

- Start each solution on a new page.
 - Provide suitable justification for using a particular equation. You can use equations given in the handouts you are carrying or directly inferable from the handout equations without proof/derivation.
 - The exam paper has 4 questions on 2 pages.
 - Symbol(s): Gas constant $R = 8.314 \text{ J / (mol-K)}$
- Best of luck!

P1: Gas solubility in a ternary system [9 Marks]

In this problem we want to determine solubility of CO_2 in a ternary system of Water (1) – Ethanol (2) – CO_2 (3). We will make following simplifying assumptions to model this system:

- CO_2 is only sparingly soluble in the water-ethanol mixture. Hence, its behaviour can be modeled using the Henry's law, with Henry's constant given by:

$$H_{\text{CO}_2} \equiv H_3 = \frac{29000}{x_2} \text{ kPa}$$

- Activity coefficients of water and ethanol in this ternary system can be taken from the data on the binary water-ethanol mixture:

$$\ln \gamma_1 = 1.3x_2^2 ; \quad \ln \gamma_2 = 1.3x_1^2$$

Where, x_1 and x_2 are liquid phase mole fractions of water and ethanol, respectively, in the ternary system.

- At given T, P the vapor phase can be modeled as an ideal gas mixture.

You are asked to determine liquid phase mole fraction of CO_2 (x_3) in the ternary system prepared at 323K and 125 kPa with x_2 (liquid phase ethanol mole fraction)=0.5. The saturation vapor pressures of pure water and pure ethanol at 323K are $P_1^{\text{sat}} = 12.34 \text{ kPa}$ and $P_2^{\text{sat}} = 26.66 \text{ kPa}$, respectively.

- Is the above posed question a determinate problem? Succinctly justify. [1M]
- Obtain the governing equation for x_3 in terms of following variables/parameters:

$$P, x_1, x_2, \gamma_1, \gamma_2, P_1^{\text{sat}}, P_2^{\text{sat}}, H_3. \text{ [5M]}$$

- Solve the equation obtained in part B above to obtain a numerical value for x_3 .
Convergence criterion: relative error in $x_3 < 1\%$. Note that if you take a physically reasonable initial guess for liquid mole fraction(s), you will get convergence in just 2 iterations. [3M].

If you're not able to obtain an equation in part B, solve the following equation to get credit (max. 2.5M) for part C: $x_3 = 10^{-5}(100 - 10x_1\gamma_1 + 5x_2\gamma_2)$

(developed model compares fairly well with published experimental data: I. Dalmolin et al. / Fluid Phase Equilibria 245 (2006) 193–200)

P2: Thermodynamics of a binary liquid mixture from regular solution model [9 Marks]

You will be analyzing mixing thermodynamics of a A-B binary liquid mixture whose molar Gibbs free energy G_{AB} is given by the following expression:

$$G_{AB} = x_A G_A + x_B G_B + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B RT \chi_{AB}$$

where, G_A and G_B are the molar Gibbs energies of respective pure species at the mixture P, T; x_A and x_B are the mole fractions of respective components, and χ_{AB} is a model parameter such that the product $T\chi_{AB} = \text{constant}$, i.e., the product is not a function of T, P, composition.

- Determine enthalpy and entropy changes of mixing for the given binary mixture. [4M]

- B. It is known that for an ideal solution $\chi_{AB} = 0$. Now determine the excess Gibbs energy G_{AB}^E for a non-zero χ_{AB} . [1M]
- C. Discuss physical significance of parameter χ_{AB} in context of your answers in part (A) and (B). Keep your answer clear and concise. [2M]
- D. Obtain an expression for infinite dilution activity coefficient for component A, $\ln \gamma_A^\infty$. [2M]

P3: Work requirement in post-combustion CO₂ separation (12 marks)

You will be determining the minimum work requirement for separation of a high pressure stream of gaseous mixture of CO₂ and H₂. The feed stream (stream 1) is at 40bar and 350K with composition 40-mol-% CO₂ and 60-mol-% H₂. This stream is split in a steady-flow process into two product streams—a H₂ rich stream (stream 2) with composition 6-mol-% CO₂ and 94-mol-% H₂ and a CO₂ rich stream (stream 3) with composition 96-mol-% CO₂ and 4-mol-% H₂. Both the product streams are at 1bar and 350K, i.e., at atmospheric pressure and same temperature as that of feed stream. You may take following assumptions:

- Feed stream 1 can be modeled as an ideal solution of gaseous CO₂ and H₂. At this high pressure, ideal gas assumption is not valid.
- Both the product streams can be modeled as ideal gas mixtures.
- The ideal gas heat capacities in the range of above mentioned conditions of feed and product streams can be taken as constant.

Data.

$$C_p^{ig}: \text{CO}_2 = (9/2)R, \text{H}_2 = (7/2)R$$

Fugacity coefficients at 40 bar and 350K: $\phi_{\text{CO}_2} = 0.85, \left(\frac{\partial \phi_{\text{CO}_2}}{\partial T}\right)_P = 0.0013; \phi_{\text{H}_2} = 1, \left(\frac{\partial \phi_{\text{H}_2}}{\partial T}\right)_P = 0$

- A. Determine the molar entropies of the three streams. The ideal gas reference state entropy @ 1bar and 350K is set to zero for both pure CO₂ and pure H₂, i.e., $S_{\text{CO}_2}^{ig}(1\text{bar}, 350\text{K}) = 0$ & $S_{\text{H}_2}^{ig}(1\text{bar}, 350\text{K}) = 0$. [8M]
- B. Determine the amount of each product stream per mole of feed stream. [1M]
- C. Determine the lost work (kJ per mole of feed) associated with the separation process. You may assume that the process is adiabatic and ignore potential & kinetic energy changes of flow streams. The surrounding temperature $T_\sigma = 300\text{ K}$. If you are not able to obtain values in part A, use following values for part C: $S/R = 0.38, 3.7$ & 3.75 for stream 1, 2 & 3. [3M]

P4: Indicate True/False (0.5M) with proper justification (2M) (4x 2.5= 10 marks)

- A. The chemical equilibrium condition for a single homogenous phase reaction for both gas phase and liquid phase can be written as: $\prod_i (t_i \hat{\phi}_i)^{\nu_i} = \left(\frac{P}{P^\circ}\right)^{-\nu} K$. Here, t_i represents species mole fractions and other symbols have usual meaning.
- B. Raoult's law is based on the assumption of zero interactions between molecules in both the gas phase and the liquid phase.
- C. An isolated system with rigid adiabatic walls is at equilibrium. The rigid adiabatic walls are replaced by rigid conducting walls such that no mass exchange occurs with surroundings. As the system evolves towards a new equilibrium state, its entropy is maximized.
- D. A binary reaction mixture of A & B forms a 2 phase liquid-vapor system. The reaction occurs only in the liquid phase and is given by: $A(l) \rightarrow B(l)$. At equilibrium all 4 chemical potentials are equal, viz. $\mu_A^l = \mu_B^l = \mu_A^v = \mu_B^v$.