Max. Marks : 80 (40+40)

Total Time : 2 hours

CHL721 – Adv Chemical Engg Thermodynamics

MAJOR

10. 5. 2016

(Part A : Answer on these sheets only; Be Precise & Relevant)

1. State the degrees of freedom for the following : **[4]**

   (a) System of two miscible, non-reacting species which exists as an azeotrope in vapour-liquid equilibrium. ________________

   (b) A system prepared by partially decomposing $CaCO_3$ into an evacuated space. Rx^n : $CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$ ________________

2. For solid-liquid equilibria, write the exact expression to evaluate ψ_i using H_i^l and H_i^s . ψ_i is the ratio of pure component fugacities f_i^s/f_i^l . _________________________ **[6]**

   If temperature effect on enthalpies can be ignored, then ψ_i can be written _________________________

   If liquid phase is an ideal soln and in the solid phase both species are completely immiscible, then liquid mole fractions x_1 and x_2 are : _________________________

3. For the micro-canonical ensemble with its natural variables (E, V, N), do E and N fluctuate ? For this ensemble, write the expression/relation for (i) probability of state ν, P_ν (ii) entropy, S and (iii) Boltzmann factor β (= $1/k_BT$). **[6]**

4. Write the natural variables for the Grand canonical ensemble. Which system does this ensemble represent and what are the two variables which fluctuate ? **[8]**

   For the g-canonical ensemble write the probability P_ν and the partition function, Ξ . Starting with the Gibbs entropy formula, obtain the expression for S in terms of Ξ and other variables. What is $\ln \Xi$ = ?

Name : ______________________ Entry # ______________________

5. What is the significance of Curie temperature ? **[8]**

In words state what is the mean field approximation (w.r.t. Ising magnet model) and what is its utility ?

Write the mean field $< H_i >$ in terms of H, J, z, s_i and μ .

6. Why do surfactant molecules 'self-assemble' ? **[8]**

When are spherical micelles more expected ?

For a system of non-interacting α-micelles the partition function is given below :

$$Q^{id} = \prod_{\alpha=1}^{N} [(V q_\alpha^{int} / \Lambda_\alpha^3)^{n_\alpha} / n_\alpha !] \quad ; \; n_\alpha = N_\alpha / \alpha$$

From this obtain the chemical potential, μ_α .

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(Part B)

1. An isomerization reaction, $A \rightarrow B$, occurs in liquid phase. A and B are miscible liquids for which

$$G^E/RT = x_A x_B$$

For the reaction $\Delta G^\circ = -1000$ J/mol at 25 °C.

(a) what is the equilibrium composition of the mixture, if the reaction occurs at 25 °C ?

(b) how much error is there if A and B are taken to form an ideal solution ? **[10]**

2. (a) Starting with entropy S which is natural function of (E, V, N), obtain the Legendre transforms of entropy that are natural functions of (i) (T, V, N) and (ii) (1/T, V, μ/T). Show all steps clearly.

(b) The canonical partition function for a gas (system of N particles each of mass m) is given below :

$$Q(N,V,\beta) = (1/N!)\left[(2\pi m/h^2\beta)^{3N/2}(V-Nb)^N e^{\beta a N.N/V} \right] \quad ; \quad a, b \text{ are constants}$$

(i) Although it is not so, assuming it to be a system of non-interacting, indistinguishable particles, what is the equivalent single particle partition function 'q' ?

(ii) From the system partition function Q, obtain the equation of state of the gas. **[10]**

3. Consider a system of N distinguishable, non-interacting spins, n_i (each of magnetic moment μ) in an applied external magnetic field, H. Each spin can take only two states, +1 or −1 , i.e. parallel or anti-parallel to the applied field H. However total magnetization M is fixed, i.e. in an ensemble all members have the same number of up spins, n_+ . $N = n_+ + n_-$ E (energy) and H, N are the natural variables of the ensemble to be used.

(a) Which ensemble should be used ? What are M and E for the above ?
(b) Obtain the entropy S and the relation for β (= $1/k_BT$)
(c) For large N, find βH in terms of μ, N, n_+ and H
(d) From (c) get n_+ and hence M **[12]**

4. In the lattice gas model, $n_i = 0$ or 1 denotes whether a cell is empty or occupied by the particle. The interaction energy between two neighbouring particles 1 and 2 is given by

$$\varepsilon_{12} = -\varepsilon \quad \text{if} \quad n_1 = n_2 = 1 \; ; \text{ and } = 0 \text{ otherwise}$$

If the lattice has N cells, find the total energy E_p and the particles N_p for use in the grand canonical partition function Ξ . Use also the variable transformation $s_i = 2n_i - 1$, i.e. s_i takes the values ± 1, as in the Ising magnet model.

Write Ξ as Q with E_{eff} to correspond to the Ising model and find the corresponding lattice gas J and H.

State also for the lattice gas what is (i) the order parameter (ii) the equivalent of Curie point. **[8]**