

U.G. 3rd Semester Examination - 2025

CHEMISTRY

[MAJOR]

Course Code : CHEM-MAT-03

Group : IB (Inorganic & Physical)

[NEP-2020]

Full Marks : 40

Time : $2\frac{1}{2}$ Hours

*The figures in the right-hand margin indicate marks.
Candidates are required to give their answers in their
own words as far as practicable.*

GROUP-A

(Inorganic-IB)

[Marks : 20]

1. Answer any one question: 1×1=1
 - a) Complete the reaction: $\text{BF}_3 + \text{B}_2\text{H}_6 + (\text{CH}_3)_2\text{O} + (\text{CH}_3)_2\text{S} \rightarrow$.
 - b) Give an example of neutralization reaction in liquid NH_3 solvent.
2. Answer any two questions: 2×2=4
 - a) The metal ion X^{2+} and Y^{2+} belong to analytical groups IIA and IIIB respectively. Which sulphide has lower solubility product, XS or YS? How can you get XS from a mixture containing both X^{2+} and Y^{2+} ions?

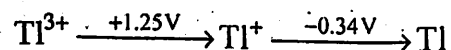
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b) Give the name and structure of a redox indicator.

c) Acidity of anhydrous HF is substantially increased in presence of SbF_5 – Explain.

3. Answer any one question: $5 \times 1 = 5$

a) i) Construct the Frost diagram from the following Latimer diagram showing the calculation for evaluation of coordinate of each point of the plot:



ii) The reducing power of Co(II) ion increases appreciably, in the presence of EDTA – Explain. $3+2=5$

b) i) Why KNH_2 is considered as a base in liquid ammonia solvent?

ii) Compare the acid strength of H_3PO_2 , H_3PO_3 and H_3PO_4 with proper justification.

iii) Why does alkaline medium inhibit rusting of iron? $2+2+1=5$

4. Answer any one question:

$10 \times 1 = 10$

a) i) Define buffer capacity. Derive Henderson equation for the calculation of pH of an acidic buffer.

ii) Calculate the pH of the mixed solution obtained by mixing 100 ml 0.1 (M) CH_3COOH to 50 ml 0.1(M) NaOH solution. [K_a for $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ mol litre $^{-1}$].

iii) HNO_3 and HCl have equal strength in aqueous medium but their strengths differ in CH_3COOH medium – Explain.

iv) In the light of solvent-system theory justify the nature of BiN in liquid NH_3 . $(1+3)+2+2+2=10$

b) i) Explain why Cl^- is oxidized by permanganate solution only at low pH below 1.5 but not in neutral medium. Given $E^0_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.52\text{V}$ and $E^0_{\text{Cl}_2/\text{Cl}^-} = 1.36\text{V}$.

- ii) Find out the equivalence point potential during the titration of a 0.1 (M) Fe^{2+} solution with 0.1 (M) Ce^{4+} solution. Given $E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77\text{V}$ and $E^0_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.57\text{V}$.

- iii) Classify the following into Hard and Soft acids and bases. Give reason.
 CN^- , H^- , Cl^- , Pt^{2+} , Mg^{2+} , CO

- iv) Calculate equilibrium constant for the following redox reaction:
 $\text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow \text{Fe}^{2+} + \text{Sn}^{4+}$

Given $E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77\text{V}$ and
 $E^0_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0.15\text{V}$. $3+2+3+2=10$

GROUP-B
(Physical-IB)
[Marks : 20]

1. Answer any **one** question: $1 \times 1 = 1$
- a) What is activation energy?
- b) State the Clausius statement of the second law of thermodynamics.
2. Answer any **two** questions: $2 \times 2 = 4$
- a) Define the heat capacities at constant volume (C_v) and at constant pressure (C_p) in terms of internal energy and enthalpy, respectively.
- b) What is homogeneous Catalysis? Give one example.
- c) A reaction has a rate law
 $\text{Rate} = k[\text{A}]^{1/2}[\text{B}]^{3/2}$
What is the overall order of the reaction? Can such an order arise from an elementary step? Justify your answer.
3. Answer any **one** question: $5 \times 1 = 5$
- a) i) A second-order reaction of the type, $\text{A} + \text{B} \rightarrow \text{Products}$, is 40% complete in 120 minutes, when the initial concentrations

of both A and B are 0.02 mol/L. Calculate the rate constant and the half-life.

- ii) Show that for a first order reaction, the half-life is independent of initial concentration. $2 \frac{1}{2} + 2 \frac{1}{2} = 5$

- b) i) Prove that the efficiency of a reversible engine is greater than that of an irreversible engine operating between the same hot and cold reservoirs.

- ii) For a first-order reaction, initial concentration of the reactant is 0.6 mol/L. After 30 minutes, it decreases to 0.3 mol/L. Calculate the rate constant.

$$3+2=5$$

4. Answer any one question: $10 \times 1 = 10$

- a) i) Derive the Gibb's-Helmholtz equation.
ii) One mole of an ideal diatomic gas ($C_v = 5 \text{ cal mol}^{-1} \text{K}^{-1}$) was initially at 25°C and 1 atm. The gas was transferred to the state when temperature is 100°C and pressure 10 atm. Calculate the entropy change.
iii). Starting from $dG = VdP - SdT$, derive the condition for chemical equilibrium and explain its physical significance.

$$4+3+3=10$$

- b) i) A reversible reaction follows first-order kinetics in both directions. Derive the integrated rate expression for the reaction, and express it in terms of the equilibrium concentration of the product formed.

- ii) Derive the expression for the rate constant based on Transition State Theory (TST) of chemical kinetics.

- iii) Calculate the maximum efficiency of a steam engine operating between 110°C and 25°C. What would be the efficiency of the engine if the boiler temperature is raised to 140°C, the temperature of the Sink remaining the same. $4+3+3=10$