

Name:

**Chem 3321, some practice questions for test #2**

I want complete, detailed answers to the questions. Show all your work to get full credit.

DATA:

$$R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ atm} = 1.01 \times 10^5 \text{ Pa} = 1.01 \text{ bar} = 760 \text{ torr}$$

$$1 \text{ mL} = 1 \text{ cm}^3$$

$$1 \text{ Pa} = 1 \text{ N m}^{-2}$$

$$0 \text{ }^\circ\text{C} = 273 \text{ K}$$

$$\text{Avogadro's constant} = N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\pi = 3.14159$$

$$1 \text{ eV} = 1.6022 \times 10^{-19} \text{ J (electron volt to joule conversion)}$$

$$\text{mass conversion from amu to kg: } 1.66 \times 10^{-27} \text{ kg/amu}$$

$$C_P - C_V = nR \text{ for any ideal gas}$$

### Problem 1

From the following data, determine the total volume change for dissolving glycine in 1 kg water to 1 molal concentration. Note: 1 kg H<sub>2</sub>O = 55.51 mol. Note: 1 molal concentration means that 1 mol of glycine is dissolved in 1 kg of water.

glycine concentration	glycine	water
molality	$\bar{V}$ , cm <sup>3</sup> mol <sup>-1</sup>	$\bar{V}$ , cm <sup>3</sup> mol <sup>-1</sup>
0	–	18.07
1	44.88	18.05
pure glycine	46.71	–

Solution:

$$\Delta V = (n_1\bar{V}_1 + n_2\bar{V}_2) - (n_1V_1^* + n_2V_2^*) \quad (1)$$

$$= 55.51(18.05) + 1(44.88) - [55.51(18.07) + 1(46.71)] = -2.94 \text{ cm}^3 \quad (2)$$

### **Problem 2**

The molar enthalpy of vaporization of water is  $40.65 \text{ kJ mol}^{-1}$  at its normal boiling point of  $100 \text{ }^\circ\text{C}$ . Determine the vapor pressure of water at  $110 \text{ }^\circ\text{C}$ .

Solution:

Using the Clausius-Clapeyron equation,

$$\begin{aligned} \ln \left[ \frac{P_2}{P_1} \right] &= \frac{-\Delta H}{R} \times \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\ \ln \left[ \frac{P_2}{1 \text{ atm}} \right] &= \frac{-40650 \text{ J/mol}}{8.3145 \text{ J/molK}} \times \left( \frac{1}{383.15 \text{ K}} - \frac{1}{373.15 \text{ K}} \right) \\ P_2 &= 1.408 \text{ atm} \end{aligned}$$

### **Problem 3**

A solution of acetone ( $A$ ) and methanol ( $M$ ) are in equilibrium at  $57.2\text{ }^\circ\text{C}$  and  $1.0\text{ atm}$ . The mole fraction of acetone in the liquid phase is  $0.400$ . Determine mole fraction of acetone in the vapor phase. For these two components,  $P_A^* = 105\text{ kPa}$  and  $P_M^* = 73.5\text{ kPa}$ .

Solution:

From Raoult's law,

$$P_A = X_A P_A^* = 0.4 \times 105\text{ kPa} = 42\text{ kPa}$$

$$P_B = X_B P_B^* = 0.6 \times 73.5\text{ kPa} = 44.1\text{ kPa}$$

From Dalton's law,  $P_{Tot} = P_A + P_B = 86.1\text{ kPa}$

Mole fraction of acetone in the vapor phase,

$$Y_A = P_A/P_{Tot} = 0.4878$$

#### Problem 4

$\text{N}_2\text{O}_3$  dissociates according to the equilibrium



At 298 K and 1 bar pressure, the degree of dissociation is  $3.5 \times 10^{-3}$ , where the degree of dissociation is defined as the ratio

$$\frac{\text{moles of NO}_2 \text{ or NO}}{\text{moles of the reactant before any dissociation occurs}} \quad (4)$$

Calculate  $\Delta G^\circ$  for this reaction.

Solution:

First, we can construct an ICE table as follows:



From the last line, the total number of moles is  $n_0 + x$ , and we are told this corresponds to 1 bar pressure. Therefore, for the partial pressure of NO, we can write

$$\frac{P_{\text{NO}}}{P^\circ} = \frac{P_{\text{NO}}}{P_{\text{total}}} = \frac{x}{n_0 + x} \quad (5)$$

and similarly for the other components. Therefore, we can assemble  $K_P$  as

$$K_P = \frac{\left(\frac{x}{n_0+x}\right)^2}{\frac{n_0-x}{n_0+x}} = \frac{x^2}{(n_0-x)(n_0+x)} \quad (6)$$

then we can multiply and divide by  $(1/n_0)^2$  to get

$$K_P = \frac{(x^2)(1/n_0)^2}{(n_0-x)(n_0+x)(1/n_0)^2} = \frac{(x/n_0)^2}{(1-x/n_0)(1+x/n_0)} = \frac{y^2}{(1-y)(1+y)} \quad (7)$$

where  $y = 3.5 \times 10^{-3}$ . This gives  $K_P = 1.225 \times 10^{-5}$  and then, using  $\Delta G^\circ = -RT \ln K$ , we get  $\Delta G^\circ = 28.02$  kJ/mol.

### **Problem 5**

a) Prove that (where  $K$  is the equilibrium constant)

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

Solution: This is actually the van't Hoff equation. To derive this equation we just need the two basic formulae involving  $\Delta G$ , namely

$$\Delta G = \Delta H - T\Delta S \text{ and}$$

$$\Delta G^\circ = -RT \ln K$$

Then we solve for  $\ln K$  to give

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ - T\Delta S^\circ}{RT} \quad (9)$$

which when simplified yields the van't Hoff equation.

b) Compute  $\Delta H^\circ$  and  $\Delta S^\circ$  for the reaction  $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$

given the following data:  $K$  at  $T = 273 \text{ K}$  is 72.9 and  $K$  at  $T = 325 \text{ K}$  is 1.30.

Solution:

First, the reaction must be exothermic due to LeChatelier's Rule because increasing the temperature causes the equilibrium to shift to the left (smaller value of  $K$ ). Second, the entropy change of this reaction is negative because we go from two moles of a gas to only one mole of a gas. Numerically, we can solve the van't Hoff equation to find the slope and intercept using the given two data points. This yields  $\Delta H^\circ = -57.1 \text{ kJ/mol}$  and  $\Delta S^\circ = -173.6 \text{ J/(K mol)}$ .