CHM2132 Midterm 2
Wednesday November 18th, 2015

Name: ___________________________________

Student #: ___________________________________

This is a closed book exam with no notes allowed.
Calculators are permitted.
Show all your work.
Remember to include units in all your calculations**.**
Marks will be deducted if units are not shown in your final answer.
You will find the equations, data and constants on the last page. You may rip this page off of the midterm and use it to cover your work during the test.

Q1: __________/4 Q2: __________/9 Q3: __________/10

Q4: __________/12 Q5 : __________/5

Total = __________/40

1. The following statements are **FALSE**. **Choose 2 of the 3 statements below** and:

(i) Change the sentence so that it becomes a correct statement.

(ii) In one sentence explain why the statement was incorrect. (4 marks)

a) If liquid water is put into a freezer held at -10°C, $\Delta G_{fus} > 0$ for this water.

Under these conditions water will spontaneously freeze. Fusion is melting, and so will not be favored. The Gibbs energy is positive for a process that cannot occur spontaneously.

b) ~~The only~~ One way to increase the entropy of an ideal gas is by allowing heat to be transferred from the surroundings.

If a gas is allowed to undergo free expansion (i.e. against zero external pressure), no heat is required for the expansion, but the increase in volume increases entropy of the gas.

In general, if a gas undergoes an irreversible adiabatic expansion, the entropy can increase because the reversible path that connects initial and final states is what determines the change in entropy.

c) If a closed system containing the gas phase reaction $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$ at equilibrium undergoes a reversible isothermal compression, the equilibrium constant K_p will ~~decrease~~ not change.

An equilibrium constant is not altered by a change in the pressure or volume of the reaction. It is constant, because it is always related to the standard Gibbs energy by:

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

2. Short calculation questions:
   a) A mad scientist excitedly explains a plan to create a heat engine that absorbs 1000 J of thermal energy at 500 K and emits 500 J at 300 K. What law of thermodynamics would be broken by this heat engine? Justify your answer with a short calculation. (4 marks)

According to the heat absorbed and released, the engine does $w = 1000 \text{ J} - 500 \text{ J} = 500 \text{ J}$ of work. However, the maximum work that can be done by a heat engine is determined by the second law of thermodynamics (the entropy of the universe must always be increasing). This says that the maximum efficiency of a heat engine is given by: $\varepsilon = \frac{T_h - T_l}{T_h}$ For this heat engine this is $\varepsilon = \frac{500 \text{ K} - 300 \text{ K}}{500 \text{ K}} = 0.4$. Therefore according to the 2nd law of thermodynamics, the maximum work that can be done by this engine is: $q \times \varepsilon = 1000 \text{ J} \times 0.4 = 400 \text{ J}$. This is less than the work that is done according to the input and output heats, so this engine violates the second law of thermodynamics.

   b) Use the data in the table to calculate the boiling point of carbon tetrachloride. (3 marks)

	CCl_4 (*l*)	CCl_4 (*g*)
ΔH_f^o (kJ mol^{-1})	-128.2	-97.7
S_m^o (J K^{-1} mol^{-1})	214.1	309.7

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{vap}}$$

$$T_{vap} = \frac{\Delta H_{vap}}{\Delta S_{vap}} = \frac{\Delta H_f^o(\text{products}) - \Delta H_f^o(\text{reactants})}{S_m^o(\text{products}) - S_m^o(\text{reactants})} = \frac{\Delta H_f^o(\text{g}) - \Delta H_f^o(\text{l})}{S_m^o(\text{g}) - S_m^o(\text{l})} = \frac{\left(-97.7 \text{ kJ mol}^{-1} - \left(128.2 \text{ kJ mol}^{-1}\right)\right)\left(10^3 \text{ J kJ}^{-1}\right)}{309.7 \text{ J K}^{-1} \text{ mol}^{-1} - 214.1 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$T_{vap} = 319 \text{ K } \left(46^\circ\text{C}\right)$$

   c) The vapor pressure of dichloromethane at 0°C is 0.176 atm. The boiling point of dichloromethane is 40 °C. Calculate its molar heat of vaporization. (2 marks)

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H_{vap}^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta H_{vap}^o = \frac{-R\ln\left(\frac{p_2}{p_1}\right)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = \frac{-\left(8.314 \text{ J K-1 mol-1}\right)\ln\frac{0.176 \text{ atm}}{\text{atm}}}{\frac{1}{273 \text{ K} + 40 \text{ K}} - \frac{1}{273 \text{ K}}} = 31 \text{ kJ mol}^{-1}$$

3. 1.75 moles of water undergoes the transition $H_2O(l, 373\text{ K}) \rightarrow H_2O(g, 610\text{ K})$ at 1 bar of pressure. Data on the physical properties of water are on the last page in the equation sheet.

a) Calculate ΔS for the water. (4 marks)

$$\begin{aligned}\Delta S &= \Delta S_{vap} + \Delta S_{\text{temperture increase}} \\ &= n\left[\frac{\Delta H^{o}_{vap}}{T_{vap}} + C_{p,m}(g)\ln\left(\frac{T_2}{T_1}\right)\right] \\ &= 1.75\text{ mol}\left[\frac{40650\text{ J mol}^{-1}}{373\text{ K}} + \left(33.6\text{ J K}^{-1}\text{ mol}^{-1}\right)\ln\left(\frac{610\text{ K}}{373\text{ K}}\right)\right] \\ &= 220\text{ J K}^{-1}\text{ mol}^{-1}\end{aligned}$$

b) If the process in a) is carried out in surroundings that are held at 610 K, calculate the entropy change of the surroundings for this process. (4 marks)

$$\begin{aligned}\Delta S_{surr} &= \frac{-q_{vap}}{T_{surr}} + \frac{-q_{\text{temperature increase}}}{T_{surr}} \\ &= \frac{n}{T_{surr}}\left[-\Delta H^{o}_{vap} - C_{p,m}(g)\Delta T\right] \\ &= -\frac{1.75\text{ mol}}{610\text{ K}}\left[40650\text{ J mol}^{-1} + \left(33.6\text{ J K}^{-1}\text{ mol}^{-1}\right)(610\text{ K-}373\text{ K})\right] \\ &= -139\text{ J K}^{-1}\text{ mol}^{-1}\end{aligned}$$

c) Based on your answers in a) and b) does this calculation predict that the process will occur spontaneously? Provide a brief justification for your answer. (1 mark)

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 220\text{ J K}^{-1}\text{ mol}^{-1} - 139\text{ J K}^{-1}\text{ mol}^{-1} = 81\text{ J K}^{-1}\text{ mol}^{-1}$$

Since the total entropy change is greater than zero, therefore this process is spontaneous.

d) Can you use Gibbs energy calculations to determine if this process will be spontaneous? Explain why or why not. (1 mark)

Although this a constant pressure process, it is not isothermal and therefore we can not use a Gibbs energy calculation to evaluate for spontaneity.

4. It is found that at 1.50 atm, 375 K, 2.73% of NOCl(g) is dissociated at equilibrium according to:

$$NOCl\ (g) \rightleftharpoons NO\ (g) + \tfrac{1}{2}\ Cl_2\ (g)$$

a) Calculate K_x. (6 marks)

Let α = fraction dissociated at equilibrium

	NOCl	NO	½ Cl_2
Initial	n	0	0
Change	-αn	αn	1/2 αn
Equilibrium	(1-αn)	αn	1/2 αn
Mole fraction	$\frac{1-\alpha}{1+\frac{1}{2}\alpha} = \frac{1-0.0273}{1.01365} = 0.9596$	$\frac{\alpha}{1+\frac{1}{2}\alpha} = \frac{0.0273}{1.01365} = 0.02693$	$\frac{\frac{1}{2}\alpha}{1+\frac{1}{2}\alpha} = \frac{\frac{1}{2}(0.0273)}{1.01365} = 0.01347$

$$K_x = \frac{\chi_{NO}\chi_{Cl_2}^{\frac{1}{2}}}{\chi_{NOCl}} = \frac{(0.02693)(0.01347)^{\frac{1}{2}}}{(0.9596)}$$
$$= 3.257 \times 10^{-3}$$

b) Calculate K_p. (2 marks)

$$K_p = \left(\frac{p_T}{p^o}\right)^{\Delta v} K_x$$

$$\Delta v = v_{\text{gas, products}} - v_{\text{gas, reactants}} = 1 + \tfrac{1}{2} - 1 = \tfrac{1}{2}$$

$$K_p = \left(\frac{1.50\ \text{atm}\left(1.01325\ \text{bar atm}^{-1}\right)}{1\ \text{bar}}\right)^{\frac{1}{2}} 3.257 \times 10^{-3}$$
$$= 4.02 \times 10^{-3}$$

c) Calculate ΔG for this reaction at 375 K, starting from 0.500 bar Cl_2, 0.500 bar NO, and 1.00 bar of NOCl gas. (4 marks)

$$\Delta G = \Delta G_R^o + RT \ln Q_P$$

$$Q_P = \frac{\frac{p_{\mathrm{NO}}}{p^o}\left(\frac{p_{\mathrm{Cl_2}}}{p^o}\right)^{\frac{1}{2}}}{\left(\frac{p_{\mathrm{NOCl}}}{p^o}\right)} = \frac{(0.500)(0.500)^{\frac{1}{2}}}{1.00} = 0.353$$

$$\Delta G = -RT \ln K + RT \ln Q_P$$

$$= \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1}\right)(375 \text{ K})\left(\ln\left(\frac{0.353}{4.02\times 10^{-3}}\right)\right)$$

$$= 13.9 \text{ kJ mol}^{-1}$$

5. Answer the questions in each box for the phase diagram below (5 marks):

What is the equation of this line?

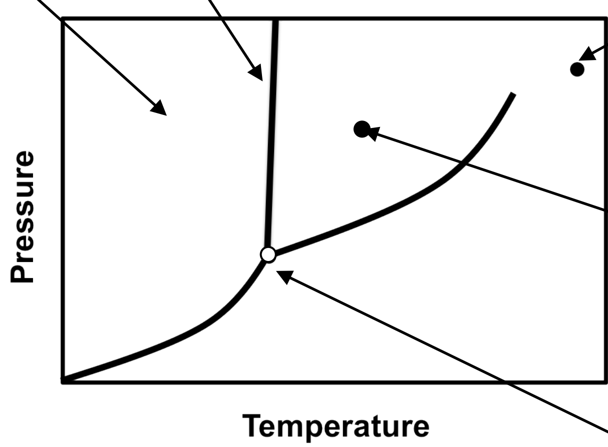
$$\frac{dp}{dT} = \frac{\Delta H^o_{fus}}{T_{fus}\Delta V_m}$$

What phase is present at this point?

Supercritical fluid

What phase has the lowest chemical potential in this region?

Solid



Show on the phase diagram the approximate vapour pressure of the substance at this point.

According to the Gibbs phase rule, how many degrees of freedom does the substance have at this point?

zero (F = 3 – p = 3 – 3)

Not covered in 2016.

Constants and Data

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 = 1.01325 bar
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}

$C_{p,m}(\mathrm{H_2O}(l)) = 75.3$ J K^{-1} mol^{-1} $C_{p,m}(\mathrm{H_2O}(g)) = 33.6$ J K^{-1} mol^{-1} $\Delta H^o_{vap}(\mathrm{H_2O}) = 40.65$ kJ mol^{-1}

Equations

$$pV = nRT$$

$$p = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$$

$$\Delta U = w + q$$

$$w = \int_{x_1}^{x_2} F \cdot dx$$

$$w = \int_0^Q \phi \cdot dQ'$$

$$w = -\int_{V_1}^{V_2} p_{ext}\, dV$$

$$C_p - C_V = nR$$

$$\Delta U = \int_{T_1}^{T_2} C_V\, dT$$

$$\Delta H = \int_{T_1}^{T_2} C_p\, dT$$

$$H = U + pV$$

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

$$p_1 V_1^\gamma = p_2 V_2^\gamma \quad \gamma = \frac{C_p}{C_V}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

$$\Delta H_r^\circ = \sum_{\text{Products}} \nu \Delta H_f^\circ - \sum_{\text{Reactants}} \nu \Delta H_f^\circ$$

$$\varepsilon = \frac{T_{high} - T_{low}}{T_{high}}$$

$$\varepsilon = \frac{\left|\oint \delta w_{rev}\right|}{q_{AB}}$$

$$\Delta H^\circ_{r,T} = \Delta H^\circ_{r,298.15\,\mathrm{K}} + \int_{T_1}^{T_2} \Delta C_p(T')\,dT'$$

$$\Delta C_p(T') = \sum_i \nu_i C_{p,i}(T')$$

$$\Delta S = \int \frac{C_V}{T} dT$$

$$\Delta S = \int \frac{C_p}{T} dT$$

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

$$\Delta_r S_m^\circ = \sum_{\text{Products}} \nu S_m^\circ - \sum_{\text{Reactants}} \nu S_m^\circ$$

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}}$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T_{\text{surr}}}$$

$$\Delta S^o_{trs} = \frac{\Delta H^o_{trs}}{T_{trs}}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$A = U - TS$$

$$G = H - TS$$

$$\Delta G = V \Delta p$$

$$\Delta(\Delta G) = \Delta V \Delta p$$

$$\Delta G_r^\circ = \sum_{\text{Products}} \nu \Delta G_f^\circ - \sum_{\text{Reactants}} \nu \Delta G_f^\circ$$

$$\Delta G = nRT \ln\left(\frac{p_2}{p_1}\right)$$

$$p_{\mathrm{A}} = x_{\mathrm{A}} p_{\mathrm{T}}$$

$$x_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{n_{\text{Total}}}$$

$$\Delta G(p_2) = \Delta G^o + nRT \ln\left(\frac{p_2}{p^o}\right)$$

$$\Delta G_m^o = -RT \ln K$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta_r H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta G_R = \Delta G_R^o + RT \ln Q_P$$

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$K_p = \prod_i \left(\frac{p_i}{p^o}\right)^{\nu_i}$$

$$K_p = \left(\frac{p_T}{p^o}\right)^{\Delta \nu_i} \prod_i x_i^{\nu_i} = \left(\frac{p_T}{p^o}\right)^{\Delta \nu_i} K_x$$

$$K = \left(\frac{c^o RT}{p^o}\right)^{\Delta \nu_i} \prod_i \left(\frac{c_i}{c^o}\right)^{\nu_i} = \left(\frac{c^o RT}{p^o}\right)^{\Delta \nu_i} K_c$$

$$\mu_i = \mu_i^o + RT \ln\left(\frac{p_i}{p^o}\right)$$

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H_{trs}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{dp}{dT} = \frac{\Delta_{trs} H_m}{T_{trs} \Delta V_m}$$

$$\int x^n\, dx = \frac{1}{n+1} x^{n+1} + c$$

$$\int \frac{dx}{x} = \ln x + c$$

$$\frac{dx^n}{dx} = n x^{n-1}$$