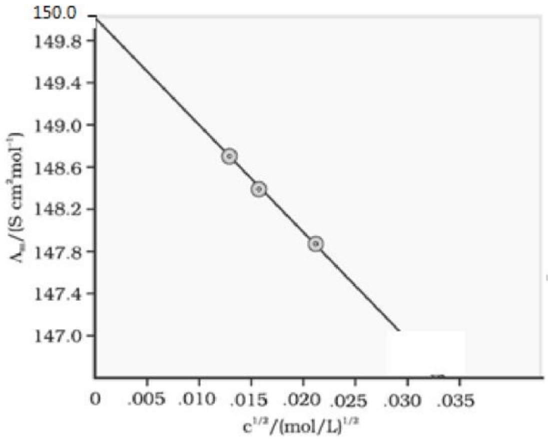
27.	Explain the followings i) delta formation ii) Freundlich adsorption isotherm iii) Two characteristics of lyophilic sols **OR** i) During hydrogenation, H_2 is adsorbed over Ni with liberation of 350 KJ mol^{-1} energy. State the type of adsorption and the nature of layer formed. ii) Explain the cause of formation of cone of light between overhead projector and screen. iii) Alum is applied on fresh wounds. Why?	
28.	i) Why Zr and Hf have same size? ii) Calculate magnetic moment of $[Fe(NH_3)_6]^{2+}$ iii) Transition elements exhibit variable oxidation states . Why?	
29.	i) Write the IUPAC name of the given compound  ii) How will you convert Cl-$(CH_2)_4$-Cl into hexan-1,6-diamine ? iii) $CH_3CH_2NH_2 \xrightarrow{1. NaNO_2+HCl\ ,\ 2. H_2O}$ A $\xrightarrow{KI\ ,\ heat}$ B . Identify A and B.	
30.	i) How will you show that glucose has five -OH groups and a -CHO group? Give reactions for the same. ii) Name one optically inactive amino acid and one essential amino acid	
	SECTION D Q .No 31 to 33 are long answer type carrying 5 marks each.	
31.	i) State Kohlrausch law. ii) Calculate the emf of the following cell at 298 K: Al(s)|Al^{3+} (0.15M)||Cu^{2+}(0.025M) |Cu(s) (Given $E^o(Al^{3+}/Al)$ = -1.66 V, $E^0(Cu^{2+}/Cu)$ = 0.34V, log 0.15 = -0.8239, log 0.025 = -1.6020) . Also calculate the value of standard Gibb's energy for the cell. **OR** (i) On the basis of Eo values identify which amongst the following is the strongest oxidising agent	

$Cl_2(g) + 2e^- \rightarrow 2Cl^-$ $E^o = +1.36$ V,

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^o = +1.51$ V

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $E^o = +1.33$ V

(ii) The following figure , represents variation of (Λ_m) vs $\sqrt{c}$ for an electrolyte. Here Λ_m is the molar conductivity and c is the concentration of the electrolyte.



a) Define molar conductivity

b) Identify the nature of electrolyte on the basis of the above plot. Justify your answer.

c) Determine the value of Λ_m^o for the electrolyte.

d) Show how to calculate the value of A for the electrolyte using the above graph.

32. i) Complete the following reactions

a) $Cu + H_2SO_4$

b) $NH_3 + Cl_2$(excess)

c) $ClF + H_2O$

ii) O_3 is thermodynamically unstable. Explain?

iii) What is meant by transition temperature of sulphur?

OR

i) Complete the following reactions

a) $PbS + O_3$

b) $C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4}$

c) $XeF_2 + H_2O$

ii) Why are interhalogen compounds more reactive than halogens?

iii) Draw the structure of Peroxodisulphuric acid .

33. i) Chlorobenzene and sodium ethoxide cannot be used to prepare anisole in accordance with Williamson synthesis . Why?

ii) Convert butanol into 2-chlorobutanoic acid.

	iii) Distinguish between phenol and benzoic acid. iv) Carry out oxidation of phenol. v) Write equation for Friedel-crafts acetylation of anisole. **OR** i) Compare acidic strength of phenol and carboxylic acid . ii) Convert phenol into aspirin . iii) How will you obtain 2-methylpropan-2-ol from CH_3MgBr using a suitable carbonyl compound? iv) Distinguish between propan-1-ol and propan-2-ol. v) Alcohols are used to form hemiacetals. Support your answer with the help of reactions.	

CBSE BOARD EXAM: 2020

General Instructions :

Read the following instructions very carefully and strictly follow them :

(i) *This question paper comprises* **four** *Sections –* **A**, **B**, **C** *and* **D**. *There are* **37** *questions in the question paper.* **All** *questions are compulsory.*

(ii) **Section A** – *Questions no.* **1** *to* **20** *are very short answer type questions, carrying* **1** *mark each. Answer these questions in one word or one sentence.*

(iii) **Section B** – *Questions no.* **21** *to* **27** *are short answer type questions, carrying* **2** *marks each.*

(iv) **Section C** – *Questions no.* **28** *to* **34** *are long answer type-I questions, carrying* **3** *marks each.*

(v) **Section D** – *Questions no.* **35** *to* **37** *are long answer type-II questions, carrying* **5** *marks each.*

(vi) *There is no overall choice in the question paper. However, an internal choice has been provided in 2 questions of two marks, 2 questions of three marks and all the 3 questions of five marks. You have to attempt only one of the choices in such questions.*

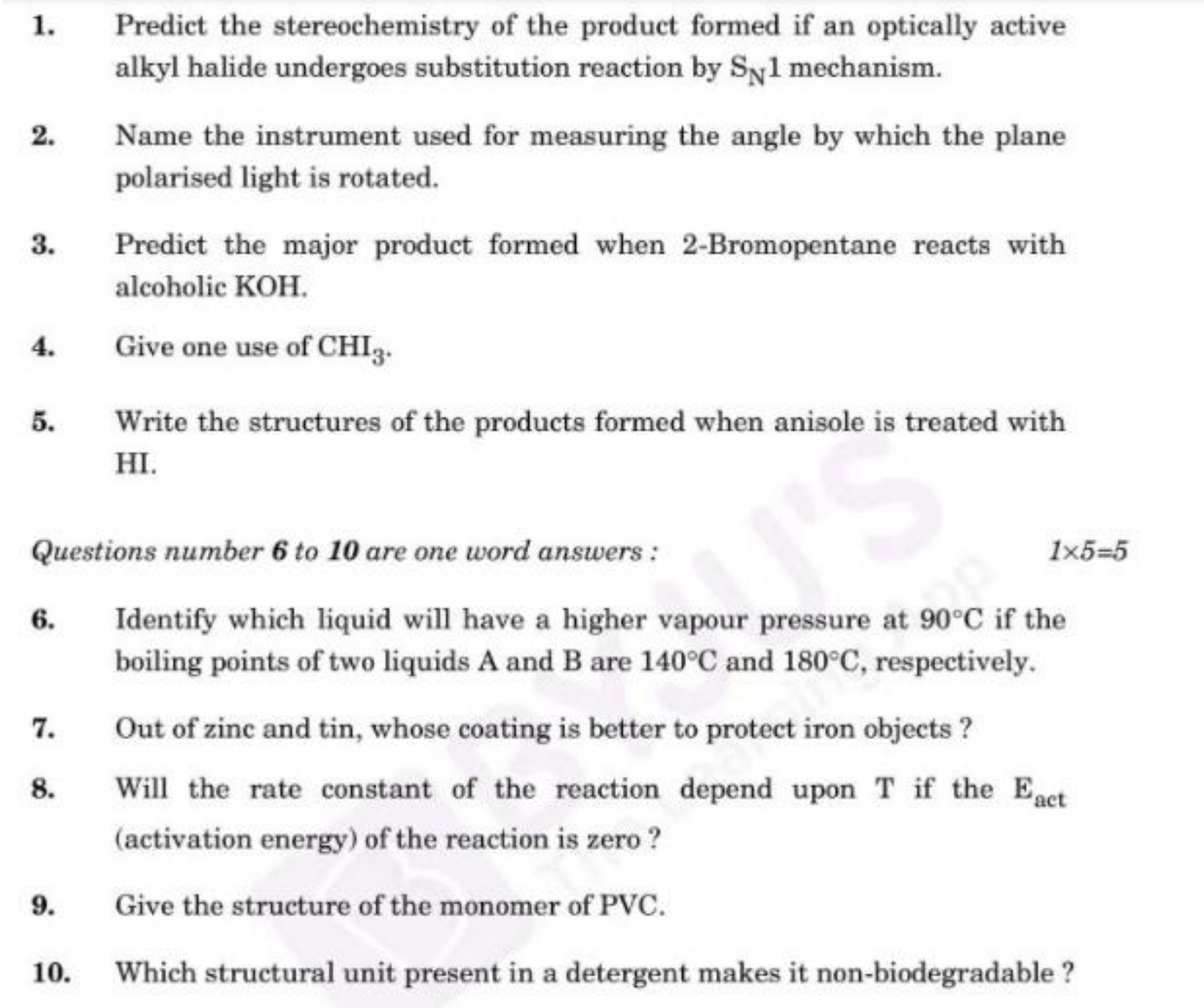
(vii) *In addition to this, separate instructions are given with each section and question, wherever necessary.*

(viii) *Use of calculators and log tables is* **not** *permitted.*

SECTION A

Read the given passage and answer the questions number **1** *to* **5** *that follow : 1×5=5*

The substitution reaction of alkyl halide mainly occurs by S_N1 or S_N2 mechanism. Whatever mechanism alkyl halides follow for the substitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of S_N1 reactions are governed by the stability of carbocation whereas for S_N2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.



1. Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by S_N1 mechanism.

2. Name the instrument used for measuring the angle by which the plane polarised light is rotated.

3. Predict the major product formed when 2-Bromopentane reacts with alcoholic KOH.

4. Give one use of CHI_3.

5. Write the structures of the products formed when anisole is treated with HI.

*Questions number **6** to **10** are one word answers :* *$1\times5=5$*

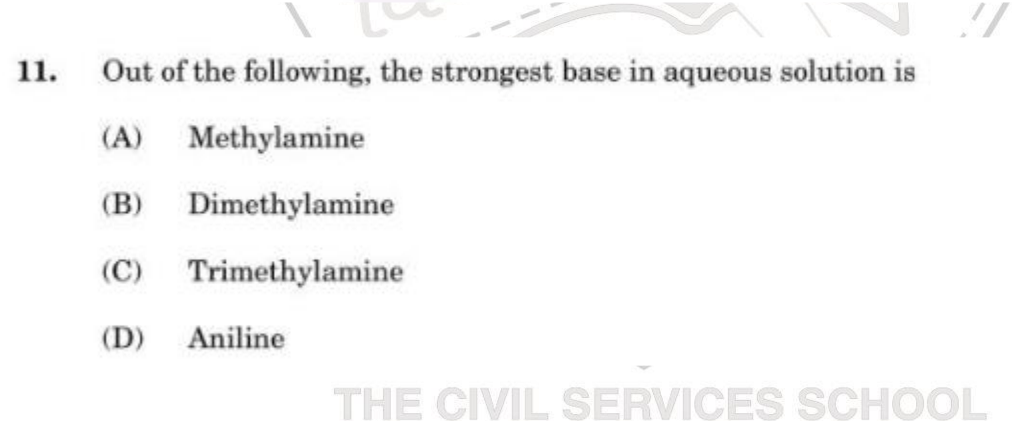
6. Identify which liquid will have a higher vapour pressure at 90°C if the boiling points of two liquids A and B are 140°C and 180°C, respectively.

7. Out of zinc and tin, whose coating is better to protect iron objects ?

8. Will the rate constant of the reaction depend upon T if the E_{act} (activation energy) of the reaction is zero ?

9. Give the structure of the monomer of PVC.

10. Which structural unit present in a detergent makes it non-biodegradable ?



11. Out of the following, the strongest base in aqueous solution is

(A) Methylamine

(B) Dimethylamine

(C) Trimethylamine

(D) Aniline

12. Iodoform test is ***not*** given by

(A) Ethanol

(B) Ethanal

(C) Pentan-2-one

(D) Pentan-3-one

13. Out of the following transition elements, the maximum number of oxidation states are shown by

(A) Sc (Z = 21)

(B) Cr (Z = 24)

(C) Mn (Z = 25)

(D) Fe (Z = 26)

14. Hardening of leather in tanning industry is based on

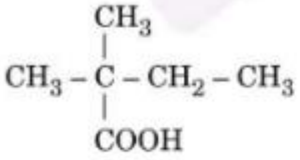
(A) Electrophoresis

(B) Electro-osmosis

(C) Mutual coagulation

(D) Tyndall effect

15. What is the correct IUPAC name of the given compound ?



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{C}}-CH_2-CH_3$$

(A) 2,2-Dimethylbutanoic acid

(B) 2-Carboxyl-2-methylbutane

(C) 2-Ethyl-2-methylpropanoic acid

(D) 3-Methylbutane carboxylic acid

For questions number 16 to 20, two statements are given – one labelled Assertion (A) and the other labelled Reason (R). Select the correct answer to these questions from the codes (i), (ii), (iii) and (iv) as given below : *1×5=5*

(i) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(ii) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is ***not*** the correct explanation of the Assertion (A).

(iii) Assertion (A) is correct, but Reason (R) is incorrect statement.

(iv) Assertion (A) is incorrect, but Reason (R) is correct statement.

16. *Assertion (A) :* Au and Ag are extracted by leaching their ores with a dil. solution of NaCN.

Reason (R) : Impurities associated with these ores dissolve in NaCN.

17. *Assertion (A) :* F – F bond in F_2 molecule is weak.

Reason (R) : F atom is small in size.

18. *Assertion (A) :* Linkage isomerism arises in coordination compounds because of ambidentate ligand.

Reason (R) : Ambidentate ligand like NO_2 has two different donor atoms i.e., N and O.

19. *Assertion (A) :* Sucrose is a non-reducing sugar.

Reason (R) : Sucrose has glycosidic linkage.

20. *Assertion (A) :* The molecularity of the reaction $H_2 + Br_2 \rightarrow 2HBr$ appears to be 2.

Reason (R) : Two molecules of the reactants are involved in the given elementary reaction.

SECTION B

21. Define the following terms : *1×2=2*

(a) Tranquilizers

(b) Antiseptic

OR

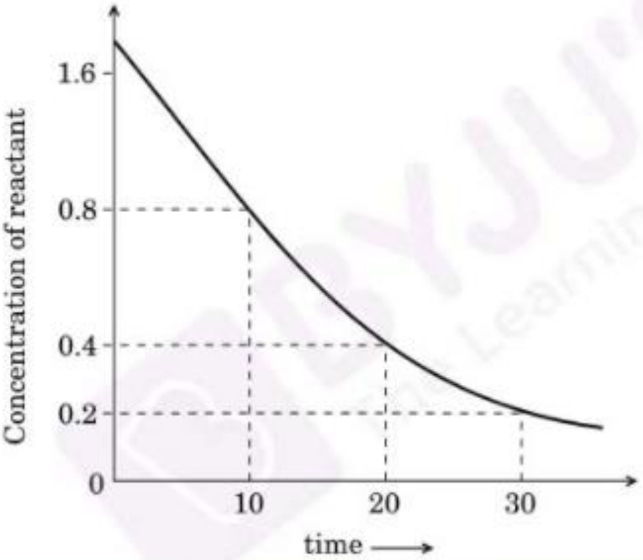
Explain the cleansing action of soaps. *2*

22. For a 5% solution of urea (Molar mass = 60 g/mol), calculate the osmotic pressure at 300 K. [$R = 0{\cdot}0821\ L\ atm\ K^{-1}\ mol^{-1}$] *2*

OR

Visha took two aqueous solutions — one containing 7·5 g of urea (Molar mass = 60 g/mol) and the other containing 42·75 g of substance Z in 100 g of water, respectively. It was observed that both the solutions froze at the same temperature. Calculate the molar mass of Z. *2*

23. Analyse the given graph, drawn between concentration of reactant vs. time. *1×2=2*



(a) Predict the order of reaction.

(b) Theoretically, can the concentration of the reactant reduce to zero after infinite time ? Explain.

24. Draw the shape of the following molecules : *1×2=2*

(a) $XeOF_4$

(b) BrF_3

25. Give the formulae of the following compounds : *1×2=2*

(a) Potassium tetrahydroxidozincate (II)

(b) Hexaammineplatinum (IV) chloride

26. What happens when

(a) Propanone is treated with methylmagnesium iodide and then hydrolysed, and

(b) Benzene is treated with CH_3COCl in presence of anhydrous $AlCl_3$? *1×2=2*

27. Write the names and structures of monomers in the following polymers : *1×2=2*

(a) Bakelite

(b) Neoprene

SECTION C

28. Give the structures of A and B in the following sequence of reactions : $\frac{1}{2}\times 6=3$

(a) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B$

(b) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[0^\circ - 5^\circ C]{NaNO_2 + HCl} B$

(c) $C_6H_5\overset{+}{N_2}Cl^- \xrightarrow[\Delta]{CuCN} A \xrightarrow{H_2O/H^+} B$

OR

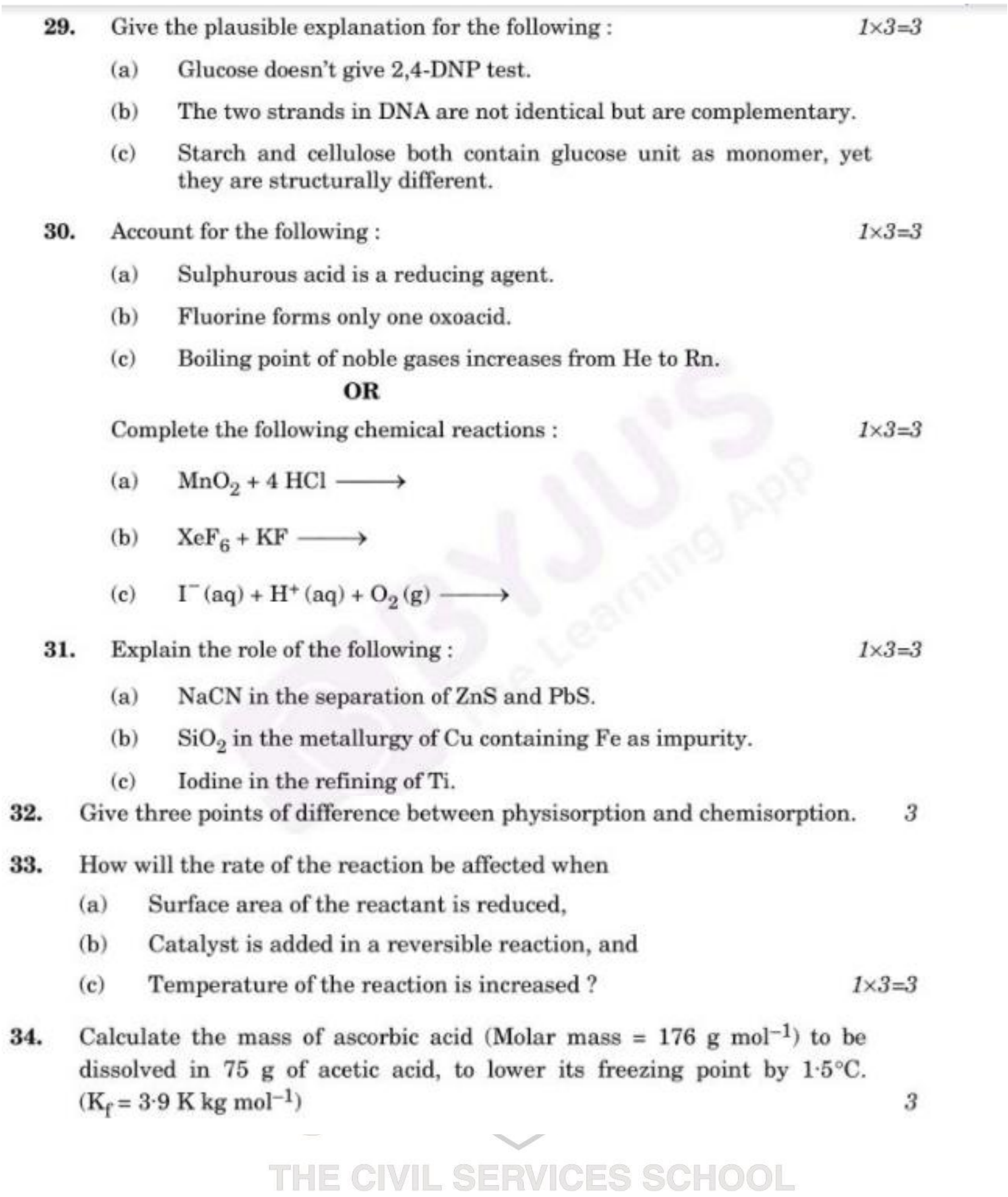
(a) How will you distinguish between the following pairs of compounds : *1×2=2*

(i) Aniline and Ethanamine

(ii) Aniline and N-methylaniline

(b) Arrange the following compounds in decreasing order of their boiling points : *1*

Butanol, Butanamine, Butane



29. Give the plausible explanation for the following : *1×3=3*

(a) Glucose doesn't give 2,4-DNP test.

(b) The two strands in DNA are not identical but are complementary.

(c) Starch and cellulose both contain glucose unit as monomer, yet they are structurally different.

30. Account for the following : *1×3=3*

(a) Sulphurous acid is a reducing agent.

(b) Fluorine forms only one oxoacid.

(c) Boiling point of noble gases increases from He to Rn.

OR

Complete the following chemical reactions : *1×3=3*

(a) $MnO_2 + 4\,HCl \longrightarrow$

(b) $XeF_6 + KF \longrightarrow$

(c) $I^-(aq) + H^+(aq) + O_2(g) \longrightarrow$

31. Explain the role of the following : *1×3=3*

(a) NaCN in the separation of ZnS and PbS.

(b) SiO_2 in the metallurgy of Cu containing Fe as impurity.

(c) Iodine in the refining of Ti.

32. Give three points of difference between physisorption and chemisorption. *3*

33. How will the rate of the reaction be affected when

(a) Surface area of the reactant is reduced,

(b) Catalyst is added in a reversible reaction, and

(c) Temperature of the reaction is increased ? *1×3=3*

34. Calculate the mass of ascorbic acid (Molar mass = 176 g mol^{-1}) to be dissolved in 75 g of acetic acid, to lower its freezing point by 1·5°C. (K_f = 3·9 K kg mol^{-1}) *3*

SECTION D

35. (a) Calculate ΔG° for the reaction

$$Zn\,(s) + Cu^{2+}\,(aq) \longrightarrow Zn^{2+}\,(aq) + Cu\,(s).$$ *3*

Given : E° for $Zn^{2+}/Zn = -\,0{\cdot}76$ V and

E° for $Cu^{2+}/Cu = +\,0{\cdot}34$ V

$R = 8{\cdot}314\ JK^{-1}\ mol^{-1}$

$F = 96500\ C\ mol^{-1}$.

(b) Give two advantages of fuel cells. *2*

OR

(a) Out of the following pairs, predict with reason which pair will allow greater conduction of electricity : *1×3=3*

(i) Silver wire at 30°C or silver wire at 60°C.

(ii) 0·1 M CH_3COOH solution or 1 M CH_3COOH solution.

(iii) KCl solution at 20°C or KCl solution at 50°C.

(b) Give two points of differences between electrochemical and electrolytic cells. *2*

36. (a) Account for the following : *1×3=3*

(i) Copper (I) compounds are white whereas Copper (II) compounds are coloured.

(ii) Chromates change their colour when kept in an acidic solution.

(iii) Zn, Cd, Hg are considered as d-block elements but not as transition elements.

(b) Calculate the spin-only moment of Co^{2+} (Z = 27) by writing the electronic configuration of Co and Co^{2+}. *2*

OR

(a) Give three points of difference between lanthanoids and actinoids. *3*

(b) Give reason and select one atom/ion which will exhibit asked property : *1×2=2*

(i) Sc^{3+} or Cr^{3+} (Exhibit diamagnetic behaviour)

(ii) Cr or Cu (High melting and boiling point)

37. (a) Out of t-butyl alcohol and n-butanol, which one will undergo acid catalyzed dehydration faster and why ? *2*

(b) Carry out the following conversions : *1×3=3*

(i) Phenol to Salicylaldehyde

(ii) t-butylchloride to t-butyl ethyl ether

(iii) Propene to Propanol

OR

(a) Give the mechanism for the formation of ethanol from ethene. *2*

(b) Predict the reagent for carrying out the following conversions : *1×3=3*

(i) Phenol to benzoquinone

(ii) Anisole to p-bromoanisole

(iii) Phenol to 2,4,6-tribromophenol

CBSE SAMPLE PAPER : 2021

SAMPLE PAPER 1
CHEMISTRY THEORY (043)

MM:70 **Time: 3 Hours**

General Instructions:

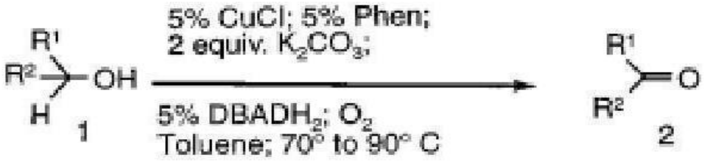
Read the following instructions carefully.

a) There are 33 questions in this question paper. All questions are compulsory.
b) Section A: Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
c) Section B: Q. No. 17 to 25 are short answer questions and carry 2 marks each.
d) Section C: Q. No. 26 to 30 are short answer questions and carry 3 marks each.
e) Section D: Q. No. 31 to 33 are long answer questions carrying 5 marks each.
f) There is no overall choice. However, internal choices have been provided.
g) Use of calculators and log tables is not permitted.

SECTION A (OBJECTIVE TYPE)

1. Read the passage given below and answer the following questions: (1x4=4)

An efficient, aerobic catalytic system for the transformation of alcohols into carbonyl compounds under mild conditions, copper-based catalyst has been discovered. This copper-based catalytic system utilizes oxygen or air as the ultimate, stoichiometric oxidant, producing water as the only by-product



A wide range of primary, secondary, allylic, and benzylic alcohols can be smoothly oxidized to the corresponding aldehydes or ketones in good to excellent yields. Air can be conveniently used instead of oxygen without affecting the efficiency of the process. However, the use of air requires slightly longer reaction times.

This process is not only economically viable and applicable to large-scale reactions, but it is also environmentally friendly.

(Reference: Ohkuma, T., Ooka, H., Ikariya, T., & Noyori, R. (1995). Preferential hydrogenation of aldehydes and ketones. Journal of the American Chemical Society, 117(41), 10417-10418.)

The following questions are multiple choice questions. Choose the most appropriate answer:

(i)The Copper based catalyst mention in the study above can be used to convert:

a) propanol to propanonic acid
b) propanone to propanoic acid
c) propanone to propan-2-ol
d) propan-2-ol to propanone

(ii)The carbonyl compound formed when ethanol gets oxidised using this copper-based catalyst can also be obtained by ozonolysis of:

a) But-1-ene
b) But-2-ene
c) Ethene
d) Pent-1-ene

OR

Which of the following is a secondary allylic alcohol?

a) But-3-en-2-ol
b) But-2-en-2-ol
c) Prop-2-enol
d) Butan-2-ol

(iii) Benzyl alcohol on treatment with this copper-based catalyst gives a compound 'A' which on reaction with KOH gives compounds 'B' and 'C'. Compound 'B' on oxidation with $KMnO_4$- KOH gives compound 'C'. Compounds 'A', 'B' and 'C' respectively are :

a) Benzaldehyde, Benzyl alcohol, potassium salt of Benzoic acid
b) Benzaldehyde, potassium salt of Benzoic acid, Benzyl alcohol
c) Benzaldehyde, Benzoic acid, Benzyl alcohol
d) Benzoic acid, Benzyl alcohol, Benzaldehyde

(iv) An organic compound 'X' with molecular formula C_3H_8O on reaction with this copper based catalyst gives compound 'Y' which reduces Tollen's reagent. 'X' on reaction with sodium metal gives 'Z' . What is the product of reaction of 'Z' with 2-chloro-2-methylpropane?

a) $CH_3CH_2CH_2OC(CH_3)_3$
b) $CH_3CH_2OC(CH_3)_3$
c) $CH_2=C(CH_3)_2$
d) $CH_3CH_2CH=C(CH_3)_2$

Read the passage given below and answer the following questions: (1x4=4)

The amount of moisture that leather adsorbs or loses is determined by temperature, relative humidity, degree of porosity, and the size of the pores. Moisture has great practical significance because its amount affects the durability of leather, and in articles such as shoes, gloves and other garments, the comfort of the wearer. High moisture content accelerates deterioration and promotes mildew action. On the other hand, a minimum amount of moisture is required to keep leather properly lubricated and thus prevent cracking.

The study indicates that adsorption of moisture by leather is a multi-molecular process and is accompanied by low enthalpies of adsorption. Further at 75-percent relative humidity, the adsorption is a function of surface area alone.

Hide is tanned to harden leather. This process of tanning occurs due to mutual coagulation of positively charged hide with negatively charged tanning material. Untanned hide and chrome-tanned leathers have the largest surface areas. The leathers tanned with vegetable tanning materials have smaller surface areas since they are composed of less hide substance and the capillaries are reduced to smaller diameters, in some cases probably completely filled by tanning materials. The result of the study indicated that untanned hide and chrome-tanned leather adsorb the most water vapour.

(Source:Kanagy, J. R. (1947). Adsorption of water vapor by untanned hide and various leathers at 100 F. *Journal of Research of the National Bureau of Standards*, *38*(1), 119-128.)

2. In these questions (Q. No 5-8 , a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

(i) Assertion: Vegetable tanned leather cannot adsorb a large amount of moisture.
Reason: Porous materials have higher surface area.

(ii) Assertion: Animal hide soaked in tannin results in hardening of leather.
Reason: Tanning occurs due to mutual coagulation.

(iii) Assertion: Adsorption of moisture by leather is physisorption.

Reason: It is a multimolecular process and is accompanied by low enthalpies of adsorption

(iv) Assertion: Leathers tanned with vegetable tanning materials have smaller surface areas

Reason: The capillaries present in leather are reduced to smaller diameters

OR

Assertion: Leather absorbs different amount of moisture.

Reason: Some moisture is necessary to prevent cracking of leather.

Following questions (No. 3 -11) are multiple choice questions carrying 1 mark each:

3 Which of the following option will be the limiting molar conductivity of CH_3COOH if the limiting molar conductivity of CH_3COONa is 91 Scm^2mol^{-1}? Limiting molar conductivity for individual ions are given in the following table.

S.No	**Ions**	**limiting molar conductivity / Scm^2mol^{-1}**
1	H+	349.6
2	Na+	50.1
3	K+	73.5
4	OH^-	199.1

a) 350 Scm^2mol^{-1}

b) 375.3 Scm^2mol^{-1}

c) 390.5 Scm^2mol^{-1}

d) 340.4 Scm^2mol^{-1}

4. Curdling of milk is an example of:

a) breaking of peptide linkage

b) hydrolysis of lactose

c) breaking of protein into amino acids

d) denauration of proetin

OR

Dissachrides that are reducing in nature are:

a) sucrose and lactose

b) sucrose and maltose

c) lactose and maltose

d) sucrose, lactose and maltose

5.When 1 mole of benzene is mixed with 1 mole of toluene The vapour will contain: (Given : vapour of benzene = 12.8kPa and vapour pressure of toluene = 3.85 kPa).

a) equal amount of benzene and toluene as it forms an ideal solution

b) unequal amount of benzene and toluene as it forms a non ideal solution

c) higher percentage of benzene

d) higher percentage of toluene

6.Which of the following is the reason for Zinc not exhibiting variable oxidation state

a) inert pair effect

b) completely filled 3d subshell

c) completely filled 4s subshell

d) common ion effect

OR

Which of the following is a diamagnetic ion: (Atomic numbers of Sc, V, Mn and Cu are 21, 23, 25 and 29 respectively)

a) V^{2+}
b) Sc^{3+}
c) Cu^{2+}
d) Mn^{3+}

7. Propanamide on reaction with bromine in aqueous NaOH gives:
a) Propanamine
b) Ethanamine
c) N-Methyl ethanamine
d) Propanenitrile

OR

IUPAC name of product formed by reaction of methyl amine with two moles of ethyl chloride
a) N,N-Dimethylethanamine
b) N,N-Diethylmethanamine
c) N-Methyl ethanamine
d) N-Ethyl - N-methylethanamine

8. Ambidentate ligands like NO_2^- and SCN^- are :
a) unidentate
b) didentate
c) polydentate
d) has variable denticity

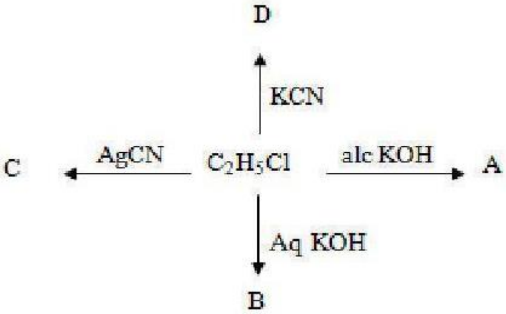
OR

The formula of the coordination compound Tetraammineaquachloridocobalt(III) chloride is
a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$
b) $[Co(NH_3)_4(H_2O)Cl]Cl_3$
c) $[Co(NH_3)_2(H_2O)Cl]Cl_2$
d) $[Co(NH_3)_4(H_2O)Cl]Cl$

9. Which set of ions exhibit specific colours? (Atomic number of Sc = 21, Ti = 22, V=23, Mn = 25, Fe = 26, Ni = 28 Cu = 29 and Zn =30)

a) Sc^{3+}, Ti^{4+}, Mn^{3+}
b) Sc^{3+}, Zn^{2+}, Ni^{2+}
c) V^{3+}, V^{2+}, Fe^{3+}
d) Ti^{3+}, Ti^{4+}, Ni^{2+}

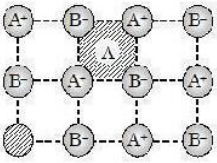
10. Identify A,B,C and D:



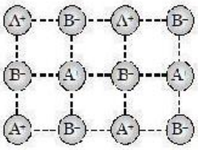
a) A = C_2H_4, B= C_2H_5OH, C= C_2H_5NC, D= C_2H_5CN
b) A= C_2H_5OH, B= C_2H_4, C = C_2H_5CN, D=C_2H_5NC
c) A = C_2H_4, B= C_2H_5OH, C= C_2H_5CN, D= C_2H_5NC
d) A= C_2H_5OH, B= C_2H_4, C= C_2H_5NC, D= C_2H_5CN

11.The crystal showing Frenkel defect is :

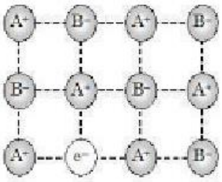
a)



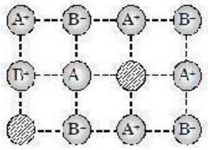
b)



c)



d)



In the following questions (Q. No. 12 - 16) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

12.Assertion: The two strands of DNA are complementary to each other
Reason: The hydrogen bonds are formed between specific pairs of bases.

13.Assertion: Ozone is thermodynamically stable with respect to oxygen.
Reason:Decomposition of ozone into oxygen results in the liberation of heat

14.Assertion: Aquatic species are more comfortable in cold waters rather than in warm waters.
Reason:Different gases have different K_H values at the same temperature

OR

Assertion: Nitric acid and water form maximum boiling azeotrope.

Reason: Azeotropes are binary mixtures having the same composition in liquid and vapour phase.

15. Assertion: Carboxylic acids are more acidic than phenols.
Reason: Phenols are ortho and para directing.

16.Assertion: Methoxy ethane reacts with HI to give ethanol and iodomethane
Reason: Reaction of ether with HI follows S_N^2 mechanism

SECTION B

The following questions, Q.No 17 – 25 are short answer type and carry 2 marks each.

17. With the help of resonating structures explain the effect of presence of nitro group at ortho position in chlorobenzene.

OR

Carry out the following conversions in not more than 2 steps:

(i)Aniline to chlorobenzene
(ii)2-bromopropane to 1- bromopropane

18. A glucose solution which boils at 101.04°C at 1 atm. What will be relative lowering of vapour pressure of an aqueous solution of urea which is equimolal to given glucose solution? (Given: K_b for water is 0.52 K kg mol^{-1})

19. (i) Using crystal field theory, write the electronic configuration of iron ion in the following complex ion. Also predict its magnetic behaviour :

$[Fe(H_2O)_6]^{2+}$

(ii)Write the IUPAC name of the coordination complex: $[CoCl_2(en)_2]NO_3$

OR

(i)Predict the geometry of $[Ni(CN)_4]^{2-}$
(ii)Calculate the spin only magnetic moment of $[Cu(NH_3)_4]^{2+}$ ion.

20. For a reaction the rate law expression is represented as follows:

$$\text{Rate} = k\,[A][B]^{1/2}$$

i. Interpret whether the reaction is elementary or complex. Give reason to support your answer.

ii. Write the units of rate constant for this reaction if concentration of A and B is expressed in moles/L.

OR

The following results have been obtained during the kinetic studies of the reaction:

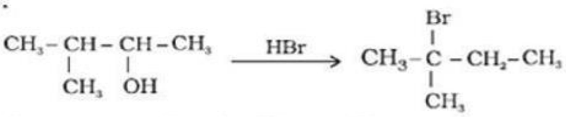
$P + 2Q \rightarrow R + 2S$

Exp.	**Initial P(mol/L)**	**Initial Q (mol/L)**	**Init. Rate of Formation of R (M min^{-1})**
1	0.10	0.10	3.0×10^{-4}
2	0.30	0.30	9.0×10^{-4}
3	0.10	0.30	3.0×10^{-4}
4	0.20	0.40	6.0×10^{-4}

Determine the rate law expression for the reaction.

21. The C-14 content of an ancient piece of wood was found to have three tenths of that in living trees. How old is that piece of wood? (log 3= 0.4771, log 7 = 0.8540 , Half-life of C-14 = 5730 years)

22. When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:



$$CH_3-\underset{CH_3}{CH}-\underset{OH}{CH}-CH_3 \xrightarrow{HBr} CH_3-\overset{Br}{\underset{CH_3}{C}}-CH_2-CH_3$$

Give a mechanism for this reaction.

23. Give the formula and describe the structure of a noble gas species which is isostructural with IF_6^-.

24. The following haloalkanes are hydrolysed in presence of aq KOH.

(i) 2- Chlorobutane (ii) 2-chloro-2-methylpropane

Which of the above is most likely to give a racemic mixture? Justify your answer.

25. Atoms of element P form *ccp* lattice and those of the element Q occupy 1/3rd of tetrahedral voids and all octahedral voids. What is the formula of the compound formed by the elements P and Q?

SECTION C

Q.No 26 -30 are Short Answer Type II carrying 3 mark each.

26. Give reasons for the following:

i. Transition elements act as catalysts

ii. It is difficult to obtain oxidation state greater than two for Copper.

iii. $Cr_2O_7^{2-}$ is a strong oxidising agent in acidic medium whereas WO_3 and MoO_3 are not.

OR

Observed and calculated values for the standard electrode potentials of elements from Ti to Zn in the first reactivity series are depicted in figure (1):

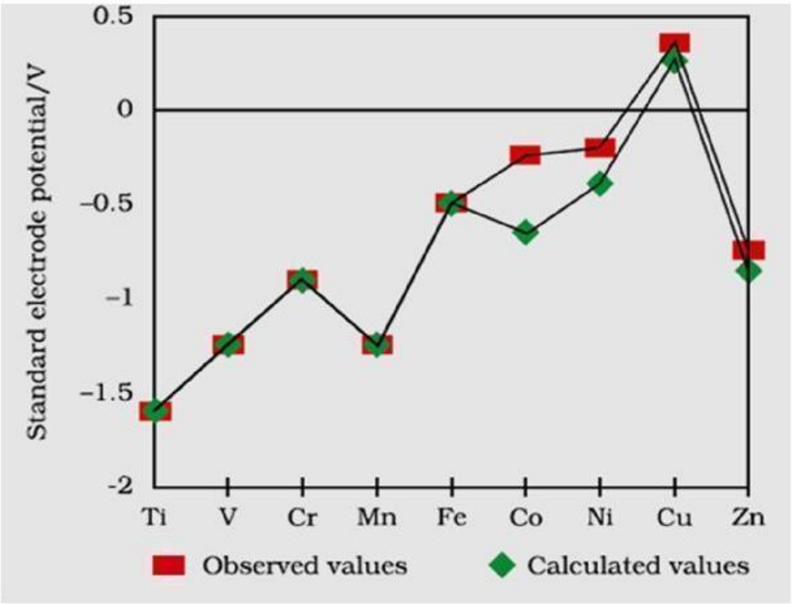


FIGURE 1 (source NCERT)

Explain the following observations:

i. The general trend towards less negative E° values across the series

ii. The unique behaviour of Copper

iii. More negative E° values of Mn and Zn

27. Arrange the following in increasing order of property specified:

i. Aniline, ethanamine, 2-ethylethanamine (solubility in water)

ii. Ethanoic acid, ethanamine, ethanol (boiling point)

iii. Methanamine, N, N- dimethylmethanamine and N- methylmethanamine (basic strength in aqueous phase)

OR

i. Give a chemical test to distinguish between N-methylethanamine and N,N-dimethyl ethanamine.

ii. Write the reaction for catalytic reduction of nitrobenzene followed by reaction of product so formed with bromine water.

iii. Out of butan-1-ol and butan-1-amine, which will be more soluble in water and why?

28. A metal crystallizes into two cubic system-face centred cubic (fcc) and body centred cubic (bcc) whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of fcc and bcc.

29. Three amino acids are given below:

Alanine $CH_3CH(COOH)(NH_2)$ Aspartic acid $HOOC\text{-}CH_2CH(COOH)(NH_2)$ and Lysine $H_2N\text{-}(CH_2)_4\text{-}CH(COOH)(NH_2)$

i. Make two tripeptides using these amino acids and mark the peptide linkage in both cases.

ii. Represent Alanine in the zwitter ionic form.

30. i. Arrange the following in decreasing order of bond dissociation enthalpy

F_2 , Cl_2 , Br_2 , I_2

ii. Bi does not form pπ-pπ bonds. Give reason for the observation.

iii.Electron gain enthalpy of oxygen is less negative than sulphur. Justify

SECTION D

Q.No 31 to 33 are long answer type carrying 5 marks each.

31. (i) Answer the following questions: **(2+3)**

a) Write the balanced chemical reaction for reaction of Cu with dilute HNO_3.

b) Draw the shape of ClF_3

(ii)'X' has a boiling point of 4.2K, lowest for any known substance. It is used as a diluent for oxygen in modern diving apparatus. Identify the gas 'X'. Which property of this gas makes it usable as diluent? Why is the boiling point of the gas 'X' so low?

OR

(i) Answer the following questions: **(2+3)**

a) Arrange the following in the increasing order of thermal stability:

H_2O, H_2S, H_2Se, H_2Te

b)Give the formula of the brown ring formed at the interface during the ring test for nitrate.

(ii) A greenish yellow gas 'A' with pungent and suffocating odour, is a powerful bleaching agent. 'A' on treatment with dry slaked lime it gives bleaching powder. Identify 'A' and explain the reason for its bleaching action. Write the balanced chemical equation for the reaction of 'A' with hot and concentrated NaOH.

32. An organic compound 'A' C_8H_6 on treatment with dilute H_2SO_4 containing mercuric sulphate gives compound 'B'. This compound 'B' can also be obtained from a reaction of benzene with acetyl chloride in presence of anhy $AlCl_3$. 'B' on treatment with I_2 in aq. KOH gives 'C' and a yellow compound 'D'. Identify A, B, C and D. Give the chemical reactions involved. **(5)**

OR

(i) Write the reaction for cross aldol condensation of acetone and ethanal.

(ii) How will you carry out the following conversions:

a) Benzyl alcohol to phenyl ethanoic acid

b) Propanone to propene

c) Benzene to *m*-Nitroacetophenone

33. (i) State Kohlrausch law. **(1+4)**

(ii) Calculate the emf of the following cell at 298 K:

$Al(s)/Al^{3+}$ (0.15M)//Cu^{2+}(0.025M) /Cu(s)

(Given $E^\circ(Al^{3+}/Al) = -1.66$ V, $E^\circ(Cu^{2+}/Cu) = 0.34$V, log 0.15 = -0.8239, log 0.025 = -1.6020)

OR

(i) On the basis of E° values identify which amongst the following is the strongest oxidising agent **(1+4)**

$Cl_2(g) + 2e^- \rightarrow 2Cl^-$ $E° = +1.36$ V,

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E° = +1.51$ V

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $E° = +1.33$ V

(ii) The following figure 2, represents variation of (Λ_m) vs $\sqrt{c}$ for an electrolyte. Here Λ_m is the molar conductivity and c is the concentration of the electrolyte.

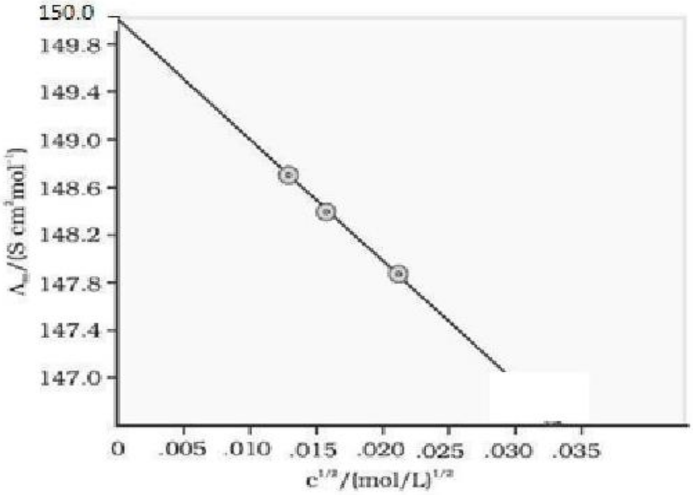
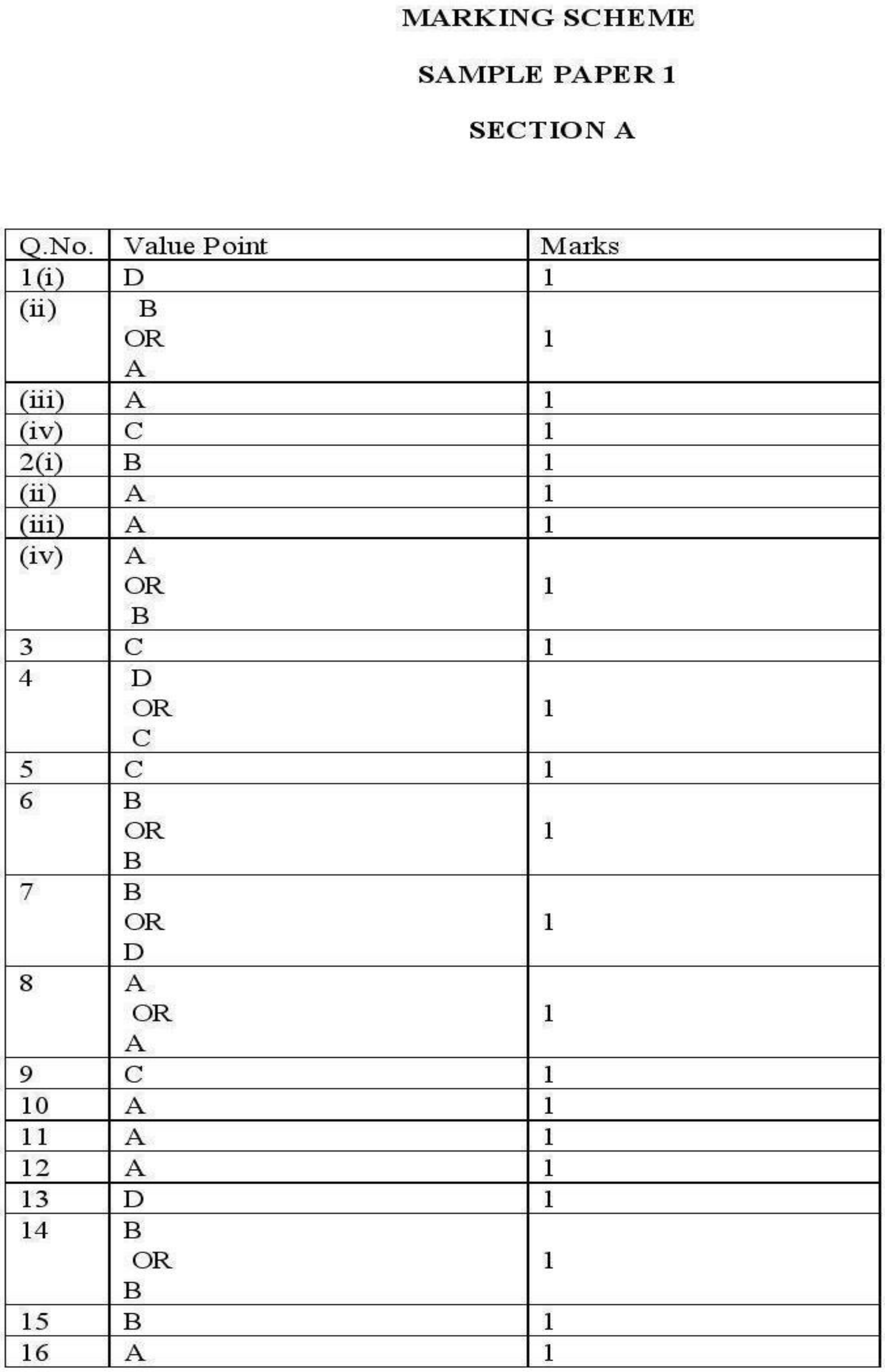


Figure 2

a) Define molar conductivity
b) Identify the nature of electrolyte on the basis of the above plot. Justify your answer.
c) Determine the value of $\Lambda_m°$ for the electrolyte.
d) Show how to calculate the value of A for the electrolyte using the above graph.



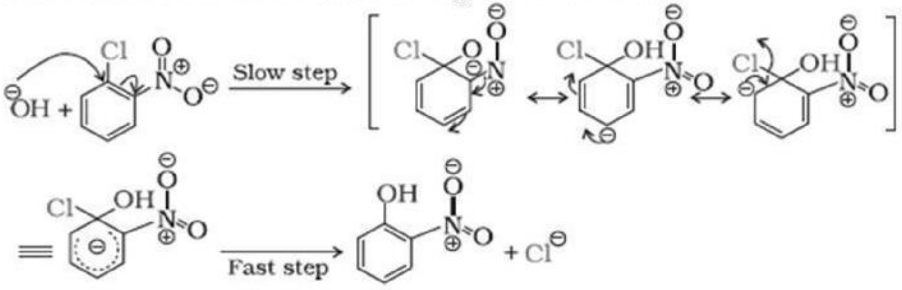
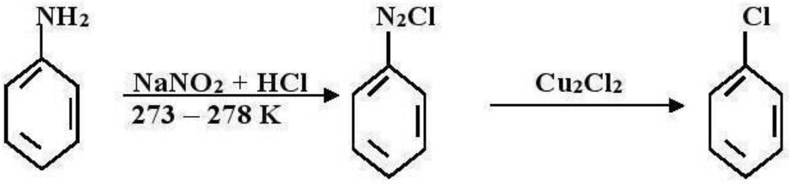
MARKING SCHEME

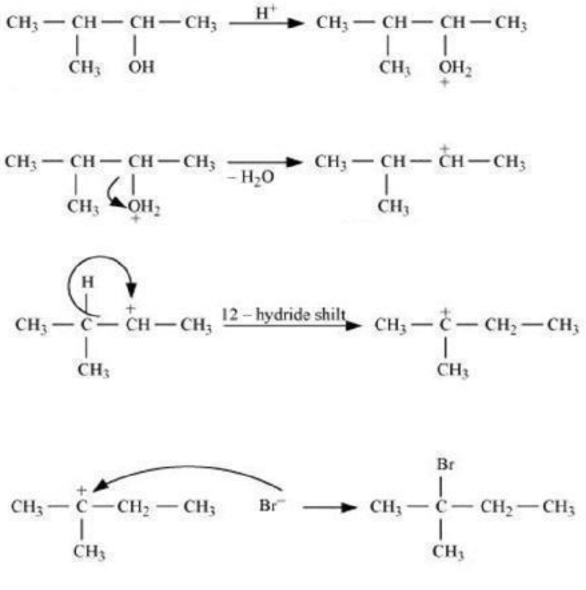
SAMPLE PAPER 1

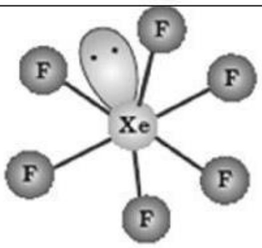
SECTION A

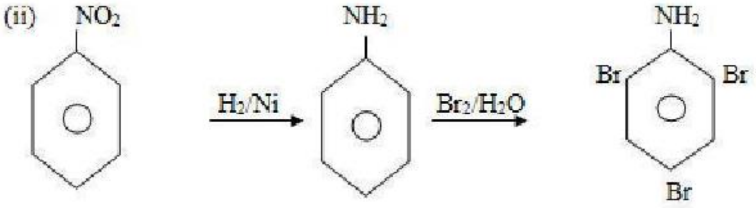
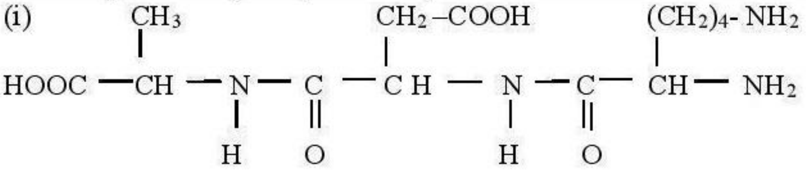
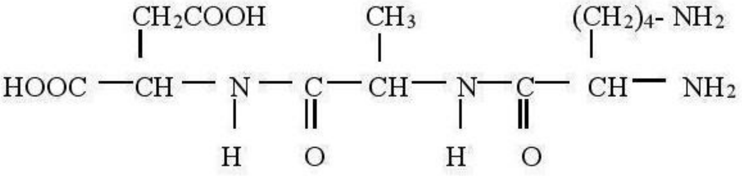
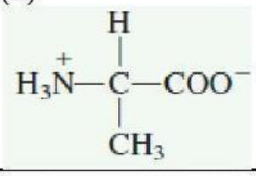
Q.No.	Value Point	Marks
1(i)	D	1
(ii)	B OR A	1
(iii)	A	1
(iv)	C	1
2(i)	B	1
(ii)	A	1
(iii)	A	1
(iv)	A OR B	1
3	C	1
4	D OR C	1
5	C	1
6	B OR B	1
7	B OR D	1
8	A OR A	1
9	C	1
10	A	1
11	A	1
12	A	1
13	D	1
14	B OR B	1
15	B	1
16	A	1

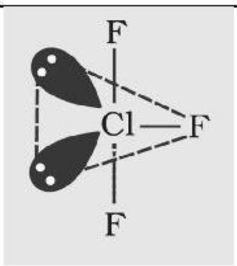
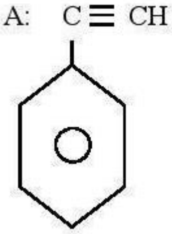
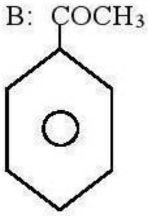
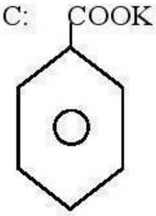
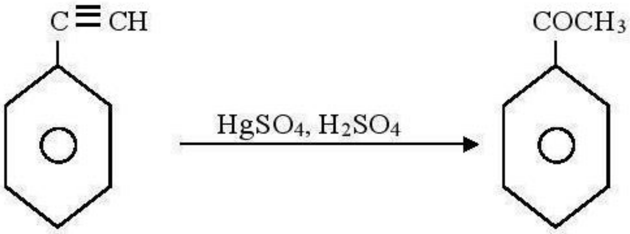
SECTION B, C, D

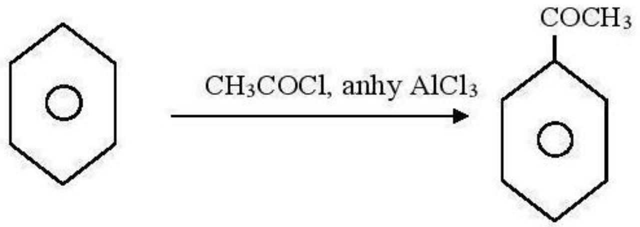
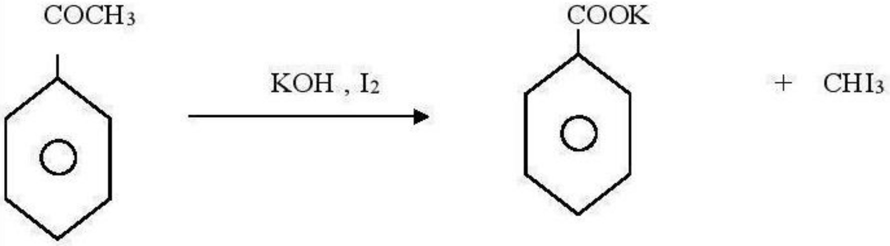
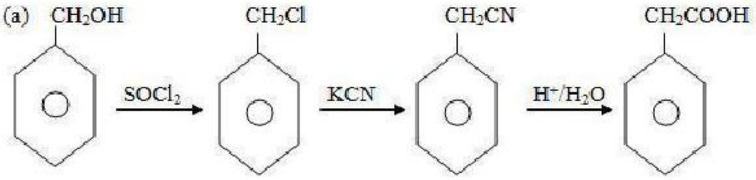
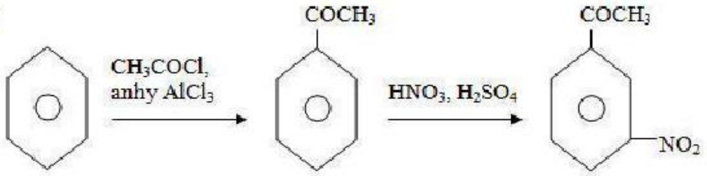
Q.No.	VALUE POINTS	MARKS
	SECTION B	
17	Nitro group at ortho position withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene.  **OR** **(i)**  **(ii)** $CH_3CH(Br)CH_3 \xrightarrow{\text{alc KOH}} CH_3CH{=}CH_2 \xrightarrow{\text{HBr, organic peroxide}} CH_3CH_2CH_2Br$	2 1 1
18	$\Delta Tb = K_b m \quad \Delta Tb = 101.04-100 = 1.04\ ^{o}C$ or $m = 1.04 / 0.52 = 2\ m$ 2 m solution means 2 moles of solute in 1 kg of solvent. 2 m aq solution of urea means 2 moles of urea in 1kg of water. No. of moles of water = 1000/18 = 55.5 Relative lowering of VP = x_2 (where x_2 is mole fraction of solute) Relative lowering of VP = n_2/n_1+n_2 (n_2 is no. of moles of solute , n_1 is no. of moles of solvent) = 2/ 2+55.5 = 2/57.5 = 0.034	1 1/2 1/2
19	(i)$t_{2g}^4e_g^2$ Paramagentic (ii)Dichloridobis(ethane-1,2-diamine)cobalt(III)nitrate OR (i)Square planar (ii)$Cu^{2+} = 3d^9$ 1 unpaired electron so $\sqrt{1(3)} = 1.73BM$	½, ½ 1 1 1
20	Reaction is a complex reaction. Order of reaction is 1.5. Molecularity cannot be 1.5, it has no meaning for this reaction. The reaction occurs in steps, so it is a complex reaction. (ii)units of k are $mol^{-1/2}L^{1/2}s^{-1}$	1/2 1/2 1

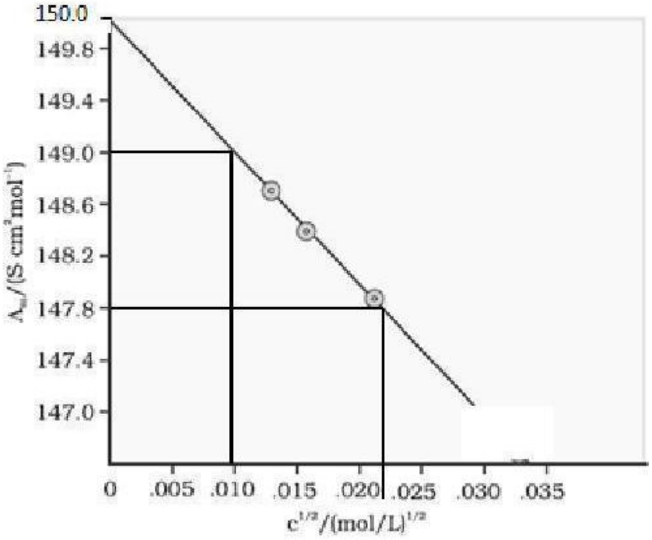
	OR Ans : let the rate law expression be Rate = k $[P]^x[Q]^y$ from the table we know that Rate 1 = $3.0 \times 10^{-4} = k\,(0.10)^x\,(0.10)^y$ Rate 2 = $9.0 \times 10^{-4} = k\,(0.30)^x\,(0.30)^y$ Rate 3 = $3.0 \times 10^{-4} = k\,(0.10)^x\,(0.30)^y$ Rate 1/ Rate 3 = $(1/3)^y$ or $1 = (1/3)^y$ So y = 0 Rate 2/ Rate 3 = $(3)^x$ or $3 = (3)^x$ So x = 1 Rate = k [P]	½ ½ 1
21	$k = 0.693/t_{1/2}$ $k = 0.693/5730\ \text{years}^{-1}$ $t = \frac{2.303}{k}\log\frac{Co}{Ct}$ let Co = 1 Ct = 3/10 so Co/Ct = 1/ (3/10) = 10/3 $t = \frac{2.303}{0.693} \times 5730\ \log\frac{10}{3}$ t = 19042 x (1-0.4771) = 9957 years	½ ½ ½ ½
22		½ ½ ½ ½
23	XeF_6 Central atom Xe has 8 valence electrons, it forms 6 bonds with F and has 1 lone pair. According to VSEPR theory, presence of 6 bp and 1 lp results in distorted octahedral geometry	1 1

		
24.	Racemic mixture will be given by 2 chlorobutane as it is an optically active compound. When 2 chlorobutane undergoes S_N^1 reaction, both front and rear attack are possible, resulting in a racemic mixture	1 1
25	Let no. of Atoms of element P be x No. of tetrahedral voids = 2x No. Of octahedral voids = x Atoms of Q = 1/3 (2x) + x = 5x/3 $P_xQ_{5x/3}$ P_3Q_5	1/2 ½ 1
	SECTION C	
26	(i)Due to large surface area and ability to show variable oxidation states (ii)Due to high value of third ionisation enthalpy (iii) Mo(VI) and W(VI) are more stable than Cr(VI). **OR** (i) The general trend towards less negative E^o V values across the series is related to the general increase in the sum of the first and second ionisation enthalpies. (ii) The high energy to transform Cu(s) to Cu^{2+} (aq) is not balanced by its hydration enthalpy. (iii) The stability of the half-filled *d* sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their more negative E^o V values	1 1 1 1 1 1
27	(i) Aniline, *N*-ethylethanamine, Etanamine (ii)Ethanamine, ethanol, ethanoic acid (iii) N, N dimethylmethanamine, methanamine, N-methylmethanamine **OR** (i) N-methyletahnamine is a secondary amine. When it reacts with benzenesulphonyl chloride, it forms N- Ethyl -N methyl sulphonamide while and	1 1 1 1

	N,N-dimethyl etahnanmine is a tertiary amine it does not react with benzenesulphonyl chloride. (ii)  (iii)Butan-1-ol Alcohol forms stronger hydrogen bonds with water than formed by amine due to higher electronegativity of O in alcohol than N in amine	1 ½ ½
28	We know that $d = zM/ N_a a^3$ For fcc, z=4 therefore $d = 4 \times M / Na (3.5 \times 10^{-8})^3$ g/cm^3 For bcc, z=2 therefore $d' = 2 \times M / Na (3.0 \times 10^{-8})^3$ g/cm^3 $d/d' = 4/(3.5 \times 10^{-8})^3 / 2/(3.0 \times 10^{-8})^3 = 1.26:1$	1/2 1 1 1/2
29	(i)  $HOOC-\overset{CH_3}{\overset{\vert}{CH}}-\underset{H}{\underset{\vert}{N}}-\underset{O}{\underset{\Vert}{C}}-\overset{CH_2-COOH}{\overset{\vert}{CH}}-\underset{H}{\underset{\vert}{N}}-\underset{O}{\underset{\Vert}{C}}-\overset{(CH_2)_4-NH_2}{\overset{\vert}{CH}}-NH_2$  $HOOC-\overset{CH_2COOH}{\overset{\vert}{CH}}-\underset{H}{\underset{\vert}{N}}-\underset{O}{\underset{\Vert}{C}}-\overset{CH_3}{\overset{\vert}{CH}}-\underset{H}{\underset{\vert}{N}}-\underset{O}{\underset{\Vert}{C}}-\overset{(CH_2)_4-NH_2}{\overset{\vert}{CH}}-NH_2$ (ii)  $H_3\overset{+}{N}-\overset{H}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-COO^-$	1 1 1
30	i. Arrange the following in decreasing order of bond dissociation enthalpy $Cl_2 > Br_2 > F_2 > I_2$ ii. Bi does not form pπ-pπ bonds as its atomic orbitals are large and diffuse so effective overlapping is not possible iii.Due to small size of oxygen, it has greater elecrton electron repulsions	1 1 1
	SECTION D	
31.	(i) (a) $3Cu + 8\ HNO_3(dilute) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ (b)	1

	 (ii)'X' is Helium It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood. It monoatomic having no interatomic forces except weak dispersion forces and has second lowest mass therefore bp is lowest. OR (a) H_2Te, H_2Se, H_2S, H_2O (b) $[Fe(H_2O)_5(NO)]^{2+}$ (ii) A is chlorine gas Its bleaching action is due to oxidation. $Cl_2 + H_2O \rightarrow 2HCl + O$, Coloured substance + O → Colourless substance $6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$	1 1 1 1 1 1 1 1 1
32	A:  B:  C:  D: CHI_3 	½ each 1 1

	 	1
	OR (i) $CH_3COCH_3 + CH_3CHO$ $\downarrow$ dil NaOH	1
	$(CH_3)_2C(OH)CH_2CHO + CH_3CH(OH)CH_2COCH_3$ $\downarrow$ Heat $(CH_3)_2C{=}CHCHO + CH_3CH{=}CHCOCH_3$	1
	(ii) (a) 	1
	(b) $CH_3COCH_3 \xrightarrow{H_2,\ Pd} CH_3CH(OH)CH_3 \xrightarrow{H_2SO_4} CH_3CH{=}CH_2$	1
	(c) 	1
33	(i) limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.	1
	(ii) $E^\circ cell = E^\circ cathode - E^\circ anode = 0.34 - (-1.66) = 2.00$ V $Ecell = E^\circ cell - \underline{0.059} \log \underline{[Al^{3+}]^2}$	1/2

	n $[Cu^{2+}]^3$	1
	Here $n = 6$	½
	$E_{cell} = 2 - \frac{0.059}{6} \log \frac{[0.15]^2}{[0.025]^3}$	1
	$= 2 - 0.059/6\ (2\log 0.15 - 3 \log 0.025)$ $= 2 - 0.059/6\ (-1.6478 + 4.8062) = 2 - 0.0311 = 1.9689V$	1
	OR	
	(i) MnO_4^-	1
	(ii)(a) Molar conductivity of a solution at a given concentration is the conductance of the volume *V* of solution containing one mole of electrolyte kept between two electrodes with area of cross section *A* and distance of unit length.	1
	(b)Strong electrolyte, For strong electrolytes, Λm increases slowly with dilution	1
	(c) $\Lambda m = \Lambda m° - A\ c^{½}$ Therefore $\Lambda m° = 150\ S\ cm^2\ mol^{-1}$	1
	(d) 	1
	$A = -$ slope $= - (149 - 147.8/ 0.010-0.022) = 100\ S\ cm^2\ mol^{-1}/(mol/L^{-1})^{1/2}$.	