Birla Institute of Technology and Science, Pilani
First Semester, 2016-17
CHE G622, Advanced Chemical Engineering Thermodynamics

Comprehensive Examination — **3rd December, 2016 (2:00 -5:00 PM)**
Max Time: 3Hr — **Total Max Marks:105**

- Concept is only important, not the answer
- Refer the equations, table and book which you have used.
- Box the final and intermediate answers
- Don't skip any mathematical steps-otherwise you will lose marks
- Mention unit for the intermediate and final answers-otherwise you will lose marks

Q1: A system consists of N numbers of noninteracting, distinguishable two-level atoms. Each atom can exist in one of two states, $E_0 = 0$, and $E_1 = \varepsilon$. The number of atoms in energy level E_1 is n_1. The total internal energy of the system is $U = n_0E_0 + n_1E_1$.

(a) Compute the entropy of the system as a function of total internal energy.
(b) Compute the heat capacity of N number of atoms. **[7]**

Q2. A lattice contains N numbers of normal lattice sites and N numbers of interstitial lattice sites. N identical atoms are on the lattice, M on the interstitial sites and N─M on the normal sites (N>>M >>1). If an atom occupies a normal sites, its energy E = 0. If an atom occupies an interstitial site, its energy is E = ε. Compute the internal energy and heat capacity as a function of temperature for this lattice. **[8]**

Q3: Consider a ternary system comprising solute species 1 and a mixed solvent (species 2 and 3). Assume that:

$$G^E/RT = A_{12}x_1x_2 + A_{13}x_1x_3 + A_{23}x_2x_3$$

(a) Show mathematically that Henry's constant H_1 for species 1 in the mixed solvent is related to Henry's constants $H_{1,2}$ and $H_{1,3}$ for species 1 in the pure solvents by:

$$\ln H_1 = x'_2 \ln H_{1,2} + x'_3 \ln H_{1,3} - A_{23}x'_2x'_3$$

Here x'_2 and x'_3 are solute free mole fractions; $x'_2 \equiv x_2/(x_2+x_3)$, and $x'_3 \equiv x_3/(x_2+x_3)$ **[10]**

Q4: For a multicomponent mixture containing any number of species, prove that

$$\bar{M}_i = M + \left(\frac{\partial M}{\partial x_i}\right)_{T,P} - \sum_k x_k \left(\frac{\partial M}{\partial x_k}\right)_{T,P}$$

where the summation is all over the species. Show that for a binary mixture this result reduces to

$\bar{M}_1 = M + x_2\left(\frac{dM}{dx_1}\right)$ and $\bar{M}_2 = M - x_1\left(\frac{dM}{dx_1}\right)$ **[10]**

Q5: Possible correlating equations for $\ln \gamma_1$ in a binary liquid system are given below. **[10]**

(a) $\ln\gamma_1 = Ax_2^2$; (b) $\ln\gamma_1 = x_2^2(A + Bx_2)$; (c) $\ln\gamma_1 = x_2^2(A + Bx_2 + Cx_2^2)$

For all these cases

a) Determine the expressions for $\ln \gamma_2$ by integrating the Gibbs/Duhem equation ($\sum_i x_i d\ln\gamma_i = 0$)
b) Derive the corresponding equations for G^E/RT. Note that by its definition, $y_i = 1$ for $x_i = 1$.

Q6: Departures from Raoult's law are primarily from liquid-phase nonidealities ($\gamma_i \neq 1$). But vapor-phase nonidealities ($\phi_i \neq 1$) also contribute. Consider the special case where the liquid phase is an ideal solution, and the vapor phase a nonideal gas mixture described by Z= PV/RT= 1+ BP/RT. Show that departures from Raoult's law at constant temperature are likely to be negative. State clearly any assumptions and approximations. **[15]**

Q7: Estimate the activity coefficients for the system CCl_4(1)-EtOH(2) at 70 °C and x_1= 0.4 using the UNIQUAC method. **[15]**

Q8: CO is burned with stoichiometric amount of Air. If CO and air enter the burner at 298.15 K and 1 bar and the burner is completely insulated, determine the temperature and composition of the gas leaving the burner. Use graphical method. **[15]**

Q9: Derive the necessary equations to determine three suffix Margules parameters starting from the three suffix Margules equations. Consider a binary system. **[15]**