

**Midterm Exam # 2**

**Answer Sheet:** (All problems are multiple choice. List the letter that corresponds to the correct answer. Maximum number of points you can get is 18 pts!)

Conceptual questions (each 0.75 pts):

- 1) D
- 2) C
- 3) D
- 4) A
- 5) B
- 6) C
- 7) B
- 8) B
- 9) C
- 10) B
- 11) C
- 12) A

Problems and Calculations (each 1.5 pts):

- 1) G
- 2) F
- 3) D
- 4) D
- 5) F
- 6) A

### Conceptual Questions:

- How many different phases can at most co-exist in a two-component system?
  - 1
  - 2
  - 3
  - d. 4
  - none of a) - d)
- An ideal solution of  $x_A$  mol fraction of A and  $x_B$  mol fraction of B, with vapor pressures  $P_A^*$  for pure component A and  $P_B^*$  for pure component B, has a vapor pressure  $P$  given by
  - $P = P_A^* + P_B^*$
  - $P = P_A^* - P_B^*$
  - c.  $P = x_A P_A^* + x_B P_B^*$
  - $P = x_A P_A^* - x_B P_B^*$
  - None of a) - d)
- At the triple point what thermodynamic quantity is the same for all three phases?
  - Entropy  $S$
  - Enthalpy  $H$
  - Internal energy  $U$
  - d. Chemical potential  $\mu$
  - None of a) - d)
- Consider an ideal solution mixture of components A and B in equilibrium with vapor. B is more volatile than A. Compared to the liquid, the vapor contains
  - a. Less of component A
  - Less of component B
  - Equal amounts of A and B
  - None of a) - c)
- Which of the following quantities has a discontinuity in a first-order phase transition?
  - a. Gibbs energy  $G$
  - Volume  $V$
  - Enthalpy  $H$
  - None of a) - c)
- Consider water above the critical temperature  $T_c$ . Which of the following statements is correct for this system?
  - The number of possible phase depends on the pressure in the system
  - There will be a liquid vapor transition
  - c. Only one phase exists.
  - None of a) - c)

7. For a chemical reaction  $A + B \rightleftharpoons C$  we measure an equilibrium constant  $K^0 < 1$ . Under standard conditions, the reaction will proceed spontaneously from
- Left to right ( $A + B \Rightarrow C$ )
  - Right to left ( $C \Rightarrow A + B$ )
8. Assume a chemical reaction  $A + B \rightleftharpoons C$  in equilibrium. When we add a certain amount of B, the equilibrium
- Shifts to the left
  - Shifts to the right
  - Stays unchanged
9. Assume two chemical reactions  $A + B \rightleftharpoons X + Y$  and  $X \rightleftharpoons Z$ , characterized by equilibrium constants  $K_1$  and  $K_2$ , that are coupled leading to a resulting reaction  $A + B \rightleftharpoons Y + Z$ . The resulting equilibrium constant  $K_3$  is given by
- $K_3 = K_1 - K_2$
  - $K_3 = K_1 + K_2$
  - $K_3 = K_1 * K_2$
  - $K_3 = K_1 / K_2$
  - None of a) - d)
10. Assume two chemical reactions  $A + B \rightleftharpoons X + Y$  and  $X \rightleftharpoons Z$ , characterized by Gibbs energy differences (between products and reactants)  $\Delta G_1$  and  $\Delta G_2$ . When coupling the two reactions, one finds for the resulting reaction  $A + B \rightleftharpoons Y + Z$
- $\Delta G = \Delta G_1 - \Delta G_2$
  - $\Delta G = \Delta G_1 + \Delta G_2$
  - $\Delta G = \Delta G_1 * \Delta G_2$
  - $\Delta G = \Delta G_1 / \Delta G_2$
  - None of a) - d)
11. A way to shift the equilibrium is to couple the reaction of interest with a second one. To make an unfavorable reaction possible, what is the requirement for the second reaction?
- $\Delta G^{0_2} > \Delta G^{0_1}$
  - $\Delta G^{0_2} < \Delta G^{0_1}$
  - $\Delta G^{0_2} + \Delta G^{0_1} < 0$
  - $\Delta G^{0_2} + \Delta G^{0_1} > 0$
  - None of a) - d)
12. In a van't Hoff plot  $\ln K^0_p$  is plotted as a function of the inverse temperature  $1/T$ . If  $\Delta H^0$  is independent of temperature one obtains a straight line with:
- Slope:  $-\Delta H^0/R$
  - Slope:  $-\Delta S^0/R$
  - Slope:  $-\Delta H^0/R - \Delta S^0/R$
  - None of a) - e)

### Problems and Calculations:

1. At 2500 K the equilibrium partial pressures of three gases A, B, and C are 0.7, 0.4, and 0.1 bar, respectively. Calculate  $\Delta G_p^0$  at 2500 K for the reaction  $4A(g) \rightleftharpoons 3B(g) + C(g)$ . (Standard state: 1 bar)
- a. -150.70 kJ/mol
  - b. -75.35 kJ/mol
  - c. -37.68 kJ/mol
  - d. -3768.21 J/mol
  - e. 3768.2 J/mol
  - f. 37.68 kJ/mol
  - g. 75.35 kJ/mol
  - h. 150.70 kJ/mol
  - i. None of a) - h)

$$K_p^0 = \frac{(0.4)^3 \cdot 0.1}{(0.7)^4} = 0.02666$$

$$\begin{aligned}\Delta G^0 &= -RT \ln K_p^0 = -8.3145 \cdot 2500 \cdot \ln 0.02666 \frac{J}{mol} \\ &= 8.3145 \cdot 2500 \cdot 3.6248 \frac{J}{mol} \\ &= 75.35 \frac{kJ}{mol}\end{aligned}$$

2. In an experiment, the vapor pressure of a liquid is measured as 15 kPa at 320K, and as 180 kPa at 450 K. Calculate from these data the enthalpy of vaporization  $\Delta_{\text{vap}}H$  of the liquid

- a. - 22.89 kJ/mol
- b. -8.50 kJ/mol
- c. -0,850 KJ/mol
- d. 0..850 KJ/mol
- e. 8.50 kJ/mol
- f. 22.89 kJ/mol
- g. None of a) - f)

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{\Delta_{\text{vap}} H_m}{R} \frac{T_2 - T_1}{T_1 T_2}$$

$$\Rightarrow \Delta_{\text{vap}} H_m = R \ln \frac{P_2}{P_1} \frac{T_1 T_2}{T_2 - T_1}$$

$$= 8,3145 \cdot \ln \frac{180}{15} \frac{320 \cdot 450}{450 - 320} \frac{\text{J}}{\text{mol}}$$

$$= 8,3145 \cdot 2,4849 \cdot \frac{320 \cdot 450}{130} \frac{\text{J}}{\text{mol}}$$

$$= 8,3145 \cdot 2,4849 \cdot 1107,6923 \frac{\text{J}}{\text{mol}}$$

$$= 22,89 \frac{\text{kJ}}{\text{mol}}$$

3. The equilibrium constant  $K_c$  for a reaction  $2A \rightleftharpoons 2Y + Z$  is  $0.02 \text{ mol/l}$  at an temperature  $T=1600 \text{ K}$ . Calculate  $k_p$  at that temperature.
- $0.0026 \text{ bar}$
  - $0.0266 \text{ bar}$
  - $0.2661 \text{ bar}$
  - $2.66 \text{ bar}$
  - $26.06 \text{ bar}$
  - none of a) - e)

$$\sum \nu = 2 + 1 - 2 = 1$$

$$K_p = K_c (RT)^{\sum \nu} = K_c RT$$

$$= 0.02 \frac{\text{mol}}{(\text{dm})^3} \cdot (8.3145 \cdot 1600) \frac{\text{J}}{\text{mol}}$$

$$= 0.02 \cdot 13303.2 \frac{\text{J}}{(\text{dm})^3}$$

$$= 266.064 \frac{\text{J}}{(\text{dm})^3}$$

$$= 266.064 \frac{\text{J}}{\text{m}^3}$$

$$= 266.064 \text{ Pa}$$

$$= 2.66 \text{ bar}$$

4. The ratio of a component A to water collected in a steam distillation is 4, when the mixture was boiled at 344 K and 80 kPa. If the vapor pressure of water at this temperature is 43.2 kPa, calculate the molar mass of A (molar mass of water: 18.02 g/mol)
- 13.71 g/mol
  - 27.41 g/mol
  - 54.82 g/mol
  - 84.62 g/mol
  - 124.82 g/mol
  - 146.88 g/mol
  - none of a) - f)

$$m = n \cdot M$$

$$\frac{m_A}{m_{H_2O}} = \frac{n_A \cdot M_A}{n_{H_2O} \cdot M_{H_2O}} = \frac{p_A^*}{p_{H_2O}^*} \cdot \frac{M_A}{M_{H_2O}}$$

$$\Rightarrow M_A = \frac{p_{H_2O}^*}{p_A^*} \cdot \frac{m_A}{m_{H_2O}} \cdot M_{H_2O} \quad \left| \begin{array}{l} P = p_A^* + p_{H_2O}^* \\ \Rightarrow p_A^* = P - p_{H_2O}^* \end{array} \right.$$

$$= \frac{p_{H_2O}^*}{P - p_{H_2O}^*} \cdot \frac{m_A}{m_{H_2O}} \cdot M_{H_2O}$$

$$= \frac{43.2}{80 - 43.2} \cdot 4 \cdot 18.02 \frac{g}{mol}$$

$$= \frac{43.2}{36.8} \cdot 4 \cdot 18.02 \frac{g}{mol}$$

$$= 1.1739 \cdot 4 \cdot 18.02 \frac{g}{mol}$$

$$= 84.62 \frac{g}{mol}$$

5. Assume a reaction  $3A \rightleftharpoons Y + 3Z$ . Initially, 7 mols of pure A are contained in a volume of 14 l. One mol of A remain at equilibrium in this volume. What is the equilibrium constant  $K_c$ ?

- a. 0.31 mol/l
- b. 3.09 mol/l
- c. 5.14 mol/l
- d. 10.29 mol/l
- e. 15.43 mol/l
- f. 30.86 mol/l
- g. none of a) - e)

Start  $\rightarrow$  equilibrium:  $\Delta n_A = -6 \text{ mol} \Rightarrow \Delta n_Z = 6 \text{ mol}$

$\Delta n_Y = 2 \text{ mol}$

$$[A] = \frac{1}{14} \frac{\text{mol}}{\text{l}}, [Y] = \frac{1}{7} \frac{\text{mol}}{\text{l}}, [Z] = \frac{3}{7} \frac{\text{mol}}{\text{l}}$$

$$\Rightarrow K_c = \frac{[Y][Z]^3}{[A]^3}$$

$$= \frac{\frac{1}{7} \left(\frac{3}{7}\right)^3}{\left(\frac{1}{14}\right)^3} \frac{\text{mol}}{\text{l}}$$

$$= \frac{1}{7} \cdot 6^3 \frac{\text{mol}}{\text{l}}$$

$$= \frac{216}{7} \frac{\text{mol}}{\text{l}}$$

$$= 30.86 \frac{\text{mol}}{\text{l}}$$

6. Assume an ideal solution of two components A and B. At  $T=300\text{ K}$ ,  $P^*(A) = 3\text{ kPa}$ , and  $P^*(B) = 9\text{ kPa}$ . Compute the vapor pressure of a solution containing 0.6 mol fraction of A. What is the mole fraction of A in the vapor over the liquid?

- a. 0.333
- b. 0.450
- c. 0.503
- d. 0.600
- e. 0.802
- f. none of a) - e)

$$P = x_A P_A^* + (1 - x_A) P_B^*$$

$$P_A = y_A P \Rightarrow y_A = \frac{P_A}{P}$$

$$= \frac{x_A P_A^*}{x_A P_A^* + (1 - x_A) P_B^*}$$
$$= \frac{0.6 \cdot 3 \cdot 10^3 \text{ Pa}}{0.6 \cdot 3 \cdot 10^3 \text{ Pa} + 0.4 \cdot 9 \cdot 10^3 \text{ Pa}}$$

$$= \frac{0.6}{0.6 + 0.4 \cdot 3}$$

$$= \frac{0.6}{1.8}$$

$$= 0.33$$

### Useful Equations and Constants:

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta G = \Delta G^0 + nRT \ln \frac{P}{P^0}$$

$$K_p = \left( \frac{\dots P_Y^y P_Z^z}{P_A^a P_B^b \dots} \right)_{eq}$$

$$\Delta G^0 = -RT \ln K_p^0$$

$$K_C = \left( \frac{\dots [Y]^y [Z]^z}{[A]^a [B]^b \dots} \right)_{eq}$$

$$\Delta G = \Delta G^0 + RT \ln \left( \frac{\dots [Y]^y [Z]^z}{[A]^a [B]^b \dots} \right)^u$$

$$K_a = \left( \frac{\dots a_Y^y a_Z^z}{a_A^a a_B^b \dots} \right)_{eq}$$

$$K_p = K_C (RT)^{\sum \nu}$$

$$K_p = K_x P^{\sum \nu}$$

$$\mu_A = \left( \frac{\partial G}{\partial n_A} \right)_{T, P, n_B, n_Y, \dots}$$

$$\frac{d \ln K_p^0}{dT} = \frac{\Delta H^0}{RT^2}$$

$$\frac{d \ln K_p^0}{d(1/T)} = -\frac{\Delta H^0}{R}$$

$$\ln K_p^0 = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R}$$

$$\frac{d \ln K_C^0}{dT} = \frac{\Delta U^0}{RT^2}$$

$$\frac{d \ln K_C^0}{d(1/T)} = -\frac{\Delta U^0}{R}$$

$$K_{overall} = \prod_i K_i$$

$$\Delta G_{overall} = \sum_i \Delta G_i$$

$$f = c - p + 2$$

$$P_i = P_i^* x_i$$

$$\frac{n_A}{n_B} = \frac{P_A^*}{P_B^*}$$

$$\frac{n_l}{n_v} = \frac{y_l - x_l}{x_l - y_l}$$

$$\frac{dP}{PdT} = \frac{\Delta_{vap} H_m}{RT^2}$$

$$L = 6.022 \times 10^{23} \text{ mol}^{-1}, k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}, h = 6.626 \times 10^{-34} \text{ J s}$$

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ atm} = 101325 \text{ Pa} = 1.01325 \text{ bar}$$

$$1 \text{ bar} = 100000 \text{ Pa}$$

$$K_W = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$