

ANSWER ANY FIVE QUESTIONS ALL QUESTIONS CARRY EQUAL MARKS

1. (a) Define and explain the following terms
 - i. system
 - ii. Thermodynamic state
 - iii. Process
 - iv. Function.
 (b) Explain how zeroth law of thermodynamics leads to the postulation of an empirical temperature scale.
2. (a) Distinguish between reversible, quasi-static; and spontaneous processes.
 (b) What is HESS's law? Explain its applications in thermodynamics with suitable examples. What are its limitations?
 (c) Does the Joule-Thomson coefficient of a substance change with temperature at a fixed pressure? Explain?
3. (a) State and explain second law of thermodynamics.
 (b) Define and explain entropy. What are its units.
 (c) Explain the principle of increase of entropy.
4. (a) What is the entropy criterion for spontaneous change in an isolated system? Give an example of a spontaneous process in an isolated system.
 (b) Give an equation that relates the entropy change in the surroundings to the enthalpy change in the system.
 (c) When heat is added to the surroundings, the entropy of the surroundings increases. How does ΔS_{sur} depend on the temperature of surroundings? Explain.
5. (a) Explain the differences between Gibb's -Duhem equation and Gibb's - Helmholtz equation.
 (b) What is the purpose of free energy functions and give the significance of these functions.
6. (a) Explain the terms fugacity and activity. Discuss the dependence of pressure and temperature on fugacity and activity.
 (b) What do you understand by entropy and explain absolute entropy with the third law of thermodynamics.
7. (a) Derive Clausius-Clapeyron equation starting from fundamentals. State the conditions under which approximation is valid.
 (b) Prove that violation of the Kelvin-Planck statement leads to violation of the Clausius statement of the second law of thermodynamics.
8. (a) The gas phase reaction of nitric oxide and Bromine Yields NOBr.

$$2 \text{NO}(\text{g}) + \text{Br}_2 \rightarrow 2 \text{NOBr}(\text{g})$$
 The rate law is $= k[\text{NO}]^2[\text{Br}_2]$.
 What is the reaction order with respect to each of the reactants, and what is the overall reaction order?
 (b) The gas phase reaction of Hydrogen and Iodine monochloride, $\text{H}_2(\text{g}) + 2 \text{ICl}(\text{g}) \rightarrow 2 \text{HCl}(\text{g}) + \text{I}_2(\text{g})$ is first order in H_2 and first order in ICl . What is the rate law, and what are the units of the rate constant.