Bachelor of Engineering in Chemical Engineering Examination, 2019

(2nd Year, 2nd Semester)

Chemical Engineering Thermodynamics

Time : Three hours Full Marks : 100

(50 marks for each Part)

Use a separate Answer-Script for each Part

PART - I

The symbols have their usual meaning
Assume any missing data
Answer any two questions

1. (a) Estimate the state of water at 150 °C and 2 bar.

(b) Determine the enthalpy of water at 150 °C and 2 bar, given that the enthalpy of liquid water (saturated) at 0 °C is –0.04 kJ/kg. (5 + 20)

The virial coefficient correlation may be assumed to give good representation of equation of state of the system

$$Z = 1 + \left(\frac{BP_c}{RT_c}\right)\frac{P_r}{T_r} = \left(B^o + \omega B^1\right)\frac{P_r}{T_r}$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

The critical temperature, pressure and accentric factor of water are 647.1 K, 220.55 bar and 0.345 respectively.

The vapor pressure of and water is given by

$$\log_{10} P(\text{Torr}) = 8.07131 - \frac{1730.63}{t\left({}^oC\right) + 233.46}$$

Other correlations:

Riedel

$$\frac{\lambda(T_n)}{RT_n} = \frac{1.092\left(\ln P_c - 1.013\right)}{0.93 - T_{r_n}}$$

Watson

$$\frac{\lambda(T_2)}{\lambda(T_1)} = \left(\frac{1 - T_{r_2}}{1 - T_{r_1}}\right)^{0.38}$$

2. (i) The partial molar volume of species 1 in a binary solution at constant t and P is given by

$$\overline{V}_1 = V_1 + \alpha x_2^2$$

(a) What is the corresponding expression of $\overline{V}_2$.

(b) What the expression of V consistent with these equations.

(c) What are the corresponding equations for V^E, $\overline{V}_1^E$ and $\overline{V}_2^E$? (7+2+10)

[Turn over

(ii) The excess Gibbs energy of a liquid mixture at T and P is given by

$$\frac{G^E}{RT} = x_1 x_2 \left(-1.2x_1 - 1.5x_2\right)$$

Find expressions for $\ln \gamma_1$ and $\ln \gamma_2$ (6)

3. The following data are available for the molar volume of liquid mixtures of cyclohexane (1) and carbon tetrachloride at 1 atm and 60 °C

x_1	$V\left(\text{cm}^3/\text{gmol}\right)$	x_1	$V\left(\text{cm}^3/\text{gmol}\right)$	x_1	$V\left(\text{cm}^3/\text{gmol}\right)$
0	101.46	0.2	104.002	0.9	112.481
0.02	101.717	0.3	105.253	0.92	112.714
0.04	101.973	0.4	106.49	0.94	112.946
0.06	102.228	0.5	107.715	0.96	113.178
0.08	102.483	0.6	108.926	0.98	113.409
0.1	102.737	0.7	110.125	1.0	113.64
0.15	103.371	0.8	111.31		

(a) Use the above data to determine V_1, V_2, $\bar{V}_1^\infty$ and $\bar{V}_2^\infty$

(b) Plot ΔV versus x_1 taking Lewis Randall standard state for both components 1 and 2. Determine $\Delta\bar{V}_1$ and $\Delta\bar{V}_2$ at x_1 = 0.35? (25)

PART II

Answer any 2 (two) questions

All symbols have their usual meanings

Assume any missing data

Q1(A)	A binary liquid mixture is in equilibrium with its vapor at 300K. The liquid mole fraction of species 1 is 0.4 and the molar excess Gibbs free energy is 200 J/mol. If $\gamma_1 = 1.09$, calculate the value of γ_2. γ_i denotes liquid-phase activity coefficient of species i in the binary mixture. [5]
Q1(B)	Starting with the simplest form of virial equation prove that the fugacity of a pure liquid species at a pressure (P) and temperature (T) is given by the following expression $$f = P^{sat} \exp\left[\frac{BP^{sat} + v^l(P - P^{sat})}{RT}\right]$$ where B, P^{sat} and v^l are second virial coefficient, saturation vapour pressure and molar volume of the pure liquid, respectively. List your assumptions [5]

[Turn over

Q1(C)

A binary liquid mixture containing 40.5 mol% ethanol (1) and the rest methylcylcohexane(2) exerts an equilibrium pressure of 152.4 mm Hg at 35 ^{0}C and the vapor phase contains 54.7 mol% ethanol. The Antoine equations for ethanol (1) and methylcyclohexane (2) are given below:

$$lnP_1^{sat} = 8.2130 - \left[\frac{1652.05}{t + 231.480}\right]$$

$$lnP_2^{sat} = 6.8230 - \left[\frac{1270.763}{t + 221.416}\right]$$

where P^{sat} and t are in mm Hg and ^{0}C, respectively

a. Based on the experimental data given in the problem statement, estimate the van Laar parameters (α and β) [8]

b. Determine the vapour composition in equilibrium with a liquid mixture containing 60 mol% ethanol at 35 ^{0}C. [7]

The van Laar equations are given below

$$\ln \gamma_1 = \frac{\alpha}{\left[1 + \frac{\alpha}{\beta}\frac{x_1}{x_2}\right]^2} \quad ; \qquad \ln \gamma_2 = \frac{\beta}{\left[1 + \frac{\beta}{\alpha}\frac{x_2}{x_1}\right]^2}$$

$$\alpha = \left[1 + \frac{x_2 \, ln\, \gamma_2}{x_1 \, ln\, \gamma_1}\right]^2 \ln \gamma_1 \ ; \qquad \beta = \left[1 + \frac{x_1 \, ln\, \gamma_1}{x_2 \, ln\, \gamma_2}\right]^2 \ln \gamma_2$$

Q2(A)

An ideal vapour-liquid mixture of n-hexane (1) and n-heptane (2) is under equilibrium conditions. Calculate the following:

(a) vapour composition at 27 ^{0}C when the liquid phase contains 20 mol% n-hexane. [4]

(b) liquid composition at 27 ^{0}C when the vapour phase contains 20 mol% n-hexane. [4]

(c) vapour composition at a total pressure of 30 kPa and the liquid phase containing 20 mol% n-hexane (show calculations for only one iteration). [7]

The Antoine constants for n-hexane and n-heptane are given below:

	A	B	C
n-hexane	13.8216	2697.55	224.37
n-heptane	13.8567	2911.32	216.64

$$\ln P^{sat}(kPa) = A - \frac{B}{t\ (^0C) + C}$$

Q2(B)	The activity coefficients of a benzene (1)–cyclohexane (2) mixture at 40 ^{0}C, are given by $RT \ln\gamma_1 = Ax_2^2$ and $RT \ln \gamma_2 = Ax_1^2$. At 40 ^{0}C benzene-cyclohexane forms an azeotrope containing 49.4 mol % benzene at a total pressure of 202.5 mm Hg. If the vapour pressures of pure benzene and pure cyclohexane at 40 ^{0}C are 182.6 mm and 183.5 mm Hg, respectively, calculate the total pressure for a liquid mixture containing 12.6 mol % benzene at 40 ^{0}C. [10]
Q3(A)	Ethanol is manufactured by catalytic vapour phase hydration of ethylene [C_2H_4 (g) + H_2O (g) $\rightleftharpoons$ C_2H_5OH (g)]. The reactor operates at 400 K and 2 bar and the feed is a gas mixture of ethylene and steam in the mol ratio 1:3. The equilibrium constant at 400 K is 0.25. Estimate the composition of the equilibrium mixture. Assume ideal gas behavior. [15]
Q3(B)	Calculate the pressure required for 50% dissociation of nitrogen tetroxide [N_2O_4 (g) $\rightleftharpoons$ 2 NO_2 (g)] at 300 K. The standard heat of formation and Gibbs free energy of formation of the reactant and product species (298.15 K and 1 atm) are given below: [10]

	Δh_f^0 (kJ/mol)	Δg_f^0 (kJ/mol)
N_2O_4 (g)	9.33	97.947
NO_2 (g)	33.304	51.295