

KEY

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 25 pts!)

Conceptual questions (each 1.0 pts):

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

Problems and Calculations (each 2.0 pts):

- 1) F
- 2) D
- 3) A
- 4) F
- 5) I
- 6) B

Conceptual Questions:

- Under constant temperature and constant volume conditions, a system is said to be in equilibrium when
 - $\Delta G < 0$
 - $\Delta G = 0$
 - $\Delta S > 0$
 - $\Delta S = 0$
 - $\Delta A = 0$
 - $\Delta A < 0$
 - None of a) - f)
- For the chemical reaction, $2H \rightarrow H_2$, at constant pressure, is the entropy change
 - $\Delta S = 0$
 - $\Delta S = \Delta H$
 - $\Delta S = \Delta U$
 - $\Delta S > 0$
 - $\Delta S < 0$
 - $\Delta S \rightarrow \infty$ for $T \rightarrow 0K$
 - None of a) - f)
- Is the change in the Gibbs energy for the above reaction
 - $\Delta G = 0$
 - $\Delta G = \Delta H$
 - $\Delta G \neq \Delta G$
 - $\Delta G = \Delta S$
 - $\Delta G < 0$
 - $\Delta G > 0$
 - None of a) - f)
- How many different phases can at most co-exist in a two-component system?
 - 1
 - 2
 - 3
 - 4
 - 5
 - none of a) - e)
- At triple point what is the thermodynamic quantity that is the same for each component in all three phases?
 - Chemical potential μ
 - Entropy S
 - Enthalpy H
 - Internal energy U
 - Concentration c
 - None of a) - e)

6. Which of the following is correct for a completely immiscible 2-component solution?
- Raoult's law applies
 - It is an ideal solution mixture
 - Its boiling point is that of the more volatile component
 - It has a higher boiling point than the individual components
 - It has a lower boiling point than the individual components
 - None of a) - e)
7. Which statement is true for an ideal solution mixture of two components A and B?
- It does not form an azeotropic mixture
 - The liquid curve in the temperature-composition phase diagram is a straight line
 - The vapor curve in the temperature-composition phase diagram is a straight line
 - The vapor curve in the pressure-composition phase diagram is a straight line
 - Raoult's law does **not** apply
 - None of a) - e)
8. The following reaction describes dissociation of chlorine into atoms: $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$. If the volume is doubled, the degree of dissociation
- increases
 - decreases
 - depending on temperature may or may not change
 - will oscillate
 - None of a) - d)
9. When equilibrium is reached, the total Gibbs energy of the reactants and products
- Is the same
 - Differs, but has the same sign
 - Differs in both value and sign
 - is both zero
 - adds up to zero
 - None of a) - e)
10. 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?
- $\Delta G^0_2 < \Delta G^0_1$
 - $\Delta G^0_2 > \Delta G^0_1$
 - $\Delta G^0_2 + \Delta G^0_1 > 0$
 - $\Delta G^0_2 + \Delta G^0_1 < 0$
 - $\Delta G^0_2 * \Delta G^0_1 > 0$
 - None of a) - e)

11. In a van't Hoff plot $\ln K_p$ is plotted as a function of the inverse temperature $1/T$. If ΔH^0 is independent of temperature one obtains a straight line. From slope and intercept one finds:
- a. Slope: $-\Delta H^0/R$
 - b. Slope: $-\Delta S^0/R$
 - c. Intercept: $-\Delta H^0/R$
 - d. Intercept: $-\Delta H^0/R - \Delta S^0/R$
 - e. Slope: $-\Delta H^0/R - \Delta S^0/R$
 - f. None of a) - e)
12. Consider water above the critical temperature T_c . Which of the following statements is correct for this system?
- a. Only one phase exists.
 - b. The number of possible phase depends on the pressure in the system
 - c. There will be a liquid vapor transition
 - d. None of a) - c)
13. Determine the number of degrees of freedom for of an olive in a solution of water and alcohol.
- a. 0
 - b. 1
 - c. 2
 - d. 3
 - e. None of a) - d)

Problems and Calculations:

1. In a 25-liter container, at 25°C, and assuming ideal gas behavior, A atoms and B atoms combine to give AB: $A(g) + B(g) \rightleftharpoons AB(g)$. Suppose, we put into the container 0.3 mol of A, 0.38 mol of B and 0.02 mol of AB. After reaching equilibrium, only 0.03 mol of A is left. Assuming a standard concentration of 0.5 mol/l, what is K_c° ?

- a. 51.132
- b. 109.85
- c. 219.70
- d. 313.86
- e. 511.32
- f. 1098.5
- g. 2197.0
- h. 313.86
- i. 5113.2
- j. none of a) - i)

$$\Delta n_A = -0.27 \text{ mol} \Rightarrow \Delta n_{AB} = 0.27 \text{ mol}, \Delta n_B = -0.27 \text{ mol}$$

$$\Rightarrow [A] = \frac{0.03 \text{ mol}}{25 \text{ l}} = 0.0012 \frac{\text{mol}}{\text{l}} \Rightarrow [A]^{\circ} = 0.0024$$

$$[B] = \frac{0.38 - 0.27}{25} \frac{\text{mol}}{\text{l}} = 0.0044 \frac{\text{mol}}{\text{l}} \Rightarrow [B]^{\circ} = 0.0088$$

$$[AB] = \frac{0.02 + 0.27}{25} \frac{\text{mol}}{\text{l}} = 0.0116 \frac{\text{mol}}{\text{l}} \Rightarrow [AB]^{\circ} = 0.0232$$

$$K_c^{\circ} = \frac{[AB]^{\circ}}{[A]^{\circ}[B]^{\circ}} = \frac{0.0232}{0.0024 \cdot 0.0088} = 1098.5$$

2. An ideal solution of 5 mol of A and 2 mol of B is at 330K in equilibrium with vapor. At this temperature, $P_A^* = 2.5$ bar and $P_B^* = 6.5$ bar. What is the mass percentage of A in the vapor phase? (molar Mass of A (B): $M_A = 30$ g/mol; $M_B = 180$ g/mol)

- a. 83.6%
- b. 78.5%
- c. 25.9%
- d. 13.8%**
- e. 10.4%
- f. 7.85 %
- g. 2.59 %
- h. 1.38 %
- i. 1.04 %
- j. None of a) - i)

$$\frac{x_A}{x_B} = \frac{5}{2} = 2.5 \quad (\text{in liquid})$$

$$\frac{y_A}{y_B} = \frac{P_A}{P_B} = \frac{x_A P_A^*}{x_B P_B^*} \quad (\text{in vapor})$$

$$\frac{y_A}{y_B} = \frac{m_A/M_A}{m_B/M_B} \Rightarrow \frac{m_A}{m_B} = \frac{y_A}{y_B} \frac{M_A}{M_B} = 2.5 \frac{P_A^*}{P_B^*} \frac{M_A}{M_B}$$

$$= 2.5 \cdot \frac{2.5}{6.5} \frac{30}{180}$$

$$= 0.16$$

$$m_A \% = \frac{m_A}{m_A + m_B} = \frac{0.16}{1.16} = 0.138$$

$$\Rightarrow m_A \% = 13.8 \%$$

3. In an experiment, the vapor pressure of a liquid is measured as 4 kPa at 280K, and as 140 kPa at 450 K. Calculate from these data the enthalpy of vaporization $\Delta_{\text{vap}}H$ of the liquid.

- a. 21.91 kJ/mol
- b. 21.57 kJ/mol
- c. 10.63 kJ/mol
- d. 3.171 kJ/mol
- e. 2.191 kJ/mol
- f. 1.063 kJ/mol
- g. 317.1 J/mol
- h. 219.1 J/mol
- i. 106.3 J/mol
- j. None of a) - i)

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

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

$$= 8.3145 \cdot \ln \left(\frac{140}{4} \right) \cdot \frac{280 \cdot 450}{170} \frac{\text{J}}{\text{mol}}$$

$$= 8.3145 \cdot \ln 35 - 741.1765 \frac{\text{J}}{\text{mol}}$$

$$= 21909.9 \frac{\text{J}}{\text{mol}}$$

$$= 21.91 \frac{\text{kJ}}{\text{mol}}$$

4. The ratio of a component A to that of water collected in a steam distillation is 6, 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)
- 11.08 g/mol
 - 21.16 g/mol
 - 42.31 g/mol
 - 63.47 g/mol
 - 84.62 g/mol
 - 126.92 g/mol**
 - 169.24 g/mol
 - 207.39 g/mol
 - 214.53 g/mol
 - none of a) - i)

$$m = n M$$

$$\frac{m_A}{m_{H_2O}} = \frac{n_A / M_A}{n_{H_2O} / M_{H_2O}} = \frac{P_A^*}{P_{H_2O}^*} \frac{M_A}{M_{H_2O}}$$

$$\Rightarrow M_A = \frac{P_{H_2O}^*}{P_A^*} \frac{m_A}{m_{H_2O}} \cdot M_{H_2O} \quad \left| \quad P = P_A^* + P_{H_2O}^* \Rightarrow P_A^* = P - P_{H_2O}^* \right.$$

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

$$= \frac{43.2 \text{ kPa}}{(80 - 43.2) \text{ kPa}} \cdot 6 \cdot 18.02 \frac{\text{g}}{\text{mol}}$$

$$= \frac{43.2}{36.8} \cdot 6 \cdot 18.02 \frac{\text{g}}{\text{mol}}$$

$$= 126.92 \frac{\text{g}}{\text{mol}}$$

5. The Gibbs energies of formation of A(g) and B(g) are 100 kJ/mol and 50.5 kJ/mol, respectively. The standard state is 2 bar and 300 K. Assume ideal behavior and a reaction $A \rightleftharpoons 2B$. Calculate the pressure where 30% of A is dissociated.

- a. 0.178 bar
- b. 0.312 bar
- c. 0.503 bar
- d. 0.734 bar
- e. 0.893 bar
- f. 0.953 bar
- g. 1.134 bar
- h. 1.693 bar
- i. 3.386 bar
- j. none of a) - i)

$$\Delta G^\circ = 101 \frac{\text{kJ}}{\text{mol}} - 100 \frac{\text{kJ}}{\text{mol}} = 1 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G^\circ = -RT \ln K_p^\circ \Rightarrow \ln K_p^\circ = -\frac{\Delta G^\circ}{RT} = \frac{-1000 \frac{\text{J}}{\text{mol}}}{8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \cdot 300 \text{K}}$$

$$= \frac{-10}{3 \cdot 8.3145} = -0.4009$$

$$\Rightarrow K_p^\circ = 0.6697$$



$$p_A = \frac{1-\alpha}{1+\alpha} P \qquad p_B = \frac{2\alpha}{1+\alpha} P$$

$$K_p^\circ = \frac{(2\alpha/(1+\alpha))^2}{(1-\alpha)/(1+\alpha)} \frac{P}{2\text{bar}} = \frac{4\alpha^2}{1-\alpha^2} \frac{P}{2\text{bar}}$$

$$\Rightarrow P = \frac{1-\alpha^2}{4\alpha^2} K_p^\circ \cdot 2\text{bar}$$

$$\alpha = 0.3 \Rightarrow P = \frac{0.91}{0.36} \cdot 0.6697 \cdot 2\text{bar}$$

$$= 2.5278 \cdot 0.6697 \cdot 2\text{bar} = 3.386\text{bar}$$

6. For a certain chemical reaction under constant volume one finds a difference $\Delta U = -110 \text{ kJ/mol}$ in internal energy between products and reactants, and an entropy difference $\Delta S = -230 \text{ J/(K mol)}$. Assume that these two values do not depend on temperature. At what temperature will be the Helmholtz's energy difference $\Delta A = 0$?

- a. 956.5K
- b. 478.3 K
- c. 239.1 K
- d. 95.65 K
- e. 47.83 K
- f. 23.91 K
- g. 0.9655 K
- h. 0.4783 K
- i. 0.2391 K
- j. none of a) - i)

$$\Delta A = \Delta U - T\Delta S = 0$$

$$\Rightarrow T\Delta S = \Delta U$$

$$\Rightarrow T = \frac{\Delta U}{\Delta S} = \frac{-110 \text{ kJ/mol}}{-230 \text{ J/mol/K}} = \frac{110 \cdot 1000}{230} \text{ K}$$

$$= 478.26$$

Useful Equations and Constants:

$$G = H - TS \quad \Delta G = \Delta H - T\Delta S \quad \Delta S = n_1 R \ln\left(\frac{V_1 + V_2}{V_1}\right) + n_2 R \ln\left(\frac{V_1 + V_2}{V_2}\right)$$

$$A = U - TS \quad \Delta A = \Delta U - T\Delta S \quad \left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \quad RT \ln \frac{f}{P} = \int_0^P \left(V_m - \frac{RT}{P'}\right) dP'$$

$$H = U + PV \quad \Delta H = \Delta U + \Delta(PV) \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G = \Delta G^\circ + nRT \ln \frac{P}{P^\circ} \quad K_P = \left(\frac{\dots P_Y^y P_Z^z}{P_A^a P_B^b \dots}\right)_{eq} \quad \Delta G^\circ = -RT \ln K_P^\circ$$

$$K_C = \left(\frac{\dots [Y]^y [Z]^z}{[A]^a [B]^b \dots}\right)_{eq} \quad \Delta G = \Delta G^\circ + RT \ln \left(\frac{\dots [Y]^y [Z]^z}{[A]^a [B]^b \dots}\right)^n$$

$$K_a = \left(\frac{\dots a_Y^y a_Z^z}{a_A^a a_B^b \dots}\right)_{eq} \quad K_P = K_C (RT)^{\sum \nu} \quad K_P = K_x P^{\sum \nu}$$

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B,n_Y,\dots} \quad \frac{d \ln K_P^\circ}{dT} = \frac{\Delta H^\circ}{RT^2} \quad \frac{d \ln K_P^\circ}{d(1/T)} = -\frac{\Delta H^\circ}{R}$$

$$\ln K_P^\circ = -\frac{\Delta H^\circ}{R} \cdot \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad \frac{d \ln K_C^\circ}{dT} = \frac{\Delta U^\circ}{RT^2} \quad \frac{d \ln K_C^\circ}{d(1/T)} = -\frac{\Delta U^\circ}{R}$$

$$K_{overall} = \prod_i K_i \quad \Delta G_{overall} = \sum_i \Delta G_i \quad f = c - p + 2$$

$$P_i = P_i^* x_i \quad \frac{n_A}{n_B} = \frac{P_A^*}{P_B^*} \quad \frac{n_l}{n_v} = \frac{y_l - x_l}{x_l - y_l}$$

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

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

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

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

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

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