Qualifying Examine-1997 Chemical Engineering Thermodynamics

Part I. (50%)

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- 1. Which of following properties are intensive? (10%)
 - (a) velocity (b) mass (c) stress (d) pressure (e) surface tension (f) surface area
 - (g) potential energy (h) specific weight (i) mole fraction.
- 2. A well-insulated rigid tank which has a negligible heat capacity is divided into two unequal parts A and B by an insulated partition. Different amounts of the same ideal gas are contained in the two parts of the tank. The initial conditions of the temperature, pressure, and volume are known for both parts of the tank (T_A, P_A, V_A; T_B, P_B, V_B). Express the equilibrium temperature (T_f) and pressure (P_f) in terms of T_A, T_B, P_A, P_B, V_A, and V_B after removal of the partition. Assume that the molar heat capacity of the gas (C_V) is constant and that the process is adiabatic. (20%)
- 3. The molar volume of a binary mixture can be expressed as

$$\underline{V}(T,P,x_1,x_2) = x_1b_1 + x_2b_2 + x_1x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i$$

- (a) What values should be used for b_1 and b_2 ? (5%)
- (b) Derive expression for the partial molar volume of component 2, $\overline{V}_{2. (5\%)}$
- (c) Derive expression for the partial molar excess volume of component 2 at infinite

dilution,
$$\overline{V}_2^{\text{ex},\infty}$$
. (10%)

Part II. (50%)

- Ethanol and dimethyl ether are isomers. However, the normal boiling point of ethanol (78°C) is much higher than that of dimethyl ether (-25°C). Explain it on the basis of knowledge of intermolecular forces. (10%)
- 2. Two-term virial equation for a gas mixture is given by

$$Z_m = \frac{P\underline{V}}{RT} = 1 + \frac{B_m}{V}$$

where B_m is the second virial coefficient for the mixture.

- (a) Define B_m. (i.e., its mixing rule) (5%)
- (b) Show that

$$\ln \phi_i = \frac{2}{V} \sum_{j=1}^{c} y_i B_{ij} - \ln Z_m$$
 (10%)

Hint:

$$\mathrm{RT} \ln \phi_i = \int_{\underline{V}}^{\infty} [(\partial P / \partial n_i)_{T,\underline{V},n_j} - (\mathrm{RT} / \underline{V})] d\underline{V} - \mathrm{RT} \ln Z_m$$

where y_i , ϕ_i , and n_i are the mole fraction, the fugacity coefficient, and the number of moles for component i, respectively.

- 3. A pressure vessel contains methane (component 1) and methanol (component 2) at 10° C and 20 bar. The solubility of methane in methanol follows Henry's law; Henry's constant is 1000 bar. The vapor pressure of methanol at 10° C is 0.05 bar. Also assume that the properties of the vapor mixture can be represented by the two-term virial equation and the second viral coefficients (cm³ mol⁻¹) at 10° C are $B_{11} = -50$, $B_{12} = -160$, and $B_{22} = -4000$.
 - (a) List the vapor-liquid phase equilibrium relationships for each species. (5%)
 - (b) Estimate the compressibility factor for the vapor mixture. (5%)
 - (c) Estimate the solubility of methane in liquid methanol (x_1) . (5%)
 - (d) Estimate the mole fraction of methanol in the saturated vapor-phase (y_2) . (10%)

Note: (1) $R = 83.1439 \text{ bar cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$

(2) Made any reasonable assumptions to simplify the calculation.