

Instructions for students

- Write your name and centre at the top of the first pages of all problems.
- This examination paper consists of 33 pages of problems including answer boxes.
- You have 4 hours to complete all the problems.
- All results must be written in the appropriate boxes on the pages. Anything written elsewhere will not be marked. If you need any more sheets for rough work, ask the supervisor.
- You must show the main steps in a calculation in the answer box provided.
- When you have finished the examination, put all the papers into the envelope provided, write your name on it and then seal the envelope.
- Do not leave the examination room until you are directed to do so.
- Use only non-programmable scientific calculator.
- Values of some fundamental constants are given on page 2.
- A copy of the Periodic Table of the Elements is provided at the end of the paper.

© Homi Bhabha Centre For Science Education
Tata Institute of Fundamental Research
V.N. Purav Marg, Mankhurd, Mumbai 400 088.

Some Useful Information

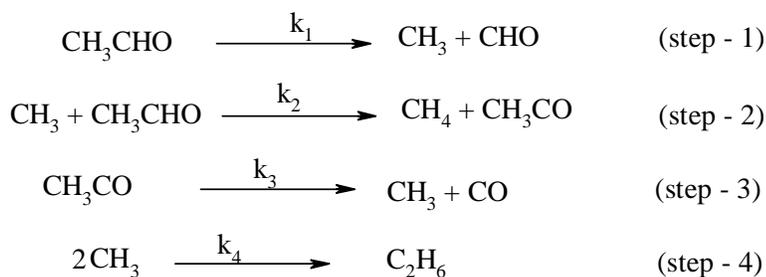
Avogadro's constant	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Electronic charge	$e = 1.602 \times 10^{-19} \text{ C}$
Molar gas constant	$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$
1 atomic mass unit (1u)	$= 931.5 \text{ MeV}/c^2$
1 Dalton	$= 1.661 \times 10^{-27} \text{ kg}$
1 eV	$= 1.602 \times 10^{-19} \text{ J}$
Mass of electron	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Planck's constant	$h = 6.625 \times 10^{-34} \text{ Js}$
Speed of light	$c = 2.998 \times 10^8 \text{ ms}^{-1}$

Problem 1

16 marks

Rates of Chemical Reactions and Arrhenius Equation

- 1.1 The rate constant of a first order reaction is $2.0 \times 10^{-6} \text{ s}^{-1}$ and the initial reactant concentration is 0.1 M. What is the initial rate in $\text{mol dm}^{-3} \text{ s}^{-1}$ and in $\text{mol mL}^{-1} \text{ min}^{-1}$?
- 1.2 Consider the rate of a simple chemical reaction $\mathbf{A} \rightarrow \mathbf{B}$. The rate generally decreases as the reaction approaches completion. Tick the correct reason from the choices below.
- (i) the reaction slows down due to cooling on progress of the reaction.
- (ii) molecules of \mathbf{A} become less active with time.
- (iii) with increasing time, a complex, \mathbf{AB} , is formed.
- (iv) the concentration of \mathbf{A} decreases with time
- (v) the sum of concentration of \mathbf{A} and \mathbf{B} decreases with time
- 1.3 It was found empirically by Hood in 1878 that the rate constant k of a reaction generally varies with temperature T as $\log k = \alpha - \beta/T$, where α and β are constants. Arrhenius gave his famous equation $k = A.e^{-E_a/RT}$ in 1886. What are the units of A for first order reactions? How do you justify the name of A as 'frequency factor' in this case?
- 1.4 For the reaction $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$, the values for k are 1.2×10^{-3} and $3.0 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 700 and 630 K respectively. Determine E_a and A .
- 1.5 The standard enthalpies of formation of gaseous CO , NO , CO_2 and NO_2 are -110.5 , 90.2 , -393.5 and 33.2 kJ mol^{-1} respectively. Calculate the enthalpy of the reaction $\text{CO}(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{NO}(\text{g})$.
- 1.6 For the forward reaction in 1.5 the energy of activation is $116.3 \text{ kcal mol}^{-1}$. What is the energy of activation for the reverse reaction?
- 1.7 Rice and Herzfeld (1934) proposed the following mechanism for the thermal decomposition of acetaldehyde.

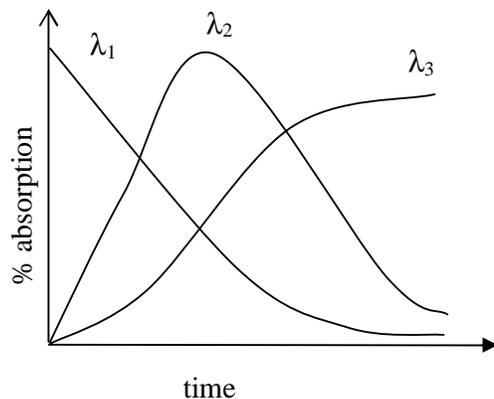


One may apply steady state approximation to CH_3 and CH_3CO radicals (i.e. the rate of formation and rate of consumption of such intermediate species are equal). Write the steady state equations for CH_3 and CH_3CO .

Obtain, using these steady state concentrations, an expression for the rate of formation of methane.

1.8 Assuming the energies of activation for steps 1- 4 to be E_1, E_2, E_3 and E_4 respectively, what will be the energy of activation for the overall reaction?

1.9



The rate of a chemical reaction between X and Y was monitored spectrophotometrically at 3 different wavelengths: λ_1, λ_2 and λ_3 . The results were found to be as shown above.

Which of the following mechanisms is in accordance with the spectral data? Tick the appropriate box.

- (i) $\text{X} + \text{Y} \rightarrow \text{Z}$
- (ii) $\text{X} + \text{Y} \rightarrow \text{Z}; \text{Z} \rightarrow \text{W}$
- (iii) $\text{X} + \text{Y} \rightarrow \text{U}; \text{X} + \text{Y} \rightarrow \text{V}$

1.10 Sketch the expected % absorption vs time curves for the other choices.

Problem 2

18 marks

Electrochemistry

- 2.1 The specific conductivity (κ) of a 0.1 M NaOH solution is 0.0221 S cm^{-1} . On addition of an equal volume (V) of 0.1 M HCl solution, the value of κ falls to 0.0056 S cm^{-1} . On further addition of the same volume V of 0.1M HCl, the value of κ rises to 0.0170 S cm^{-1} . Calculate the equivalent conductivity (Λ) for
- a) NaOH b) NaCl c) HCl d) H^+ and OH^- together
- 2.2 A conductivity cell containing distilled water has a resistance of $454 \text{ k}\Omega$, while the same cell containing KCl solution prepared in the same sample of water shows a resistance of 2150Ω . If the plates of the conductivity cell have area of 0.5 cm^2 each and are separated by 1 cm, find the cell constant and also calculate the specific conductance of KCl.
- 2.3 The same quantity of electricity that liberates 2.158 g silver is passed through a solution of a gold salt, and 1.314 g gold is deposited. The equivalent weight of silver is 107.9. Calculate the equivalent weight of gold. What is the oxidation state of gold in this gold salt?
- 2.4 Consider the following equations for a cell reaction
- $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} \dots\dots\dots (1)$
- $2\text{A} + 2\text{B} \rightleftharpoons 2\text{C} + 2\text{D} \dots\dots\dots (2)$
- How are the E° and K values for the two reactions related?
- 2.5 A cell, $\text{Ag} | \text{Ag}^+ || \text{Cu}^{2+} | \text{Cu}$, initially contains 1M Ag^+ and 1M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A current for 1 hour.
- 2.6 The standard reduction potentials for the half cells Cu^{++}/Cu and Cu^+/Cu are 0.337 V and 0.530 V, respectively. Find the equilibrium constant of the cell reaction:
- $2\text{Cu}^+ \rightleftharpoons \text{Cu}^{++} + \text{Cu}$ at 25°C . Which of the two oxidations $\text{Cu} \rightarrow \text{Cu}^+$ and $\text{Cu}^+ \rightarrow \text{Cu}^{++}$ is easier to carry out?

Problem 3

14 marks

Molecular Structure and Spectroscopy

A monochromatic light of wavelength λ , passes through a layer of sample containing an absorbing species. For an infinitesimally small thickness of the layer, the reduction of intensity of the light is proportional to the thickness, the concentration (c) of the species and the intensity (I) of the light.

- 3.1 Obtain an expression for the light intensity (I) that emerges from a sample of thickness l , if the intensity of the incident light is I_0 .
- 3.2 What is the unit of the proportionality constant in the above relation?
- 3.3 Show graphically how the light intensity (I) changes with the sample thickness l .
- 3.4 Anthracene has an absorption band with maximum at wavelength of 365 nm. Calculate the energy absorbed to promote one mole of anthracene to its first excited state.
- 3.5 Calculate the momentum of photons of wavelength 750 nm. What should be the speed of an electron having the same value of momentum?
- 3.6 Calculate the minimum uncertainty in the speed of a ball of mass 500 g that is known to be within 1.0 μm of a certain point on a bat.
- 3.7 The vibration of a diatomic molecule can be described by the motion of a simple harmonic oscillator. The corresponding equation of motion can be represented as $\mu (d^2x/dt^2) + kx = 0$, where μ is the reduced mass, k is the force constant, and $x (= r - r_e)$ is the displacement from the equilibrium position. Express x as a function of t . Establish a relation between the vibrational frequency ν (in cycles s^{-1}), μ and k .
- 3.8 If the fundamental vibrational frequency of H^{35}Cl is 2990 cm^{-1} , find the force constant of the molecule.

Problem 4

16 marks

Cyclooctatetraene and Aromaticity

The chemists in the early 1900s believed that the only requirement of aromaticity was the presence of a cyclic conjugated system. Cyclooctatetraene (**A**) defied this assumption. It was first prepared by German chemist Richard Willstater in 1911 and found to resemble an open chain polyene!

4.1 Draw the structure of cyclooctatetraene **A**.

4.2 Cyclooctatetraene is expected to have –

- (a) a planar structure
- (b) a tub-shaped structure
- (c) open chain isomeric structure
- (d) tautomeric bicyclic structure

Cyclooctatetraene reacts readily with potassium metal to form a dianion (**B**) ($C_8H_8^{2-}$).

4.3 Draw the structure of the dianion.

4.4 The geometry of this dianion is

4.5 The reaction of cyclooctatetraene with potassium takes place very easily as -

- (a) cyclooctatetraene is highly electron deficient
- (b) the oxidation potential of cyclooctatetraene is low
- (c) the dianion is aromatic
- (d) potassium metal is highly electropositive

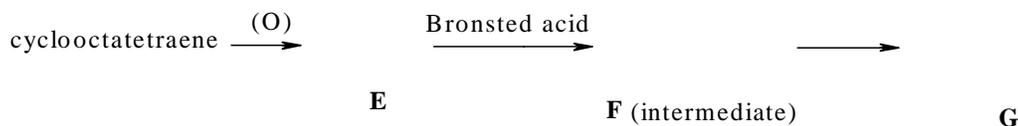
The dianion reacts with two moles of acetone to form a mixture of two compounds (**C** and **D**).

4.6 Draw the structures of **C** and **D**.

Any olefin on reaction with a per acid gives an epoxide ($>C=C< \rightarrow >C \begin{matrix} O \\ \diagup \quad \diagdown \end{matrix} C <$)

Cyclooctatetraene gives epoxide **E**, which on treatment with a Bronsted acid gives compound **G** (C_8H_8O). **G** gives 2,4-DNP derivative and also reacts with Tollen's reagent.

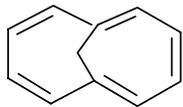
4.7 Identify **E**, **F** and **G** and complete the following reaction.



In an analogous manner, cyclooctatetraene on reaction with HBr gives compound **H** (C_8H_9Br).

4.8 Identify the structure of **H**.

E. Vogel is well known for his work on bridged annulenes. **I** is such a compound prepared by him in 1964.



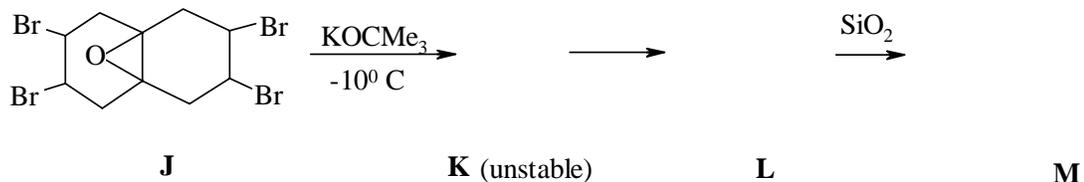
I

4.9 Mark the reaction/s possible on this compound by \checkmark and not possible by **X**

- | | | |
|-----|--|--------------------------|
| (a) | substitution by an electrophile | <input type="checkbox"/> |
| (b) | addition of bromine | <input type="checkbox"/> |
| (c) | catalytic hydrogenation under mild condition | <input type="checkbox"/> |
| (d) | addition reaction with maleic anhydride | <input type="checkbox"/> |

Drawn below is the structure of a tetrabromo compound **J**, which on treatment with potassium tert-butoxide gives compound **L** ($C_{10}H_8O$) through an unstable intermediate **K**. **L** on treatment with silica gives compound **M** ($C_{10}H_8O$).

4.10 Identify **K**, **L** and **M**



Is **L** aromatic?

Yes

No

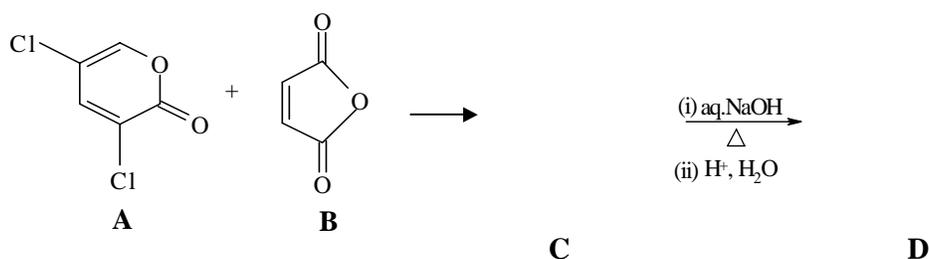
Problem 5

14 marks

Diels-Alder Reaction

2-Pyrones function as 'dienes' in Diels-Alder reaction and react with suitable dienophiles to provide products which are otherwise inaccessible. 2-Pyrone (**A**) undergoes Diels-Alder reaction with maleic anhydride (**B**) to give a primary adduct **C**, which is unstable. It gives **D** ($C_8H_5O_4Cl$) on heating with aqueous NaOH followed by acidification. **D** is a dicarboxylic acid and does not form an anhydride.

5.1 Identify the structure of **D** and that of **C**.



4-Pyrones are isomeric with 2-Pyrones.

5.2 Draw the structure of 4-Pyrone.

5.3 Draw the structure of the **most favourable** protonated species of 4-pyrone and its resonance structures.

5.4 Will 4-Pyrone undergo Diels-Alder reaction as a diene?

Yes No

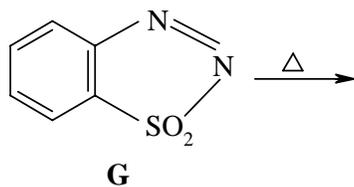
Aromatic compounds are reluctant to undergo Diels-Alder reaction. Benzene is particularly stubborn. However, it reacts with hexafluoro-2-butyne (**E**) at 250°C to give the adduct **F**.

5.5 Draw the structure of **E** and identify the adduct **F**.

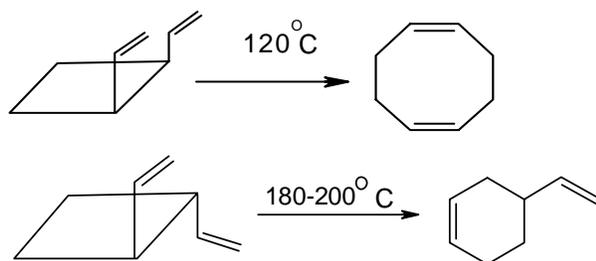


Benzyne are intermediates which are usually described by a benzene ring with a triple bond. They are good dienophiles. **G** on heating forms a benzyne **H**.

5.6 Identify the structures of the products of the following reaction:



5.7 The following reactions take place thermally. With curly arrows, drawn on the reactants, indicate how these reactions take place.



Olefins undergo a photochemical dimerization reaction to form cyclobutanes. It is called a $(2+2)\pi$ cycloaddition reaction. Benzene does not react with maleic anhydride under normal conditions. However, in the presence of light, it undergoes a reaction with two moles of maleic anhydride, through two steps to give products **H** and **I**.

5.8 Identify **H** and **I** in the following reaction.



Problem 6**12 marks****Chemical Thermodynamics and Kinetic Theory of Gases**

- 6.1** You are asked to consider the suitability of $\text{H}_2(\text{g})$, $\text{CH}_3\text{OH}(\text{l})$, $\text{CH}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{C}_6\text{H}_{14}(\text{g})$ as rocket fuels. You may pick the best fuel by calculating maximum heat of combustion per gram of all the substances. Calculate these values. Which is the most suitable fuel based on this criterion? The standard heats of formation (in kJ mol^{-1}) of $\text{H}_2\text{O}(\text{g})$, $\text{CH}_3\text{OH}(\text{l})$, $\text{CH}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{C}_6\text{H}_{14}(\text{g})$ are -241.8 , -74.8 , -393.5 , -238.7 and 167.2 , respectively.

In the kinetic theory of gases, the probability distribution (normalized to unity) for the gas particles (of mass m each) having velocities in the range v and $v + dv$ is given by

$$f(v)dv = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT} v^2 dv$$

where k is the Boltzmann constant and T is the temperature.

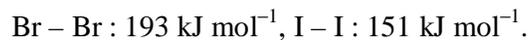
- 6.2** Plot a qualitative sketch of $f(v)$ against v at temperatures $T_1=100$ K and $T_2=200$ K.
- 6.3** Find the most probable value (v_{mp}) of the velocity.
- 6.4** Find the average velocity (v_{av}) of the gas particles.
- 6.5** Which of the above two velocities, v_{mp} and v_{av} , is higher?

Problem 7

10 marks

Halogen Compounds

7.1 The halogens are among the most reactive non-metallic elements. Most of the halogens exist as diatomic molecules. The bond dissociation enthalpies are as follows:



Thus, the F – F bond dissociation enthalpy is anomalous. The probable reason for this is:

- (a) strong electronegativity of fluorine
- (b) F atom does not have d orbitals
- (c) F – F bond is weakened by strong repulsion between nonbonding electrons in small F₂ molecule

7.2 Fluorine can be stored in a metal container, whereas other halogens cannot be stored. The reason for this is:

- (a) very low F – F bond dissociation enthalpy
- (b) fluorine does not react with metals
- (c) fluorine reacts with a metal to form a non-reactive metal fluoride film
- (d) other halogens are more reactive towards metals

7.3 Arrange the following compounds in the order of decreasing Lewis acidity:
SiBr₄, SiF₄, SiI₄, SiCl₄.

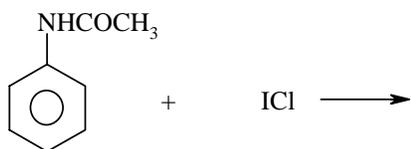
7.4 Arrange the following oxyacids in the order of decreasing acidity:
HClO₂, HClO₃, HClO₄, HOCl.

7.5 Draw the structures of the anions of the oxyacids in 7.4

7.6 Give the reason why fluorine **cannot** form such oxyanions.

7.7 The halogens form compounds among themselves. These binary inter-halogen compounds have molecular formulae XY, XY₃, XY₅, XY₇. VSEPR model is a good tool for predicting the shapes of various interhalogen compounds. Write the structure of IF₅ based on VSEPR. Also write the outer electronic configuration of the central atom in the molecule.

- 7.8 Interhalogen compounds are useful for electrophilic aromatic substitution reactions, as the halogen-halogen bond in them is polarized. Based on this observation, predict the product of the following reaction.



Problem 8

16 marks

Proteins, amino acids, nucleic acids and buffers

8.1 Insulin is a hormone, regulating blood glucose of our body. This hormone is a protein consisting of two polypeptide chains. The native structure of the protein contains both intrachain and interchain disulfide linkages which are contributed by cysteine. Draw the likely structure of the disulphide linkage.

In order to identify the primary structure of the hormone, the chains can be separated by different reactions as given below. Identify the correct products formed in each reaction.

- The disulfide linkage is reacted with β -mercaptoethanol (HS-CH₂-CH₂-OH).
- The reduced polypeptide chain (from (a) above) is reacted with sodium iodoacetate.
- The disulphide linkage is reacted with performic acid.

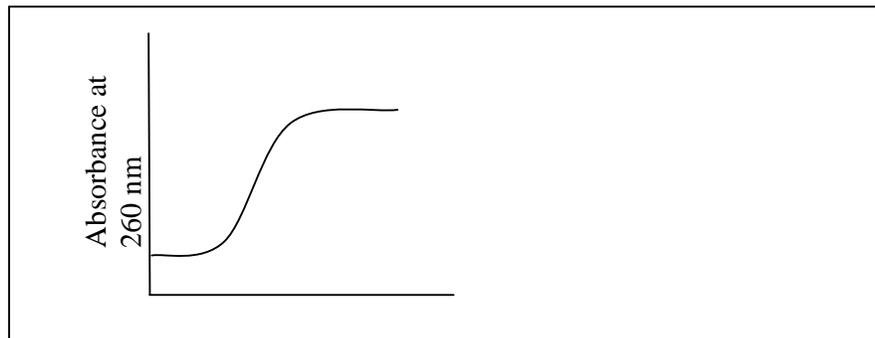
8.2 Unlike carbohydrates, which can be stored as glycogen in human body, the excess amino acids cannot be stored and hence the nitrogen is excreted in the form of urea (H₂N – CO – NH₂). This process involves a sequence of reactions known as “urea cycle” of which amino acid ornithine is an important intermediate (structure given below). Draw the structures of different species one would get while titrating ornithine against aq. KOH.



8.3 Two bacterial strains were isolated, one (**A**) from the Gangotri glacier and the other (**B**) from a hot spring. The genomic DNA's of both bacteria were isolated and the stability of the DNA studied.

- Both the DNA samples were gradually heated. Which of these two DNA samples will lose its double helix structure first and why?

- (b) Given in the box is the melting curve of a normal DNA sample, draw the melting curves of the samples **A** and **B** in the same figure.

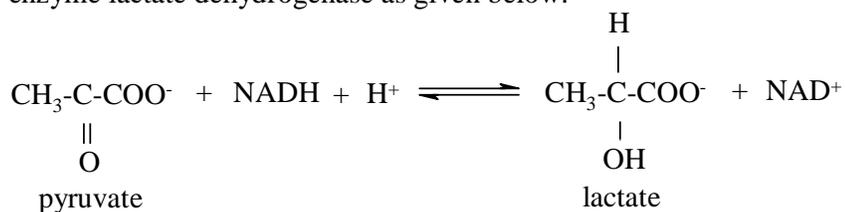


- (c) Given below is the nucleotide sequence of a stretch of DNA obtained from sample **A**. This sequence of DNA transcribes and makes an mRNA which ultimately acts as a template for protein synthesis. Find out the sequence of mRNA.



- (d) How many amino acids will be present in the protein synthesized when the above mRNA sequence acts as a template?
- (e) What will be the expected average molecular weight of the above protein?

8.4 Lactic acid bacteria help to make curd from milk by producing lactic acid from pyruvic acid during the fermentation process. This reaction is catalyzed by the enzyme lactate dehydrogenase as given below.



The optimum pH for the enzyme activity is found to be in the range of 7.9 – 8.4, beyond which the rate decreases markedly. The enzyme activity for the production of lactate was assayed in Tris buffer until the concentration of the product reached 0.05 M (pK_a of $\text{Tris}^+ = 8.1$). The buffering action of Tris is given as



- (a) Indicate the starting pH of the assay mixture with reason.

- (b) Find out the total buffer (Tris) concentration. Also find out the concentration of the conjugate acid and base at the end of the assay and the final pH.

Problem 9

13 marks

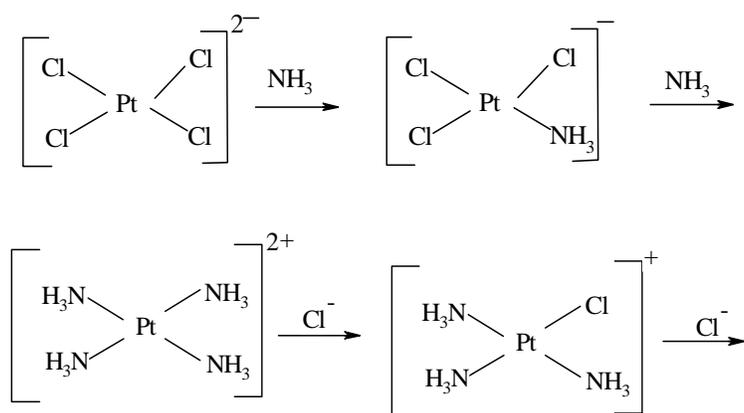
Transition Metal Chemistry

Different properties of transition elements such as multiple oxidation states, formation of coloured complexes, paramagnetism, etc. are related to the presence of electrons in d orbitals. In the first transition metal series, that begins with Sc, two elements exhibit electronic configurations different from the normal expectation.

- 9.1 Identify these two elements, write their outer electronic configurations and explain the reason for the observed configurations.
- 9.2 Covalent radius of transition metal elements decreases from left to right across a row. Explain this trend briefly.
- 9.3 Transition element chemistry is dominated by the co-ordination complexes that have specific three-dimensional structures. The ligands that are involved in complex formation play an important role in determining the geometry of the complexes. Write the IUPAC name of $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$. Draw the 3D structures of the possible isomers.
- 9.4 For the following complexes, draw d orbital splitting, indicating the distribution of electrons for the metal ion. Calculate the magnetic moment in B.M for the paramagnetic species.



- 9.5 Some ligands have directional effect on the other incoming ligands. In the following substitution reaction, write the structures of the products formed.



9.6 For the following complexes, (a) to (c), draw the structures of the most stable isomers. Indicate whether the complexes are optically active or inactive.

(a) $[\text{Ru}(\text{L})_3]^{2+}$ where L = bipyridine, to be represented by $\overset{\text{N}}{\curvearrowright} \text{N}$

active

inactive

(b) $[\text{PtCl}(\text{L})]^+$ where L = dienyl, to be represented by $\overset{\text{N}}{\curvearrowright} \overset{\text{N}}{\curvearrowright} \text{N}$

active

inactive

(c) $[\text{PtCl}_2(\text{L})_2]^+$ where L = ethylenediamine, to be represented by $\overset{\text{N}}{\curvearrowright} \text{N}$

active

inactive