The Richard Stockton College of New Jersey
Chemistry Program, School of Natural Sciences and Mathematics
PO Box 195, Pomoma, NJ

CHEM 3410: Physical Chemistry I — Fall 2008

Exam 2 — Model Solutions

November 7, 2008

12:45–2 PM

Name: ____

Read all of the following information before starting the exam:

- This is a closed book exam. You are permitted an aid sheet consisting of two sides of a 8.5" x 11" piece of paper. **Your aid sheet must be turned in with your exam.**
- Show all work, clearly and in order, if you want to get full credit. I reserve the right to take off points if I cannot see how you arrived at your answer (even if your final answer is correct).
- Please keep your written answers brief; be clear and to the point. I will take points off for rambling and for incorrect or irrelevant statements.
- Justify your answers. Clearly state any assumptions you make.
- Circle or otherwise indicate your final answers.
- You have 75 minutes to complete the exam. There are a total of 67 points on the exam, so budget your time accordingly.
- For problems involving calculations, set up your calculations first and then do the computation if time permits.
- Be sure to read all the questions first. You do not have to complete the problems in any particular order.
- Good luck!

Use of wireless communication devices at any time during the exam is strictly prohibited.

Question	Score	Total
1		16
2		18
3		17
4		16
Total		67

1. (*16* points) Consider two possible processes for the vaporization of one mole of $\mathrm{H_2O}$ at 95°C and 1 atm.

A. The $\mathrm{H_2O}$ is the only substance in the container which is kept at constant pressure and temperature giving the process:

$$H_2O\ (l,\ 95°C, 1\ atm) \rightarrow H_2O\ (g,\ 95°C, 1\ atm)$$

B. One mole of He is present in the container along with one mole of $\mathrm{H_2O}$. The container is kept at constant pressure and temperature. The $\mathrm{H_2O}(l)$ and $\mathrm{He}(g)$ are initially not mixed since one is a liquid and the other is a gas. But after vaporizing, the $\mathrm{H_2O}(g)$ then mixes with the $\mathrm{He}(g)$ in the container, giving the total process:

$$H_2O\ (l,\ 95°C, 1\ atm) + He\ (g,\ 95°C, 1\ atm) \rightarrow (H_2O + He)_{mixed}\ (g,\ 95°C, 1\ atm)$$

You can assume that $\mathrm{He}(g)$ and $\mathrm{H_2O}(g)$ are ideal gases.

The following data may be useful:

The equilibrium boiling temperature of water is 100°C at 1 atm.

$\Delta H_{vap} = 40,525$ J/mol

$\Delta S_{vap} = 108.6$ J/molK

Assume that both the enthalpy of vaporization and the entropy of vaporization are independent of temperature in the range of 95°C to 100°C.

(a) Find ΔG for process **A**. Is this process spontaneous? (*4*)

We are told to assume that the enthaply and entropy of vaporization are independent of temperature. Therefore, for process **A** we can find ΔG in the following manner:

$$\Delta G_A = \Delta H_{vap} - T\Delta S_{vap} = 40525\ J - (95 + 273\ K)(108.6\ J/K)$$

$$\boxed{\Delta G_A = 560.2\ J \text{ and the process is not spontaneous } (\Delta G > 0)}$$

(b) What are ΔS_{mixing} and ΔG_{mixing} for mixing one mole of $\mathrm{He}(g)$ with one mole $\mathrm{H_2O}(g)$ at a constant pressure of 1 atm and a constant temperature of 95°C? (*4*)

We mixing one mole of water gas and one mole of He gas. Therefore the mole fraction of each gas (X) is equal to 0.5.

$$X_{He} = \frac{1\ mole\ He}{2\ total\ moles\ gas} = 0.5$$

The free energy of mixing is:

$$\Delta G_{mix} = RT(X_{He}\ln X_{He} + X_{H_2O}\ln X_{H_2O}) = (8.314\ J/molK)(368\ K)(.5\ln .5 + .5\ln .5)$$

$$\Delta G_{mix} = -2121\ J/mol$$

Since $\Delta H_{mix} = 0$ for an ideal gas:

$$\Delta S_{mix} = \frac{-\Delta G_{mix}}{T} = \frac{2121 J/mol}{368\ K} = +5.76 J/molK$$

Both this quantities make sense since the mixing of two ideal gases is always spontaneous ($\Delta G_{mix} < 0$ and $\Delta S_{mix} > 0$).

$$\boxed{\Delta G_{mix} = -2121 \text{ J/mol and } \Delta S_{mix} = 5.76 \text{ J/molK}}$$

(c) What is ΔG for the complete process **B**. Is this process spontaneous? (*4*)

For the complete process **B**, we need to take into account the free energy of the vaporization (part a) and the mixing free energy (part b).

$$\Delta G_B = \Delta G_A + \Delta G_{mix} = 560.2\ J/mole + (-2121\ J/mol) = -1560.8\ J/mol$$

$$\boxed{\Delta G_B = -1560.8 \text{ J/mol and is spontaneous because } \Delta G_B < 0}$$

(d) Predict whether $\Delta S_{universe}$ for process **B** will be positive, negative, or equal to zero. Briefly explain your choice. [*Bonus +4 if you calculate* $\Delta S_{universe}$ *for process* **B**] (*4*)

Since the process is spontaneous, $\Delta S_{universe}$ must be greater than zero.

$$\Delta S_{system} = 5.76\ J/K + 108.6\ J/K = 114.36\ J/K$$

$$\Delta S_{surr} = \frac{-40525\ J}{368\ K} = -110.12 J/K$$

$$\boxed{\Delta S_{univ} = 114.36 + (-110.12) = +4.24 J/K}$$

2. (*18* points) The gas phase dissociation of molecule A is given by:

$$A(g) \rightleftharpoons B(g) + C(g)$$

Initially pure A is placed in a container.

(a) At 80°C and 1 bar, the fraction α of "A" that is dissociated is 0.4. (If n moles of A are initially placed in the container, then αn moles will have dissociated leaving $n - \alpha n$ moles of A at equilibrium). Calculate the equilibrium constant K_p and the standard free energy change ΔG° for the dissociation of A at 80°C. (***6***)

We can set up the following table to keep track of the equilibrium amounts of each substance

	A (g)	$\rightleftharpoons$	B (g)	+	C (g)
Initial number of moles	n		0		0
Moles at equilibrium	$n - \alpha n$		αn		αn
Total number of moles at equilibrium	$n - \alpha n + \alpha n + \alpha n$	$=$	$n + \alpha n$		
Mole fraction at equilibrium	$\frac{n-\alpha n}{n+\alpha n}$		$\frac{\alpha n}{n+\alpha n}$		$\frac{\alpha n}{n+\alpha n}$
Partial pressure at equilibrium ($P_i = X_i P$)	$\left(\frac{n-\alpha n}{n+\alpha n}\right) P$		$\left(\frac{\alpha n}{n+\alpha n}\right) P$		$\left(\frac{\alpha n}{n+\alpha n}\right) P$

We are told the total pressure ($P = 1$ bar) and that $\alpha = 0.4$. We can use this information along with the equilibrium expression to find K_p.

$$K_p = \frac{P_B P_C}{P_A} = \frac{\left(\frac{\alpha n}{n+\alpha n}\right) P \left(\frac{\alpha n}{n+\alpha n}\right) P}{\left(\frac{n-\alpha n}{n+\alpha n}\right) P} = P \frac{\alpha^2 n^2}{(n+\alpha n)(n-\alpha n)}$$

$$K_p = P \frac{\alpha^2 n^2}{n^2(1+\alpha)(1-\alpha)} = P \frac{\alpha^2}{1-\alpha^2}$$

Inserting $P = 1$ bar and $\alpha = 0.4$ we get

$$\boxed{K_p = 0.190}$$

We could have also used the relationship:

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

where $\Delta\nu$ is the difference in the stoichiometric coefficients (products - reactants) and is equal to 1 in this case, K_x is the equilibrium constant written in terms of mole fraction and K_p is the equilibrium constant in terms of partial pressures.

We can now solve for ΔG°_{rxn} using the relationship between ΔG and K_p along with the equilibrium constant solve for above and the temperature:

$$\ln K_p = \frac{-\Delta G^\circ_{rxn}}{RT}$$

$$\boxed{\Delta G^\circ_{rxn} = +4874 \text{ J/mole}}$$

(b) Calculate the pressure at which the fraction α that is dissociated is 0.9 at 80°C. (***6***)

We can use the expression for K_p we solved for above to find P if $\alpha = 0.9$. We should expect that the pressure required should decrease since if α increases, more products are formed. The product side of the reaction contains more moles of gas which would be favored only if the pressure was reduced.

$$K_p = P\frac{\alpha^2}{1-\alpha^2}$$

$$0.190 = P\frac{0.9^2}{1-0.9^2}$$

$$\boxed{P = 0.045 \text{ bar}}$$

(c) At 320°C, $K_p = 1.076$. Calculate the standard heat of reaction $\Delta H°$ for the dissociation of "A" if $\Delta H°$ is assumed to be independent of temperature.
[If you were unable to do part (a), then use (incorrectly) $K_p(80°C) = 0.30$]. (***6***)

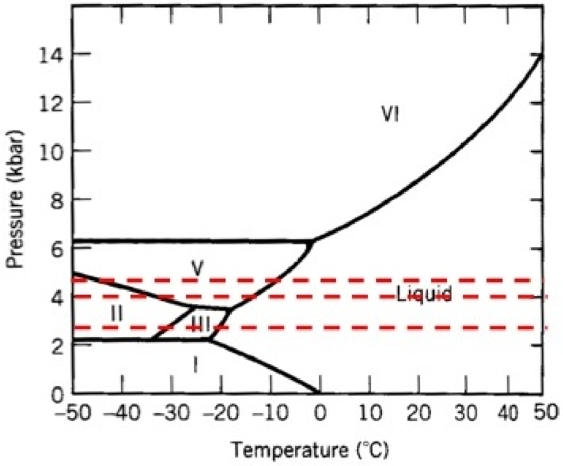
To find the enthalpy of the reaction we can employ the van't Hoff Equation since we know K_p at two temperatures. Since the equilibrium constant increases with temperature, we should expect the reaction to be endothermic.

$$\ln K_p(T_2) = \ln K_p(T_1) + \frac{\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

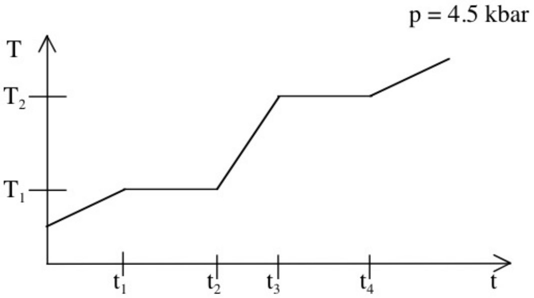
Inserting values for K_p for each temperature T_1 and T_2 we find:

$$\boxed{\Delta H^\circ_{rxn} = 12.6 \text{ kJ/mol}}$$

3. (*17* points) Unary phase diagrams, such as the one for water shown below,



are often constructed from data obtained using a constant pressure calorimeter. A carefully measured number of moles of the compound is placed in the calorimeter. Heat is added to the calorimeter at a constant rate and T is measured vs. time, t. A T vs. t plot for H_2O at $P = 4.5$ kbar might look like the sketch below:



(a) What is happening at T_1 and T_2? (*3*)

The horizontal regions represent two-phase equilibria. According to the phase diagram, the two-phase equilirbium we would observe at 4.5 kbar are: T_1 (II → V) and T_2 (V → Liquid).

(b) Based on the above phase diagram for H_2O, what are the approximate values of T_1 and T_2? (*3*)

Using the phase diagram, $T_1 \approx -40°$C and $T_2 \approx -10°$C.

(c) If P is decreased from $P = 4.5$ kbar to $P = 4.0$ kbar, how will the temperatures of the horizontal regions of the T vs. t plot change? What do these changes tell you about the sign of ΔV for the II → V and V → liquid phase transitions? (*4*)

According to the phase diagram, if we reduce the pressure to 4 kbar, T_1 will increase and T_2 will decrease.

We know that changes of P and T along the coexistence curve are governed by the Clapeyron equation:

$$\left(\frac{dP}{dT}\right)_{coexist} = \frac{\Delta H}{T\Delta V}$$

For both transitions, $dP < 0$ and $\Delta H > 0$. Therefore, for the II $\rightarrow$ V transition since $dT > 0$, ΔV must be negative to make $\frac{dP}{dT}$ negative. For the V $\rightarrow$ liquid, ΔV must be positive since $dT < 0$ and $\frac{dP}{dT} > 0$.

This should also make sense by looking at the slopes of the coexistence curves. For II $\rightarrow$ V the coexistence curve has a positive slope, while for V $\rightarrow$ liquid it has a negative slope.

(d) Sketch a similar heating curve for a pressure of 2.5 kbar. Indicate any relevant transformation temperatures on the sketch.

(*4*)

The heating curve would have the same form as the one given at the beginning of the problem. However, at 2.5 kbar we cross different two phase equilibria: $II \rightarrow III$ at approximately -30°C and $III \rightarrow L$ at around -20°C.

(e) Why do the non-horizontal portions of the heating curve have different slopes? (*3*)

The non-horizontal regions indicate a single phase is present. The slopes are difference since each phase has a different heat capacity. The heating rate is constant, so each phase will require a different amount of heat transfered to raise the temperature. Hence the slopes are different.

4. (*16* points) Please identify each of the following statements as true or false. Give a brief justification for each answer.

   (a) The mixing of ideal gases is spontaneous at high temperatures but non-spontaenous at low temperatures. (*4*)

   FALSE. The mixing of ideal gases is spontaneous at any temperature since entropy is the only driving force for mixing.

   (b) The entropy of a *system* is always maximized at equilibrium. (*4*)

   FALSE. This statement is only true in the case of an **isolated** system. In general, the entropy of the <u>universe</u> is maximized at equilibrium.

   (c) The chemical potential of 12 grams of ice at 0°C and 1 atm is equal to the chemical potential of 12 grams of liquid water at 0°C and 1 atm. (*4*)

   TRUE. At 0°C and 1 atm, liquid water and ice are in equilibrium (at the melting point). Therefore the chemical potential of the two phases are equal.

   (d) Increasing the pressure on a gas-phase reaction will always shift equilibrium towards the products. (*4*)

   FALSE. This is not true in general. The impact of changes in pressure on equilibrium depends on the particular gas stoichiometry of the reaction of interest. We demonstrated in class that as you increase the pressure on a gas-phase reaction the equilibrium will shift towards this side with *less* moles of gas.

Potentially useful information

R = 0.0821 L·atm/mol·K = 8.314 J/mol·K

$PV = nRT$ for an ideal gas

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

The Periodic Table of the Elements

1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)