B. E. (MET) 3rd Semester Examination, December 2011

Subject: METALLURGICAL THERMODYNAMICS AND KINETICS   Code: MT 302

Time: Three hours   Answer any Seven   **Full marks: 70**

1. Answer all questions by writing only True (T) or False (F). Write nothing else. Answer at one place please. 10x1=10

a. For carbon reduction of stable metal oxides, equilibrium p_{co}/p_{Co2} increases with increasing temperature.
b. In exothermic reactions, reaction rate decreases with increase in temperature.
c. In industrial operations, productivity depends more on kinetics than thermodynamics.
d. For some reactions, activation energy can have zero value.
e. For a rate controlling step, materials accumulate at the input end and not at the output end.
f. Both vibrational and configurational entropy become zero at absolute zero temperature.
g. According to Ellingham's diagram carbon reduces Fe_2O_3 at a lower temperature compared to Al_2O_3.
h. No $CaCo_3$ can decompose below its decomposition temperature.
i. The entropy of mixing of two components A and B is identical for ideal and regular solutions.
j. In a binary A-B solution, when X_B (mole fraction of B), approaches zero then the activity coefficient approaches unity.

2. Answer any two 5x2=10

a. A fused salt mixture has equal number of moles of $CaBr_2$, NaCl and KI. Calculate activity of $CaCl_2$.
b. Derive the kinetic equation for reaction of spherical solid with a gas when the reaction rate depends on solid surface area.
c. Derive the parabolic rate law for reaction of a flat plate of solid with gas when reaction is controlled by diffusion across a product layer.
d. In a reaction, a product starts accumulating from a zero value at 20% per hour. What is the rate constant and what is the rate equation?

3. Discuss validity/invalidity of any two of the following statements. 10

a. Reduced time plots can be used to calculate activation energy of a reaction.
b. If Johnson-Mehl equation is applicable for a reaction then the rate constant can be directly obtained from the α-t plot.
c. The heat of mixing in a binary A-B system follows the following equation: $(\Delta H_m)/X_A.X_B = a+bX_B$; where X is mole fraction and a and b are constants. The solution is regular.
d. The limiting current density during electrolysis arises out of slow discharge [i.e., $M^{n+} + n_e - M$] at the cathode surface

4. Justify the following: 10

a. The stability of a phase depends not only on free energy but also on entropy.
b. The common tangent points in the free energy vs. composition curve always reflect the stability of the co-existing phases.
c. Regular solution may be considered as in between ideal and non-ideal solution.
d. Henry's law is only applicable for dilute solution.

5. Prove the following: 4+3+4

a. In a binary solution, if the solute follows Henry's Law, the solvent follows Raoults Law.
b. Heat of formation of an ideal solution is zero
c. The volume of thermal expansion coefficient α of a substance is defined as: $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and the compressibility β is defined as $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$
Prove: $C_P = C_V + \frac{\alpha^2 VT}{\beta}$

6. a. Discuss third law of thermodynamics. How is this law different from other two laws of thermodynamics? 2+2=4
b. Mathematically establish the expression for entropy using the concept of statistical thermodynamics. 6

7. a. Discuss the effect of temperature on free energy. 5
b. State the necessity for the introduction of Gibbs free energy over Helmholtz free energy. 4
c. Why is Gibbs free energy called 'free'? 1

8. a. State the properties of an ideal solution. 3
b. Define fugacity. How is this related with activity? 5
c. What is activity coefficient? 2

9. a. Justify the shape of free energy vs. composition curve for a binary regular solution. 8
b. Define congruent melting. 2

10. a. The activity coefficient of Zn in liquid Zn-Cu alloy in the temperature range of 1070 to 1300 K can be expressed as:
$RT\ln\gamma_{Zn} = -31{,}600\, N^2_{Cu}$ where R=8.314 J/mol/K
Calculate the activity of Cu in Cu-Zn binary solution of $N_{Cu} = 0.7$ at 1300 K 5
b. A solution is composed of benzene and toluene. The Raoult's law holds for both benzene and toluene. The equilibrium vapour pressures of benzene and toluene are 102.4 kPa and 39.0 kPa respectively at 81°C. Calculate the mole fraction of benzene in the vapour which is in equilibrium with $N_B = 0.5$ solution. 5