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

**II B.Tech II Semester Regular Examinations, Apr/May 2006**
**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) 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. (a) Explain the limitations of first law of Thermodynamics.
   (b) How is irreversibility explained by classical thermodynamics?
   (c) Derive an expression for work done in a process in which PV=constant. [4+4+8]

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. [6+5+5]

4. (a) Explain in which phenomenon the number of distributions have any connection with energy? Explain it in detail with neat sketches.
   (b) What are the causes for deviation from perfect order in a solid material? Explain them fully. [10+6]

5. (a) Distinguish between Gibb's and Helmholtz free energies. What is their significance?
   (b) From fundamentals, derive Maxwell's relations. [6+10]

6. (a) Discuss the importance of sigma function in evaluation of fugacity.
   (b) Explain the effect of temperature on equillibrium constant.
   (c) How is equillibrium constant determined at any time. [6+5+5]

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 the standard free energy change for any reaction.

(b) Determine the equillibrium constant at $25^0C$ for the reaction. $CH_4(g) + H_2O(\ell) \rightarrow CO(g) + 3H_2(g)$. [6+10]

Data

| Component | $\Delta^0G$ *at* $25^0C$ |
|---|---|
| CO $(g)$ | - 137.8 KJ/mole |
| $CH_4(g)$ | - 50.09 KJ/mole |
| $H_2O(l)$ | - 238.0 KJ/mole |

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Code No: RR221801 **Set No. 2**

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1. (a) Name the following systems with proper explanation.
   i. A container having water and ice exchanging heat with surrounding.
   ii. A system consisting of sugar in water.
   iii. A system consisting of air in a closed container having perfectly insulated walls.
   (b) Bring out the differences among the following.
   i. Thermodynamic system
   ii. Thermodynamic process
   iii. Thermodynamic cycle. [8+8]

2. (a) For an adiabatic process prove $pv^{\gamma}$= constant.
   (b) Explain the usefulness of Kirchoff's equation in thermodynamics.
   (c) Calculate the percentage error in the determination of heat of reaction of pure solid $Na_2o$ with $Hcl$ gas at 1 atmosphere pressure to form solid and $NaCl$ water at $25^0$. The standard heats of formation in $Kcal.Mol^{-1}$are.
   $NaCl(s)$ : $-98.6 \pm 0.2$
   $Na_2O(s)$ : $-100.7 \pm 1.2$
   $HCl(g)$ : $-22.0 \pm 0.1$
   $H_2O(l)$ : $-68.32 \pm 0.01$ [5+5+6]

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) Explain the applications of Boltzmann equation.
   (b) Explain the differences between classical thermodynamics and statistical thermodynamics. [8+8]

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) 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) 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* $T_1$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. [10+6]

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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. (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'.
   [8+8]

3. (a) What is entropy and discuss how it is related to the degree of disorder.
   (b) Derive equations for the entropy changes in ideal gases for the following processes.
      i. Adiabatic process
      ii. Isothermal process
      iii. Isobaric process. [6+10]

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. [6+10]

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 the relation between free energy and equillibrium constant for any reaction and explain.
   (b) At equillibrium of any reaction what is the relation of free energy change and equillibrium constant and explain. [8+8]

7. (a) Derive the Classius-Clapeyron equation for liquid-vapor equilibrium.

   (b) The vapour pressure of a substance A at $34.7^0$C is 100 mm Hg and the heat of vaporization of A is 38.6 kj/mole. What is the vapour pressure of A at $65^0C$? $(Data : \Delta\ H_{vap} : 38.6\ kj/moleR = 8.3145\ J/mol/K)$. [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) Define and explain the following terms
   i. system
   ii. Thermodynamic state
   iii. process
   iv. Function.
   (b) Explain how $zero^{th}$ law of thermodynamics leads to the postulation of an empirical temperature scale. [8+8]

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) State and explain second law of thermodynamics.
   (b) Define and explain entropy. What are its units.
   (c) Explain the principle of increase of entropy. [6+5+5]

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+5+6]

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. [8+8]

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. [8+8]

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) The gas phase reaction of nitric oxide and Bromine Yields NOBr.
   $2\ NO(g) + Br_2 \rightarrow 2\ NOBr(g)$.
   The rate law is $= K[NO]^2[Br_2]$.
   What is the reaction order with respect to the each of the reactants, and what is the overall reaction order?

   (b) The gas phase reaction of Hydrogen and Iodine monochloride,
   $H_2(g) + 2\ ICl(g) \rightarrow 2\ Hcl(g) + I_2(g)$ 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. [8+8]

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