國立成功大學

114學年度碩士班招生考試試題

編　號：57

系　所：化學工程學系

科　目：化工熱力學

日　期：0210

節　次：第 2 節

注　意：1.可使用計算機
2.請於答案卷(卡)作答，於試題上作答，不予計分。

1. **(33%)** If the *PVT* behavior of *n*-hexane is described well with the van der Waals Equation of State, $\boldsymbol{P = \frac{RT}{V-b} - \frac{a}{V^2}}$, in which ***a*** and ***b*** are constants, please

   (1) estimate the values of ***a*** and ***b***. The critical properties of *n*-hexane are known as $T_C = 507.6$ K, $P_C = 30.25$ bar, and $V_C = 371$ cm^3/mol, while the normal boiling point of *n*-hexane is $T_n = 341.9$ K. **(15%)**

   (2) determine the heat required to expand isothermally the volume of 1 mol of *n*-hexane initially at $P = 1.013$ bar and $T = 300$ K by 1,000 times. **(12%)**

   (3) If the virial equation of state in density, *i.e.* reciprocal of molar volume, is alternatively applied to describe the *PVT* behavior of *n*-hexane, please express the second (***B***) and the third (***C***) virial coefficients in terms of ***P***, ***V***, ***T***, ***a*** and ***b***. **(6%)**

Please detail your calculation schemes and write down all assumptions you have made leading to your answers.

2. **(4%)** Please answer "True" or "False". **2%** each.

   (1) For a cyclic process, $\Delta S = 0$. For a reversible and adiabatic process, it is isentropic, i.e., $\Delta S = 0$. Therefore, the (isentropic) reversible and adiabatic process is always a cyclic process.

   (2) On the *H* vs *S* diagram, the isobaric line of a higher pressure is always below that of a lower pressure.

3. **(9%)** Please choose **three** equations all of which are used to construct the equations for flow systems such as

$$VdP + \left(1 + \frac{\beta u^2}{C_P}\right) \cdot TdS - \frac{u^2}{A} dA = 0 \qquad udu - \left(\frac{\frac{\beta u^2}{C_P} + M^2}{1 - M^2}\right) \cdot TdS + \left(\frac{1}{1-M^2}\right) \cdot \frac{u^2}{A} dA = 0$$

   [Note] deduct **1%** for every wrong answer

   (1) $\frac{dV}{V} - \frac{du}{u} - \frac{dA}{A} = 0$ (2) $dH = -udu$ (3) $dH = TdS + VdP$

   (4) $\frac{dV}{V} = \frac{\beta T}{C_P} dS - \frac{V}{c^2} dP$ (5) $TdS + VdP = -udu$

4. **(21%)** For the open system of a single species without chemical reaction, please derive from $d(nG/RT)$ to obtain the expressions of (1) $\left[\frac{\partial(nG/RT)}{\partial T}\right]_{P,n}$, (2) $\left[\frac{\partial(nG/RT)}{\partial P}\right]_{T,n}$ and (3) $\left[\frac{\partial(nG/RT)}{\partial n}\right]_{T,P}$ **(12%)**

   Further, use the answers of (1), (2), (3) to establish Maxwell relations. **(9%)**

   [Note] Those variables kept constant must be written by subscript.

5. **(20%)**

   (1) Please show the composition of the binary system at vapor/liquid equilibrium: $x_1 = \frac{1-K_2}{K_1-K_2}$ and $y_1 = \frac{K_1(1-K_2)}{K_1-K_2}$, here x_1: composition of component 1 in the liquid phase; y_1: composition of component 1 in the vapor phase; $K_1 = \frac{y_1}{x_1}$: *K* value of component 1; $K_2 = \frac{y_2}{x_2}$: *K* value of component 2. **(6%)**

(2) Please calculate the equilibrium composition (x_1 and y_1) at 600°C and 1 atm under the following conditions: **(9%)**

a. Molar Gibbs energy of liquid to vapor transition for component 1 at 600°C and 1 atm: $\Delta G_m^{1,\ l\to V} = -7.5\ kJ/mole.$

b. Molar Gibbs energy of liquid to vapor transition for component 2 at 600°C and 1 atm: $\Delta G_m^{2,\ l\to V} = 6.8\ kJ/mole.$

(3) If there is a liquid at 1 atm with a composition of $x_1 = 0.35$ at $T < 600$°C, and then the liquid is heated to $T = 600$°C and the pressure is kept constant, a gas-liquid equilibrium will be formed. What is the weight ratio of liquid phase to gas phase? **(5%)**

6. (13%) The molar volume (cm^3/mol) of a binary liquid mixture at given T and P is given by the equation: $V = Ax_1 + Bx_2 + (Cx_1 + Dx_2)x_1x_2$

(1) Find expressions for the partial molar volume of species 1 and 2 at T and P. **(5%)**

(2) Show that these expressions satisfy the Gibbs/Duhem equation. **(4%)**

(3) Show that $(\frac{dV_1}{dx_1})_{x_1=1} = (\frac{dV_2}{dx_1})_{x_1=0} = 0.$ **(4%)**