LAST Name: ____

FIRST Name: ____

Student #: ____

CHM2132 Midterm #2
Fall 2013

This is a closed book exam with no notes allowed. Non-graphing, non-programmable calculators are permitted. An equation sheet is provided on the last page. You may rip this page off of the exam and use it for rough work.

You must show all work to receive partial credit.

Remember to include units in all your calculations**. Marks will be deducted if units are not shown in your final answer. Marks will be deducted if an unreasonable number of sig figs is shown in final answer.** If data calculated in previous sections of a multi-part question and used for subsequent calculations is incorrect, <u>no additional mark deductions</u> will be applied.

Data for H_2O

ΔH^o_{vap} = 40.65 kJ mol^{-1} ΔH^o_{sub} = 46.66 kJ/mol T_{vap} = 373.15 K T_{fus} = 273.15 K

M_{H2O} = 18.01 g mol^{-1} ρ_{ice} = 920 kg m^{-3} $\rho_{\text{liquid water}}$ = 997 kg m^{-3} $p^*_{H_2O}$ = 3200 Pa at 298 K

$m^*_{H_2O}$ = 55.555 mol kg^{-1}

Constants

R = 8.314 J K^{-1} mol^{-1} = 0.08206 L atm mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}

1 L = 10^{-3} m^3 1 kJ = 1000 J 1 atm = 101325 Pa 760 Torr = 1 atm

1 bar = 10^5 Pa 1 L atm = 101.325 J 1 J = 1 kg m^2 s^{-2} 1 Pa = 1 kg m^{-1} s^{-2}

Q1: __________/8 Q2: __________/9 Q3: __________/12 Q4: __________/8

Q5: __________/8

Total = __________/45

Question 1. The following statements are **FALSE**. **Choose 4 of the 5 statements below** and:

(i) Change the sentence so that it becomes a correct statement.
(ii) In one sentence explain why the statement was incorrect. (8 marks)

a) The Clausius-Clapeyron equation can be used to calculate the vapour pressure of water at non-standard pressure.

i) The Clausius-Clapeyron equation can be used to calculate the boiling point of water at non-standard pressure.

ii) This equation only tells us how the vapour pressure of a solid or liquid varies with temperature. Like any equilibrium system, the application of pressure does not change the equilibrium constant (which is equal to the vapour pressure in this case). However, we can calculate the temperature at which the vapour pressure of a liquid equals that of the atmosphere (as is required for boiling) at standard and non-standard pressures.

b) The chemical potential of the vapour phase of a boiling aqueous salt solution decreases during this phase transition.

We have not covered this yet.

c) The standard change in Gibbs energy for an isothermal reaction run in an open vessel tells us whether or not a reaction will be spontaneous.

i) The ~~standard~~ change in Gibbs energy for an isothermal reaction run in an open vessel tells us whether or not a reaction will be spontaneous.

ii) The standard Gibbs energy (ΔG^o) tells us if the products or reactants are favored at equilibrium. It can not tell us if the reaction will go forward without including information about the starting conditions. The Gibbs energy equation ($\Delta G = \Delta G^o + RT\ln Q$) includes the reaction quotient Q – this provides us with the information about the starting conditions that we need to know to tell if the reaction will go forward or backwards.

d) If the heat of dissolving NaCl into water in an open vessel is measured, this can be combined with the enthalpy of Cl^- (*aq*) formation to calculate ΔH_f^o for Na^+ (*aq*).

We have not covered this yet.

e) A solution is not ideal if the molecules in this solution interact with each other.

We have not covered this yet.

Question 2.

In the gas-phase equilibrium system at 400 K, 5.00 bar, NO_2 is 1.4% decomposed in the following reaction:

$$NO_2\,(g) \rightleftharpoons NO\,(g) + \tfrac{1}{2}\,O_2\,(g)$$

a) Calculate K_p under these conditions. (6 marks)

	NO_2	**NO**	**½ O_2**
Initial	*n*	0	0
Change	*-xn*	*xn*	½ *xn*
Equilibrium	*n-xn*	*xn*	½ *xn*
Mole fraction (x=0.014)	(1-x)/(1+0.5x) = 0.9791	x/(1+0.5x) = 0.01390	½ x/(1+0.5x) = 0.006951
Partial pressure $p_A = x_A p_T$	4.896 bar	0.06950 bar	0.03476 bar

$$Kp = \frac{\left(\dfrac{p_{O_2}}{p^o}\right)^{\frac{1}{2}}\dfrac{p_{NO}}{p^o}}{\dfrac{p_{NO_2}}{p^o}} = \frac{(0.03476)^{\frac{1}{2}}(0.06950)}{(4.896)} = 2.6\times10^{-3}$$

$Kp = 2.6 \times 10^{-3}$

b) If the reaction at 5.00 bar was started with equimolar amounts of NO_2, NO and O_2, will the decomposition of NO_2 at 400 K be spontaneous? Provide justification for your answer with a calculation. (3 marks)

Since $n_{NO2} = n_{NO} = n_{O2}$
Therefore $p_{NO2} = p_{NO} = p_{O2} = 5/3$ bar

$$Q = \frac{\left(\dfrac{p_{O_2}}{p^o}\right)^{\frac{1}{2}}\dfrac{p_{NO}}{p^o}}{\dfrac{p_{NO_2}}{p^o}} = \left(\frac{p_{O_2}}{p^o}\right)^{\frac{1}{2}} = \left(\frac{5}{3}\right)^{\frac{1}{2}} = 1.3$$

Since Q > K, there are more products in this reaction mix compared to the amount of products at equilibrium. Therefore the decomposition of NO_2 will not be spontaneous.

It is possible, but not necessary to calculate the Gibbs energy of the reaction to evaluate for spontaneity:

$$\Delta G = \Delta G^o + RT\ln Q = -RT\ln K + RT\ln Q$$

$$= -\left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right)\left(400\text{ K}\right)\left[\ln\left(\frac{2.6\times10^{-3}}{1.3}\right)\right]$$

$$= 21\text{ kJ mol}^{-1}$$

Since $\Delta G > 0$, therefore it is not spontaneous.

Question 4

The pressure exerted on ice by the blade of an ice-skater is approximately 200.0 atm.

a) What is the new melting point of ice under this pressure? (6 marks)

$$\frac{dp}{dT}=\frac{\Delta H^o_{fus}}{T_{fus}\Delta V_m}$$ Data for water is on the first page.

However, we only have enthalpies for vaporization and sublimation, so we must calculate:

$$\Delta H^o_{sub}=\Delta H^o_{fus}+\Delta H^o_{vap}$$

$$\Delta H^o_{fus}=\Delta H^o_{sub}-\Delta H^o_{vap}=\left(46.66-40.65\right)\text{ kJ mol}^{-1}=6.01\text{ kJ mol}^{-1}$$

Also, we do not have volumes for H_2O in the two different states; instead we have densities:

$$V_m=\frac{V}{n}=\frac{VM}{m}=\frac{VM}{V\rho}=\frac{M}{\rho}$$

Substitute back into the Clapeyron equation:

$$\frac{dp}{dT}=\frac{\Delta H^o_{fus}}{T_{fus}\Delta V_m}=\frac{\Delta H^o_{fus}}{T_{fus}M\left(\rho^{-1}_{liquid}-\rho^{-1}_{solid}\right)}$$

$$=\frac{6010\text{ kJ mol}^{-1}}{\left(273.15\text{ K}\right)\left(18.01\text{ g mol}^{-1}\right)\left(10^{-3}\text{ kg g}^{-1}\right)\left(997^{-1}-920^{-1}\right)\text{m}^{-3}\text{ kg}^{-1}}=-1.4553\times10^{7}\text{ Pa K}^{-1}$$

Now solve for the new melting point:

$$\frac{dp}{dT}=\frac{p_2-p_1}{T_2-T_1}$$

$$T_2=\frac{p_2-p_1}{\frac{dp}{dT}}+T_1=\frac{\left(200.0\text{ atm}\right)\left(101325\text{ Pa atm}^{-1}\right)-101325\text{ Pa}}{-1.4553\times10^{7}\text{ Pa K}^{-1}}+273.15\text{ K}$$

$$=271.76\text{ K}$$

Or -1.38°C.

b) If the temperature of the ice is kept at -4.0°C, will this pressure from the skate melt the ice? Explain your answer with ~one sentence. (2 marks)

The ice will not melt.

Since the new melting temperature is still above the temperature of the ice, the pressure from the skate is not sufficient to melt the ice that is at -4°C. (The new melting temperature would have to be below -4°C for the ice to melt.)