

**II B.Tech. II Semester Regular Examinations, April/May -2005**  
**THERMODYNAMICS AND KINETICS**  
**(Metallurgy & Material Technology)**

Time: 3 hours

Max Marks: 80

Answer any FIVE Questions  
All Questions carry equal marks

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1. (a) State and explain *zero<sup>th</sup>* law of thermodynamics.  
(b) Distinguish clearly between integral and excess thermodynamic properties.  
(c) Explain the limitations of thermodynamics.  
(d) What are excess thermodynamic properties? Explain them with examples
2. (a) Show that internal energy is function of temperature only.  
(b) The internal energy of a closed system is given by  $U = 100 + 50T + 0.04T^2$  in Joules. The heat absorbed  $Q = 4000 + 16T$  in joules. (T is in Kelvin). If the system changes from 500 K to 1000K, what is the work done.  
(c) Calculate the work transfer and change in internal energy if the gas is changing it's state from 1 bar,  $27^0C$  to 20 bar,  $400^0C$  polytropically.
3. (a) A carnot's engine cannot be realised in actual practice. Explain why?  
(b) Assuming that the working substance in a carnot's engine is a perfect gas. Show that the ratio of heat rejected at the sink to that extracted at the source equals the ratio of absolute temperatures of the sink and source.
4. (a) Explain the applications of Boltzmann equation.  
(b) Explain the differences between classical thermodynamics and statistical thermodynamics.
5. (a) Explain the following:
  - i. Gibb's free energy
  - ii. Helmholtz function.  
(b) Prove that where w is maximum possible arrangements  $W = \frac{n!}{n_0!n_1!n_2!}$
6. (a) 'Fugacity of a component is equal to its activity for ideal solution'. Say true or false and then explain why is it so.  
(b) Derive an expression for the change in free energy when 1 gm mole of a pure substance goes in solution.
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) Mention some applications of kinetics to Metallurgical processes.  
(b) Distinguish between molecularity and order of a reaction.

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1. State and explain the following laws.
  - (a) Boyle's law
  - (b) Charle's law
  - (c) Dalton's law
  - (d) Henry's law
  - (e) Avagadro's hypothesis.
2. (a) Derive an expression for the work done in isothermal process.  
(b) calculate the work done when a gas of 'n' moles is
  - i. expanded to twice the original volume
  - ii. compressed to half its original volume isothermally at temperature 'T'.
3. (a) Discuss the second law of thermodynamics using classical viewpoint. How is entropy defined in this approach? Can the entropy of a system decrease? Explain.  
(b) Calculate standard entropy of a metal at  $650^{\circ}\text{C}$  if its entropy at  $27^{\circ}\text{C} = 5 \text{ Cal/gm/mole}$  and  $C_p = 5.4 + 1.2 \times 10^{-3}T \text{ Cal/gm/mole}$ .
4. (a) What is statistical thermodynamics.  
(b) Explain the basic postulates of statistical thermodynamics.  
(c) Differentiate between microstate, macro state and most probable macrostate.  
(d) 'According to statistical thermodynamics each macrostate consists of a very large number of quantum states'. 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) State and explain third law of thermodynamics. What is it's importance.  
(b) Derive an expression to show variation of equilibrium constant with temperature.
7. (a) From the Classius-Clapeyron equation, derive the following expression for the vapor pressure of liquid metal.  
 $\text{Log } P = \frac{A}{T} + B$  where A and B are constants.

- (b) The vapor pressure 'p' of liquid A is given by  $\log P(mm) = \frac{-2450}{T} + 6.69$  and that of solid A by  $\log P(mm) = -6947/T + 10.8$   
Calculate the temperature at which liquid and solid will have the same vapour pressure.
8. (a) Suppose that the absolute rate of a certain process cannot be measured but the ratio of the rates  $\frac{r_2}{r_1}$ , at the two temperatures  $T_2$  and  $T_1$  can be measured. Find the activation energy of this process in terms of  $T_2, T_1$  and  $r_2/r_1$ .
- (b) Distinguish between the molecularity and order of a reaction.

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1. (a) Define and explain the following:
  - i. Critical temperature of gas
  - ii. Critical pressure of gas
  - iii. Critical volume of gas.(b) Write notes on the following:
  - i. Equation of state
  - ii. Assumptions of kinetic theory of gases
  - iii. Closed system & isolated system.
2. (a) Show that internal energy is function of temperature only.  
(b) The internal energy of a closed system is given by  $U = 100 + 50T + 0.04T^2$  in Joules. The heat absorbed  $Q = 4000 + 16T$  in joules.(T is in Kelvin). If the system changes from 500 K to 1000K, what is the work done.  
(c) Calculate the work transfer and change in internal energy if the gas is changing it's state from 1 bar,  $27^{\circ}C$  to 20 bar,  $400^{\circ}C$  polytropically.
3. (a) A carnot's engine cannot be realised in actual practice. Explain why?  
(b) Assuming that the working substance in a carnot's engine is a perfect gas. Show that the ratio of heat rejected at the sink to that extracted at the source equals the ratio of absolute temperatures of the sink and source.
4. (a) 'Entropy is a non conserved property'. Explain satisfactorily with suitable examples.  
(b) Explain the follows:
  - i. Thermodynamic probability
  - ii. Isentropic process
  - iii. Entropy generation.
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) From the Classius-Clapeyron equation, derive the following expression for the vapor pressure of liquid metal.  
Log  $P = \frac{A}{T} + B$  where A and B are constants.
- (b) The vapor pressure 'p' of liquid A is given by  $\log P(mm) = \frac{-2450}{T} + 6.69$  and that of solid A by  $\log P(mm) = -6947 + 10.8$   
Calculate the temperature at which liquid and solid will have the same vapour pressure.
8. (a) Explain unimolecular reactions with examples.
- (b) Describe a few methods of determination of standard free energy changes of reactions.

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1. (a) Define and explain the following terms
  - i. system
  - ii. Thermodynamic state
  - iii. process
  - iv. Function.
- (b) Explain how *zero<sup>th</sup>* law of thermodynamics leads to the postulation of an empirical temperature scale.
2. (a) Derive an expression for the work done in isothermal process.
- (b) calculate the work done when a gas of 'n' moles is
  - i. expanded to twice the original volume
  - ii. compressed to half its original volume isothermally at temperature 'T'.
3. (a) Discuss the second law of thermodynamics using classical viewpoint. How is entropy defined in this approach? Can the entropy of a system decrease? Explain.
- (b) Calculate standard entropy of a metal at  $650^{\circ}\text{C}$  if its entropy at  $27^{\circ}\text{C} = 5 \text{ Cal/gm/mole}$  and  $C_p = 5.4 + 1.2 \times 10^{-3}T \text{ Cal/gm/mole}$ .
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  $\Delta S_{surr}$  depend on the temperature of surroundings? Explain.
5. (a) What are Maxwell relations and what is their necessity.
- (b) Why Gibb's free energy is called a thermodynamic potential? Explain
- (c) Show that the work done by a system during an adiabatic process is equal to the decrease in the internal energy of the system.
6. (a) What is the relation between free energy and equilibrium constant for any reaction and explain.
- (b) At equilibrium of any reaction what is the relation of free energy change and equilibrium constant and explain.

7. (a) Explain the practical importance of Classius-Clapeyron equation.  
(b) List the assumptions made in deriving the integrated form of the Clausius-Clapeyron equation.
8. (a) Derive an expression for half-life of a first order reaction.  
(b) What is a catalyst? What is the importance of catalysis in chemical reactions?

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