Ref. No.: Ex/ChE/T/223/2017

B.E. Chemical Engineering 2nd year 2nd Semester Examination 2017
Chemical Engineering Thermodynamics

Assume any missing data
All symbols have their usual meaning
Answer any *four* questions

Time: 3 hours Marks: 100

1(a) Derive the following relation using Jacobian method (7)

$$dS = \frac{C_p}{T}dT - \beta v T dP$$

(b) Derive Clausius-Clapeyron equation $\frac{d\ln P}{dT} = \frac{\Delta h_v}{RT^2}$ (7)

(c)

(i) Determine the state of pure acetone at 70 °C and 2.5 atm. (3)

(ii) Determine the fugacity at this temperature and pressure (8)

The vapor pressure of acetone is given by $\log_{10} P^{sat}(\text{torr}) = 7.117 - \frac{1210.595}{t(^\circ C) + 229.664}$.

The volumetric behavior of acetone in the vapor phase can be represented by $Z = 1 - 10.12\frac{P}{T}$

The density of liquid acetone is 790 kg/m^3 and may be assumed to be constant.

2(a) Calculate the enthalpy of n-octane vapor at 450K and 0.2 MPa. Choose the reference state to be saturated liquid at 0 °C. (25)

The following data are provided

$T_c = 569.4K$, $P_c = 24.97\text{bar}$, $\omega = 0.398$ Normal boiling point = 398.4 K

$C_p^o(\text{J/molK}) = 6.907 + 0.741T - 397.2\text{x}10^{-6}T$, T is in K

[Turn over

Riedel correlation $$\Delta h_m = 1.093 T_c \left[T_{br} \frac{\ln P_c - 1.013}{0.93 - T_{br}} \right]$$

Watson correlation $$\frac{\Delta h_{v2}}{\Delta h_{v1}} = \left(\frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38}$$

The compressibility factor may be estimated by the following relation

$$Z = 1 + \frac{BP}{RT}; \qquad \frac{BP_c}{RT_c} = B_o + \omega B_1;$$

$$B_o = 0.083 - \frac{0.422}{T_r^{1.6}}; \qquad B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

The vapor pressure of n-octane can be estimated from the following relation

$$\log_{10} P^{sat}\,(\text{mm Hg}) = 6.918 - \frac{1351.99}{t(^{\circ}C) + 209.155}$$

3(a) At 25 °C and 20 atm, the fugacity $\hat{f}_1$ of component 1 in binary liquid mixtures of component 1 and 2 is given by

$$\hat{f}_1\,(\text{atm}) = 50x_1 - 80x_1^2 + 40x_1^3$$ where, x_1 is the mole fraction of component 1.

For the stated T and P, determine **(2+3+3)**

(i) The fugacity coefficient of pure component 1?

(ii) The Henry's law constant of component 1?

(iii) The expression of activity coefficient of component 1 assuming that standard state is given by Lewis-Randall rule

(b) If the equation $\mu_1 = G_1 + RT \ln x_1$ is a valid expression for the chemical potential of component 1 in a binary liquid system at constant T and P, show that $\mu_2 = G_2 + RT \ln x_2$ for component 2. G_1 and G_2 are the Gibbs free energy for pure liquid components 1 and 2 at T and P. (8)

(c) The volumetric data for liquid mixtures of benzene(b) and cyclohexane (c) are represented by the expression

$$V\left(\frac{\text{cm}^3}{\text{g mol}}\right) = 109.4 - 16.8x_b - 2.64x_b^2; \quad x_b \text{ is the mole fraction of benzene}$$

Find the expression of $\bar{V}_b$, $\bar{V}_c$ and ΔV. (9)

4(a)

(i) Starting from criterion of equilibrium between two phases in terms of chemical potential, derive the expression of liquid-liquid equilibrium between two liquid phases I and II i.e.

$$(x_i\gamma_i)_I = (x_i\gamma_i)_{II}. \qquad (5)$$

(ii) The excess Gibbs free energy for organic acid(1)-water(2) and organic acid(1)-hexane(3) system is given by $G_{12}^E = 80x_1x_2$ and $G_{13}^E = 260x_1x_3$ respectively. Determine the equilibrium concentration of organic acid in hexane phase if it is contacted with the water phase containing 5 mole percent organic acid. Hexane and water can be considered to be immiscible. (10)

(b) The excess Gibbs free energy for a binary liquid solution of *A* and *B* at 70 °C is given by the following relation $\dfrac{G^E}{RT} = 0.33x_Ax_B$

The vapor pressure of pure *A* and *B* can be estimated by

$$\ln P_A^{sat}(\text{mm Hg}) = 18.1 - \frac{4050}{T(K)};\ \ln P_B^{sat}(\text{mm Hg}) = 18.37 - \frac{4050}{T(K)}$$

Determine the equilibrium vapor phase composition in contact with the liquid solution containing 40 mole percent *A* at 70 °C. (10)

5(a) In the steam cracking of methane H_2O, CO, CO_2 and H_2 only are present in a significant amount in the product gas. Determine a set of primary equations. (9)

(b) Butadiene can be prepared by the gas phase catalytic dehydrogenation of 1-butane

$$C_4H_8 \Leftrightarrow C_4H_6 + H_2$$

The butane is diluted with steam to prevent side reaction. Estimate the equilibrium constant of the reaction if 30 percent of 1-butene is converted to 1,3 butediene at a reactor pressure of 2 atm from a feed consisting of 12 mole of steam per mole of 1-butene. (8)

(c) Methanol can be manufactured by the vapor phase hydrogenation of carbon monoxide according to the following reaction $CO(g) + 2H_2(g) \Leftrightarrow CH_3OH(g)$. The reaction is carried out at 2 atm and 350K. The product contains 30 mole percent H_2. Determine the equilibrium constant for reaction from the above data. (8)