UNIVERSITY CEU SAN PABLO SCHOOL OF PHARMACY DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

COMPLEMENTARY PROBLEMS OF PHYSICAL CHEMISTRY

2018-19

LESSON 3

- **8.** Calculate the melting temperature of mercury at 100 atm and 500 atm, knowing that its normal melting temperature is -38.9 °C.
 - **Data:** ρ (Hg _{(l),} 38.9 ° C and 1 atm) = 13,690 g·cm⁻³; ρ (Hg _{(s),} - 38.9 ° C and 1 atm) = 14,193 g·cm⁻³; $\overline{\Delta H}_{\text{fus}}$ (Hg) = 2.82 cal·g⁻¹

Solution: T_{melt} (100atm) = 234.51 K; T_{melt} (500atm) = 236.61 K

9. To sterilize laboratory equipment, the boiling point of water must be 150 °C. Indicate the pressure that should be inside the autoclave. Determine the pressure when water boils at 90° C.

Data: $R = 0.082 \text{ atm} \cdot 1 \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 1.987 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $\Delta H_{vap} (H_2O) = 539.4 \text{ cal} \cdot \text{g}^{-1}$

Solution: P (150°C) = 4.683 atm; P (90°C) = 0.693 atm

10. Vapour pressure of Acetonitrile changes 0.03 atm per °C when the system is closed to the normal boiling point (80 °C). Calculate the heat of vaporization of acetonitrile.

Data: $R = 0.082 \text{ atm} \cdot 1 \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 1.987 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$;

Solution: $\Delta \overline{H}_{vap} = 7339.43 \text{ cal} \cdot \text{mol}^{-1}$

- **11.** The vapour pressure of diethyl ether is $0.247 \cdot 10^5 \text{ N} \cdot \text{m}^{-2}$ at 0 °C and $1.228 \cdot 10^5 \text{ N} \cdot \text{m}^{-2}$ at 40 °C. Calculate:
 - **a**) The enthalpy of vaporization, assuming that it remains constant throughout the temperature range.
 - **b**) The boiling point of diethyl ether at $1.013 \cdot 10^5 \text{ N} \cdot \text{m}^{-2}$
 - c) The normal entropy of vaporization.
 - d) Has diethylether a trend of self-association? (Check using Toruton's Rule)

Data: 1 atm = $1.013 \cdot 10^5 \text{ N} \cdot \text{m}^{-2}$; R = $0.082 \text{ atm} \cdot 1 \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 1.987 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ **Solution: a)** $\Delta \overline{H}_{vap} = 6791.388 \text{ cal} \cdot \text{mol}^{-1}; \mathbf{b}) T_b^o = 307.658 \text{ K};$

c) $\Delta \overline{\mathbf{S}}_{vap} = 22.071 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \mathbf{d}$) Yes, it has.

12. The following table shows the values of vapour pressure of neon at different temperatures:

T (°C)	-228.7	-233.6	-240.2	-243.7	-245.7	-247.3	-248.5
P (mmHg)	19800	10040	3170	1435	816	486	325

Determine the:

- a) molar vaporization enthalpy.
- **b)** normal boiling point.
- c) standard molar entropy of vaporization.

Data: $R = 0.082 \text{ atm} \cdot 1 \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 1.987 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $M_{\text{Ne}} = 20.79 \text{ a.m.u.}$

Solution: a) $\Delta \overline{H}_{v}^{\circ} = 447.168 \text{ cal·mol}^{-1}$; b) $T_{b}^{\circ} = 27.07 \text{ K}$; c) $\Delta \overline{S}_{v}^{\circ} = 16.519 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

13. The sublimation pressure of Cl_2 (solid) is 352 Pa at -112 °C and 35 Pa at -126.5 °C. The vapour pressures of Cl_2 (liquid) are 1590 Pa at -100 °C and 7830 Pa at -80 °C. Determine the triple point.

Data: $R = 0.082 \text{ atm} \cdot 1 \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 1.987 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; 1 atm = 1.013 \cdot 10⁵ Pa

Solution: a) T_{triple} = 168.918 K. P_{triple} = 1096.304 Pa

- **14.**20 moles of an equimolecular mixture of A and B are distilled, this mixture begins to boil at 65 °C until the boiling point of the residue reaches 75 °C. Draw approximately the phase diagram T vs. X, and answer each of the following questions:
 - a) What is the composition of the residue?
 - **b**) What is the composition of the distillate?
 - c) How many moles does the distillate contain?

Data: The boiling temperature of A is greater than B.

Solution: a) $x_{B}^{L} \approx 0.44$; b) $x_{B}^{V} \approx 0.87$; c) $n^{V} \approx 12.12$ moles

15.Water and phenol are partially miscible at 55 C. When these two liquids are mixed, at 55 °C and 1 atm., the mole fraction of water in both phases in equilibrium are 0.9 and 0.4: If 4 moles of phenol and 6 moles of water are mixed, at 55 °C and 1 atm. calculate the number of moles of phenol and water in each of the phases that are in equilibrium.

Solution: $n_{H_{2O}}^{L,1} = 2.4; n_{phenol}^{L,1} = 3.6; n_{H_{2O}}^{L,2} = 3.6; n_{phenol}^{L,2} = 0, 4$

16.For a liquid-liquid, partially miscible system containing 0.050 kg of A and 0.050 kg of B, calculate, at a temperature T, the masses of the phases in equilibrium. At this temperature the compositions of B in both phases are 30 and 85.5% (w/w), respectively.

Solution: $m^{L,1} = 0.064; m^{L,2} = 0.036$

- **17.** According to the following phase diagram, a mixture of 50 g of n-hexane and 50 g of nitrobenzene is heated to 290 K.
 - a) What is the mass of each phase?
 - b) What is the mass of each component in each of the phases?



Solution: a) $w_I = 55 \text{ g}; w_{II} = 45 \text{ g};$ **b)** $w_{I,A} = 12.65 \text{ g}; w_{I,B} = 42,31\text{g}; w_{II, A} = 37.35 \text{ g}; w_{II, B} = 7.65 \text{ g}$

- 18.A system presents the solid-liquid phase diagram of the figure. Determine:
 - a) the phases and components that are present in every region of the diagram.
 - **b**) the degrees of freedom and the thermodynamic properties required to define the system state in the points.
 - c) What would be the maximum number of moles of pure A that can be obtained by crystallization from an initial melted mixture of 80 moles and $X_A = 0.9$?



Solution: c) $n_A^s = 63.2566$ moles