B.Tech- 3rd (MME)

Metallurgical Thermodynamics & Kinetics

Full Marks : 50

Time : $2\frac{1}{2}$ hours

Answer **all** questions

The figures in the right-hand margin indicate marks

Symbols carry usual meaning

1. Answer *all* questions : 2×5

(*a*) Consider a reaction with activation energy of 8.314 kJ/mol that takes place at 300K. If the reaction rate is to be tripled, what should be the temperature of the reaction ?

(*b*) The melting point and latent heat of fusion of copper are 1356 K and 13 kJ/mol, respectively. Assume that the specific heats of solid and liquid are same. Calculate the free energy change for liquid to solid transformation at 1250 K.

(*c*) Write any two important features of Ellingham diagram. What are its limitations ?

(*d*) Derive the combined expression for 1st and 2nd Faraday's laws of electrolysis.

(*e*) Differentiate between TGA and DSC, any four differences.

2. (*a*) Prove that (δq) is not perfectly differentiable but (δq/T) is perfectly differentiable. 4

(*b*) State the laws of thermodynamics and write their importance in metallurgy. Derive the necessary equations for the combined statements of first and second laws of thermodynamics. 4

Or

(*a*) What is Hess's law, explain with an example ? Calculate the heat of the reaction

for the formation of solid WO_3 from solid W and O_2 gas at 298 K. Given the following data at 298 K and 1 atm pressure : 5

$$\langle W \rangle + (O_2) = \langle WO_2 \rangle ; \Delta H^0_{298} = -134 \text{kcal}$$

$$\langle W_3O_8 \rangle = 3\langle WO_2 \rangle + (O_2); \Delta H^0_{298} = -48.83 \text{kcal}$$

$$3\langle WO_3 \rangle = \langle W_3O_8 \rangle + \frac{1}{2}(O_2); \Delta H^0_{298} = -22.17 \text{kcal}$$

(*b*) Prove that $C_P - C_V = R$ and $C_P > C_V$. 3

3. (*a*) Calculate the equilibrium constant and equilibrium partial pressure of oxygen at 1800°C for the reaction : $ZrO_2 = Zr + O_2$; $\Delta G^0 = 1087589 + 18.12T \log T - 247.36\ T$ J. Also predict the possibility of decomposing a pure zirconia crucible under a vacuum of 10^{-5} mm of Hg at that temperature. 4

(*b*) Prove that the entropy of a perfect gas is

$$\Delta S = S_2 - S_1 = R \ln\left(\frac{V_2}{V_1}\right) = -R \ln\left(\frac{P_2}{P_1}\right).$$ 4

Or

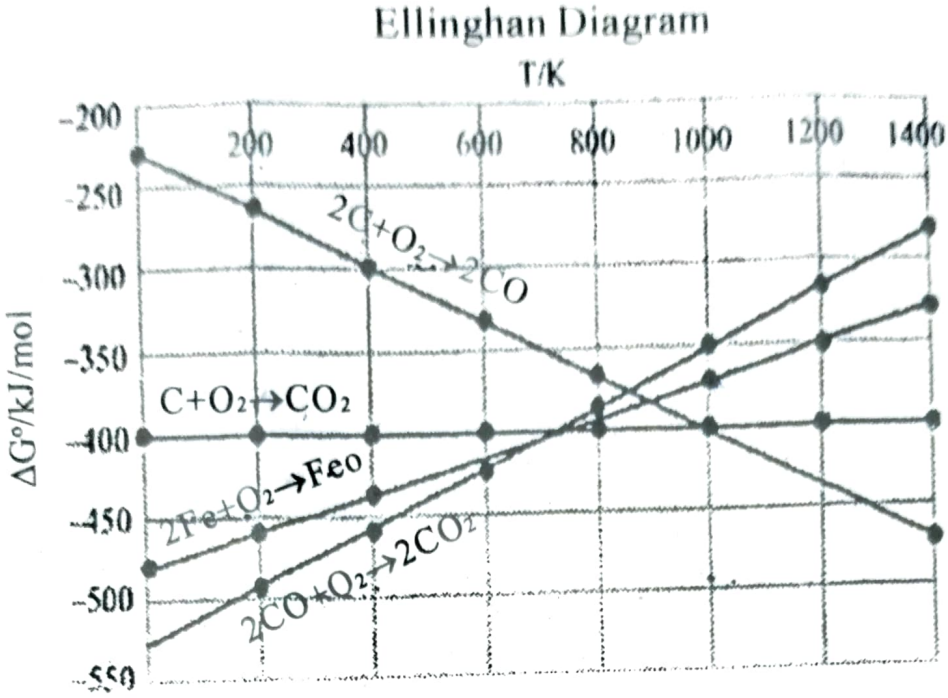
(*a*) Derive Gibbs-Duhem equation and express in terms of G, A, H, S. 4

(*b*) Pure orthorhombic sulfur transforms to stable monoclinic sulfur above 368.5K. Using third law of thermodynamics, calculate the value of entropy of transformation at 368.5 K. Given : 4

(*i*) Entropy change associated with heating orthorhombic sulfur from 0 K to 368.5 K is 36.86 J/K.

(*ii*) Entropy change associated with cooling monoclinic sulfur from 368.5 K to 0 K is –37.8 J/K.

4. (*a*) The following Ellingham diagram depicts the oxidation of 'C', 'CO' and 'Fe'. Which of the following statements are correct, explain with full justification ? 4



I. FeO can be reduced by C below 600K.

II. FeO can be reduced by CO below 600K.

III. FeO can be reduced by C above 1000K.

IV. FeO can be reduced by CO above 1000K.

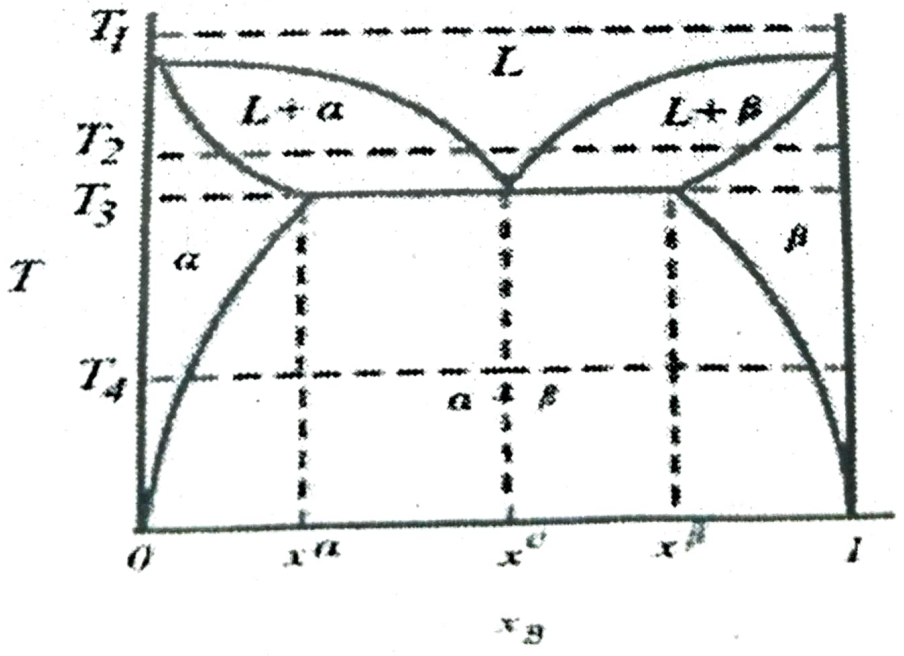
(*b*) Derive the relation, $\Delta H^m = \Omega X_A X_B$ using quasi-chemical approach. 4

Or

(*a*) Discuss the steps to determine the point O, H, C and equilibrium gas pressure using Ellingham diagram. 5

(*b*) For the given reaction :
$Ni + 0.5O_2 = NiO$, $\Delta G^0 = -250000 + 100T$ J.
At 927°C, calculate the p_{o_2} in equilibrium with Ni/NiO ? 3

5. (*a*) Draw the free energy (G) vs composition (X) diagram for the given phase diagram at temperatures T_1, T_2, T_3, T_4. 4



(*b*) What is chemical potential ? Write the equation of chemical potential of species i and also write the combined equations of 1st law and 2nd law of thermodynamics in relation to chemical potential. What are the applications of chemical potential in metallurgy ? 4

Or

(*a*) Draw the free energy-composition curves for a regular solid solution of AB alloy system under below given conditions :

i. $\Delta H_{mix} = 0$, at low temperature and higher temperature

ii. $\Delta H_{mix} > 0$, at low temperature and higher temperature

iii. $\Delta H_{mix} < 0$, at low temperature and higher temperature. 5

(*b*) What is Raoult's law of ideal solutions ? Express the Henry's law. What is the

significance of these two laws in forming solid solution in a binary alloy system, explain ? 3

6. (*a*) Draw the cooling curves (i) for a pure metal without supercooling, (ii) for a pure metal with supercooling, (iii) for a solid solution alloy, (iv) for a hypoeutectic alloy. What difference you observe from these cooling curves, explain ? 5

(*b*) What is the voltage required to electronically refine impure copper of activity = 0.9 (Raoultion standard state) to pure copper at 27°C. 3

Or

(*a*) How the rate-controlling step is determined and state its importance in metallurgy with a suitable example ? 5

(*b*) State and express Sievert's law. Calculate solubility of N_2 gas under 1 atm pressure & 1600°C in an iron-based alloyed having the composition C = 3.5%, Mn = 1%, Si = 1.2%, P = 0.5%. The interaction parameters for various components are $\epsilon_N^C = 0.25 \times 2.3$, $\epsilon_N^P = 0.51 \times 2.3$, ϵ_N^{Mn} 0.02×2.3, $\epsilon_N^N = 0$, $\epsilon_N^{Si} = 0.047 \times 2.3$, Sievert's constant for $N_2(K_P) = 0.045$. 3