國立臺灣大學95學年度碩士班招生考試試題

題號:238 科目:物理化學(B)

題號:238

頁之第

# ※ 注意:請於試卷上「非選擇題作答區」依序作答,並應註明作答之大題及小題題號。

## Problem 1 [10 pts]

A two-component mixture behaves ideally in both the vapor and liquid (i.e., obeying the Raoult's law) phases.

- (a) Suppose the vapor pressures of the two compounds at 350 K are 100 kPa and 60 kPa, respectively, determine the equilibrium composition (mole fraction of both species) of the vapor and liquid phases when the total pressure of the system is 80 kPa.
- (b) Sketch the vapor-liquid equilibrium phase diagram of the binary mixture at 350 K (i.e., pressure vs. mole fraction). On the diagram, draw the tie line for the two phases you determined in part (a).

## Problem 2 [10 pts]

It is known that compound AB2 decomposes to gases A and B at 298 K as  $AB_{2(g)} = A_{(g)} + 2B_{(g)}$ 

If the degree of dissociation of AB2 is found to be 20% at 298 K and 10 bar, determine  $K_a$  (equilibrium constant in terms of activity) and  $K_p$  (equilibrium constant in terms of pressure)

- (a) if the reference state is chosen to be 1 bar.
- (b) if the reference state is chosen to be 0.5 bar.

## Problem 3 [15 pts]

The vapor pressure of carbon tetrachloride (CCl<sub>4</sub>) are measured at two temperatures

| 710000 | - CONT. CONT. CONT. |  |
|--------|---------------------|--|
| T (°C) | Pvap (bar)          |  |
| 141.7  | 5.065               |  |
| 178.0  | 10.13               |  |

Suppose that the heat of vaporization of CCl4 is temperature independent

- (a) Determine the heat of vaporization of CCl<sub>4</sub>?
- (b) What is the entropy change of vaporization of CCl<sub>4</sub> at 141.7°C?
- (c) Estimate the normal boiling point (temperature) of CCl<sub>4</sub>.

#### Problem 4 [10 pts]

The van der Waals EOS is  $P = \frac{RT}{V - b} - \frac{a}{V^2}$ 

(a) Show that the constants a and b are related to the critical temperature  $T_c$  and

pressure 
$$P_c$$
 as  $a = \frac{27 R^2 T_c^2}{64 P_c}$  and  $b = \frac{1}{8} \frac{RT_c}{P_c}$ .

(b) Determine the value of compressibility factor at the critical point for a gas obeying the van der Waals EOS.

國立臺灣大學95學年度碩士班招生考試試題

題號:238 科目:物理化學(B)

頁之第

## Problem 5 [10 pts]

Estimate the heat required to raise the temperature of 10 moles of helium from 0°C to 100°C if

- (a) the volume of the system is kept constant during heating.
- (b) the pressure of the system is kept constant during heating.

## Problem 6 [20 pts]

The solubility process for lead sulfate  $(PbSO_4)$  in water at 25  $^{\circ}$ C is  $PbSO_4(s) = Pb^{2+}(aq) + SO_4^{2-}(aq)$ 

Available data: Gibbs free energy of formation,  $\Delta_r G^o$  at 25 °C.

|                                | $Pb^{2+}(aq)$ | $SO_4^{2-}(aq)$ | $PbSO_4(s)$ |
|--------------------------------|---------------|-----------------|-------------|
| $\Delta_f G^o / \text{kJ/mol}$ | - 24.43       | - 744.53        | - 813.14    |

- (a) Calculate the solubility product of PbSO<sub>4</sub>.
- (b) Calculate the solubility of PbSO<sub>4</sub> in pure water.
- (c) Calculate the solubility of PbSO<sub>4</sub> in a solution containing 0.008 M Na<sub>2</sub>SO<sub>4</sub>. Assume that the Debye-Hückel limiting law applies.
- (d) Is it a salting-in or salting-out phenomenon in case (c)?

## Problem 7 [15 pts]

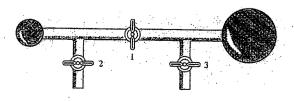
The mechanism for the dinitrogen-pentoxide-catalyzed decomposition of ozone (20 $_3$ =  $3O_2$ ) is given below.

- (1)  $N_2O_5 \rightarrow NO_2 + NO_3$
- $(2) NO_2 + NO_3 \rightarrow N_2O_5$
- (3)  $NO_2 + O_3 \rightarrow NO_3 + O_2$
- (4)  $2NO_3 \rightarrow 2NO_2 + O_2$

Derive a rate law in terms of concentrations of  $O_3$  and  $N_2O_5$  by using the steady-state approximation for  $NO_2$  and  $NO_3$ .

# Problem 8 [10 pts]

Shown below is a tube equipped with three valves, and on either end of the tube are soap bubbles with different radii. With valve 1 closed, valve 2 was opened to blow the small bubble, then it was closed and the large bubble was blown through valve 3. What will happen if valve 1 is opened so that the two bubbles are connected by an open tube? Does the large bubble get larger or does the small bubble get larger? Give your explanation.



試題隨卷繳回