Code No: RR221801 **Set No. 1**

II B.Tech II Semester Supplementary Examinations, November/December 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) Explain the deviations of gases from ideal behavior.
   (b) Calculate the pressure of 2 moles of air at 400K, with a total volume of $0.5m^3$. Use ideal gas and vander waal's equation. [6+10]

2. (a) Distinguish between steady flow and unsteady flow.
   (b) Explain the importance of adiabatic portions in the conceptualization of thermodynamic equilibrium.
   (c) State the Hess law of reaction of heats and explain its use. [4+4+8]

3. (a) Is it possible for the entropy change of a closed system to be zero during an irreversible process? Explain.
   (b) What three different mechanisms can cause the entropy of a control volume to change? Explain.
   (c) If the value of $C = a + bT + cT^{-2}$, find the expression for $S_T - S_{298}$ in terms of T (S is entropy;) [5+6+5]

4. (a) What is Nernst heat theorem. Define and explain the theorem with the help of relevant equation.
   (b) What is entropy generation? Can the entropy generation be negative? Explain. [10+6]

5. (a) Explain the following:
      i. Gibb's free energy
      ii. Helmholtz function.
   (b) Prove that where w is maximum possible arrangements $W = \frac{n!}{n_0!n_1!n_2!}$. [8+8]

6. (a) Explain the deductions of third law of thermodynamics.
   (b) Explain various methods of calculation of $\Delta\ S^0$ for a chemical reaction. [8+8]

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. [10+6]

8. (a) Define the term 'specific reaction rate constant'. From consideration of the theory of absolute reaction rates, derive an expression for the specific reaction rate constant of a reaction.

   (b) Explain the kinetic equation for first order reaction. [8+8]

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1. (a) Derive an expression for Boyle temperature in terms of vanderwall's constants.
   (b) Explain the term 'internal energy' of a system.
   (c) Calculate the increase in internal energy of a gaseous system at a constant pressure of one atmosphere when 10 calories of heat (or energy) are added and the volume of the system increases by 100^0C. [6+4+6]

2. Compare and contrast the following.
   (a) Open system and closed system.
   (b) Intensive property and extensive property
   (c) State property and path property.
   (d) Heterogeneous and homogeneous systems. [16]

3. (a) Prove that Kelvin-Plank and clausius statements of second law of thermodynamics are identical
   (b) Prove that $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$. [8+8]

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_{surr} depend on the temperature of surroundings? Explain. [5+5+6]

5. (a) Define Helmholtz energy function and explain its significance.
   (b) Derive the relationship between the standard free energy change and the equilibrium constant of a reaction. [8+8]

6. (a) What is meant by the 'standard free energy change' of a reaction? Derive an expression relating it to the equilibrium constant of the reaction.
   (b) What is the significance of the sign of free energy change? [10+6]

7. (a) Derive the equation dG = Vdp-sdt and explain its significance.
   (b) Using the above equation, derive Clausius-Clapeyron equation. [8+8]

8. (a) Explain unimolecular reactions with examples.

(b) Describe a few methods of determination of standard free energy changes of reactions. [6+10]

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1. (a) Derive equations relating critical temperatures, critical pressure and critical volume with vanderwaal's constants.
   (b) How is the most probable macrostate determined with in a given system? [10+6]
2. (a) Distinguish between steady flow and unsteady flow.
   (b) Explain the importance of adiabatic portions in the conceptualization of thermodynamic equilibrium.
   (c) State the Hess law of reaction of heats and explain its use. [4+4+8]
3. (a) Prove that Kelvin-Plank and clausius statements of second law of thermodynamics are identical
   (b) Prove that $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$. [8+8]
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.
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   (c) When heat is added to the surroundings, the entropy of the surroundings increases. How does ΔS_{surr} depend on the temperature of surroundings? Explain. [5+5+6]
5. (a) Explain the following:
      i. Gibb's free energy
      ii. Helmholtz function.
   (b) Prove that where w is maximum possible arrangements $W = \frac{n!}{n_0!n_1!n_2!}$. [8+8]
6. (a) Derive the relationship between the standard free energy change and the equillibrium constant of a reaction.
   (b) Explain the vapour pressure of an element. [12+4]
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+8]

8. (a) Explain the steps involved in the determination of order of a reaction.
   (b) Explain the theory of absolute reaction rates. [8+8]

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1. (a) Explain kinetic theory of gases.
   (b) Explain the following:
      i. Heat capacity at constant volume.
      ii. Heat capacity at constant pressure. [6+10]

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? [6+6+4]

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 650^0C if its entropy at 27^0C = $5\ Cal/gm/mole$ and $C_p = 5.4 + 1.2 \times 10^{-3}T\ Cal/gm/mole$. [8+8]

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_{surr} depend on the temperature of surroundings? Explain. [5+5+6]

5. (a) Define Helmholtz energy function and explain its significance.
   (b) Derive the relationship between the standard free energy change and the equilibrium constant of a reaction. [8+8]

6. (a) State and explain third law of thermodynamics. What is it's importance.
   (b) Derive an expression to show variation of equillibrium constant with temperature. [6+10]

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+8]

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_1can 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. [10+6]

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