

Roll No.

Total Pages : 04

GSM/J-21

1623

CHEMISTRY

Paper XII (CH-205)

Physical Chemistry (Theory)

Time : Three Hours]

[Maximum Marks : 32

Note : Attempt *Five* questions in all, selecting *two* questions from each Section. Q. No. **1** is compulsory. Use of calculator and log table is allowed.

1. (a) State and explain Carnot Theorem. How can efficiency of a heat engine be increased ? **2**
- (b) Justify the statement "Entropy of Universe is Increasing". **2**
- (c) Explain, why KCl is used as electrolyte in salt bridge ? **1**
- (d) What is a reversible cell ? How do you measure its E.M.F. ? **2**
- (e) What is standard electrode potential ? Explain. **1**

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Section A

2. (a) What is Carnot Cycle ? Calculate the efficiency of a Carnot engine working between temperatures T_1 and T_2 . **3**
- (b) Derive Gibbs-Helmholtz equation in the form as below : **3**

$$\left[\frac{\partial(\Delta G/T)}{\partial T} \right]_P = -\frac{\Delta H}{T^2}$$

3. (a) Explain the term Entropy. Show that entropy is a state function. **3**
- (b) Calculate the molar entropy change of mixing 0.6 mole of Nitrogen and 0.2 mole of Helium at 298 K assuming that they are ideal gases. **3**
4. (a) Prove that in a reversible process net entropy change for the system and surrounding is zero. **2**
- (b) 5 moles of an ideal gas expands reversibly from a volume of 6 dm³ to 60 dm³ at a temperature of 25°C. Calculate the change in entropy. **2**
- (c) What is Residual Entropy ? What is its origin and How can it be calculated ? **2**

5. (a) Derive the relationship : 1½

$$\Delta S = C_p \ln \frac{P_1}{P_2}$$

- (b) State and explain Nernst Heat Theorem. 2
- (c) State third law of thermodynamics. How absolute entropy of a substance can be determined from the heat capacity data. 2½

Section B

6. (a) What are reversible electrodes ? Explain the following electrodes :
- (i) Metal-Metal Ion Electrode
- (ii) Hydrogen Electrode. 3
- (b) A zinc electrode is placed in 0.1 m solution of zinc sulphate at 25°C. If the degree of dissociation of salt at this concentration is found to be 0.95, calculate the electrode potential of the electrode at 25°C. Given that $E_{Zn^{2+}, Zn}^0 = -0.76$ volt. 3
7. (a) Explain the construction and working of electrochemical cell. 3

- (b) Calculate the standard E.M.F. of a cell which involves the following cell reaction :



Given that $E_{\text{Zn},\text{Zn}^{2+}}^0 = 0.76$ volt and $E_{\text{Ag},\text{Ag}^{2+}}^0 = -0.80$ volt. 2

- (c) What is Liquid Junction Potential ? How can it be minimized ? 1

8. (a) Derive an expression for EMF of electrode concentration cell without transference. 3

- (b) Calculate the free energy change of the following cell at 25°C :



Standard EMF of cell is 0.014 volt. 3

9. (a) Derive Nernst equation for the potential of Hydrogen electrode. 3

- (b) Discuss the applications of E.M.F. measurement in potentiometric titrations :

HCl acid vs. NaOH Base. 3