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B.E. Chemical Engineering 2nd Year 2nd Semester Examination, 2025

Chemical Engineering Thermodynamics

Time : Three hours | Full Marks : 100

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

Question 1 **[CO-1]**

(a) Derive the expression $dS = C_v \frac{dT}{T} + \frac{T\beta}{k} dv$. Obtain the expression of dS for ideal gas.[10]

(b) Calculate the fugacity of $CHClF_2$ at -18 °C and 138 bar from the following data [10]

The vapor pressure of $CHClF_2$ at -18 °C is 2.6 bar. The volumetric data at -18 °C is given below

P (bar)	0.7	2.75	34.5	69	104	138
V (m^3/mol)x10^6	182	3.9	3.2	2.5	1.8	1.15

The compressibility factor for saturated vapour at -18 °C is 0.932.

© At 25 oC and 20 bar, the fugacity $\hat{f1}$ of component 1 in binary mixture of component 1 and 2 is given by $\hat{f}1 = 50x_1 - 80x_1^2 + 40x_1^3$. Determine [5]

(I) Fugacity coefficient of pure component 1
(II) Henry's constant for component 1
(III) Expression of activity coefficient of component 1 as a function of x_1

Question 2. **[CO-1, CO-3]**

Calculate the change in enthalpy between the two states of benzene [25]
State 1: Temperature = 55 °C, Pressure = 900 mm Hg
State 2: Temperature = 200 °C, Pressure = 1500 mm Hg

The following data is given
The vapor pressure of liquid benzene is given by:

$$log_{10}P(\text{mm Hg}) = 6.88 - \frac{1196.76}{t(oC\ ) + 219.161}$$

The substance is known to follow generalized virial equation of state

$$Z = 1 + \frac{BP_c}{RT_c}\frac{P_r}{T_r}$$

$$\frac{BP_c}{RT_c} = B^o + \omega B_1, B_o = 0.083 - \frac{0.422}{T_r^{1.6}}, B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

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The critical temperature, pressure and acentric factor of benzene are 562.1 K, 49.24 bar and 0.212 respectively.
The heat capacity of liquid benzene may be taken as 2 kJ/kg K
The density of liquid benzene may be assumed constant at 0.77 g/cm^3
The isobaric molar heat capacity of benzene in ideal gas state can be estimated from
$C_p^o(\text{J/molK}) = -33.89 + 0.472T$ where T is in kelvin
The latent heat of vaporization Δh_{vn} may be calculated using the following equations

$$\Delta h_{vn}(kJ/kg) = 1.093RT_c\left[T_{br}\frac{\ln lnP_c - 1.013}{0.93 - T_{br}}\right]$$

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

Sketch the path used for calculation on a P-v diagram

Question 3. **[CO-1, CO-3]**

(a) The solution behavior of a certain class of substances is derived by the expression

$$G = \sum_i x_i\varepsilon_i + RT\sum_i x_i ln(x_i P)$$

Where $\varepsilon_i's$ are function of T only. Obtain the expression of $\bar{G}_i, \bar{S}_i$ and $\bar{H}_i$ [10]

(b) The enthalpy change of mixing (ΔH) for a binary liquid solution of components 1 and 2 at 25 °C and 1 atm is given by the equation [15]

$$\Delta H = x_1x_2(10x_1 + 5x_2)$$

The enthalpy of pure liquid at the same T and P are: $H_1 = 100$ cal/gmol and $H_1 = 150$ cal/gmol. Determine the following

(I) Enthalpy of the solution at x_1=0.4.
(II) Excess enthalpy of the solution at x_1=0.5. Show relevant derivation
(III) Numerical value of partial molar enthalpy of the two components at infinite dilution.

Question 4. **[CO-2, CO-3]**

(a) A large body of water is in equilibrium with a large mass of air. Starting with the thermodynamic equilibrium criterion of equality of chemical potential and making reasonable assumptions (and state them) derive the following formula $y_{H2O} = \frac{P_{H2O}^{sat}}{P}$ [7]

(b) The vapour liquid equilibrium data of 1-propanol (1)-chlorobenzene (2) at 95 °C is given below

P (mm Hg)	x_1	y_1
518.0	0.212	0.6
609.0	0.43	0.70

The vapour pressure (in mm Hg) of pure 1-propanol and chlorobenzene at 95 °C is given by

$$log_{10}P_1^{sat} = 8.38 - \frac{1788}{t(oC) + 227.4}$$

$$log_{10}P_2^{sat} = 7.12 - \frac{1549.2}{t(oC) + 229.26}$$

The excess Gibbs free energy for this system can be represented by three suffix Margules equation $\frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2)x_1x_2$. Determine the following

(I) Whether the VLE exhibit positively or negative deviation from ideality
(II) Liquid phase activity coefficient of 1-propanol and chlorobenzene from the above data making suitable assumptions (state them).
(III) Value of Margules parameter A_{21} and A_{12}
(IV) Total pressure P and vapour phase composition of 1 –propanol, (y_1) at 95 °C and liquid phase mole fraction of 1 –propanol (x_1) = 0.5 assuming liquid phase is non-ideal
(V) Derive the expression relating Gibbs free energy change due to mixing (ΔG) to activity coefficient and mole fraction. Determine (ΔG) for the liquid phase at x_1=0.5. [18]

Question 5 **[CO-2, CO-3]**

(a) Ethanol is produced from the following reaction $C_2H_4(g) + H_2O(g) \leftrightarrow C_2H_5OH(g)$. Estimate the following [18]

(I) Standard heat of reaction and standard Gibbs Free energy change due to reaction at 298.15 K.
(II) Suppose the reaction is carried out at 800 K and 3 bar and the initial moles of C_2H_4, H_2O and C_2H_5OH is 2.0, 1.0 and 0.5, determine the equilibrium composition of the reaction mixture.

	$\Delta H^o_{f,298}$ (kJ/mol)	$\Delta G^o_{f,298}$ (kJ/mol)
$C_2H_4(g)$	52.3	68.3
$H_2O(l)$	-286	-238
$C_2H_5OH(g)$	-235	-168

The latent heat of vaporization and vapor pressure of water at 298.15 K is 44 kJ/mol and 24 kPa respectively.

(b) Calculate the equilibrium pressure of gaseous species that results from the decomposition of calcium carbonate $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$ at 298.15 K:
$\Delta G_f^o[CO_2(g)] = -394\ kJ/mol$; $\Delta G_f^o[CaO(s)] = -604\ kJ$ /mol
$\Delta G_f^o[CaCO_3(s)] = -1129\ kJ/mol$ [7]