

CHEM 3410: Physical Chemistry I — Fall 2009

Exam 1 — Model Solutions

October 5, 2009

12:45–2 PM

Name: Key

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 72 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		16
3		20
4		20
Total		72

1. (16 points) For the following processes, predict whether q , w , ΔU , and ΔH will be positive (+), negative (-), or equal to zero (0) for the system. Explain **briefly** in the space provided.

- (a) An ideal gas is compressed **isothermally** against an external pressure of 1 atm. (8)

q	w	ΔU	ΔH
-	+	0	0

The process involves an ideal gas and is isothermal. This immediately means that $\Delta U = \Delta H = 0$ because for an ideal gas the internal energy and enthalpy are only functions of temperature. Because $\Delta U = q + w$ this means that since $\Delta U = 0$ that $q = -w$. The gas is being compressed, so work is being done on the system, so $w > 0$ and therefore $q < 0$.

- (b) An ideal gas is heated at **constant volume**. (8)

q	w	ΔU	ΔH
+	0	+	+

The process is being done at constant volume, thus $dV = 0$ and no work can be done ($\partial w = -PdV$). The gas is being heated, so heat is flowing into the system and $q > 0$. Since $\Delta U = q + w$, then ΔU is also greater than zero. Also, $\Delta H = \Delta U + \Delta(PV)$, so since V is constant, P must be increasing and ΔH will also be positive.

2. (16 points) One mole of ideal gas is expanded at 400.0 K *isothermally* from a volume of 3.3 L to 10.9 L.

Calculate w , q , ΔU , ΔH , and ΔS for the **system** when the process is done in the following two manners. Show your work below and enter your results in the table. Be sure to include the appropriate units.

It is important to note that part (a) and (b) end up in the same state, so values of state functions (ΔU , ΔH , ΔS) for the processes are going to be the same for both parts. Also for both parts the process is isothermal and since this is an ideal gas, $\Delta U = \Delta H = 0$.

- (a) the process is done reversibly (8)

Since $\Delta U = 0$, we know that $q = -w$, so we can first solve for the work done:

$$\partial w = -PdV \rightarrow w = \int_{V_1}^{V_2} -PdV$$

Using the ideal gas law to write P in terms of V (P IS NOT CONSTANT, so it cannot be pulled out of the integral):

$$w = \int_{3.3}^{10.9} -\frac{nRTdV}{V} = -nRT \ln \frac{10.9}{3.3} = -(1 \text{ mol})(8.314 \text{ J/molK})(400\text{K}) \ln \frac{10.9}{3.3}$$

$$w = -3974 \text{ J} \quad q = -w = +3974 \text{ J}$$

The process is isothermal, so we can solve for the entropy change of the system as follows:

$$\Delta S_{sys} = \int \frac{\partial q_{rev}}{T} = \frac{q_{rev}}{T} = \frac{3974 \text{ J}}{400 \text{ K}} = 9.93 \text{ J/K}$$

- (b) the process is done irreversibly against a constant zero external pressure ($P_{ext} = 0$, i.e. a "free" expansion)

(8)

ΔU , ΔH , and ΔS are the same as in part (a) because they are state functions and the starting and ending states for both processes are the same. The external pressure on the system is a constant zero pressure meaning no work is done during the expansion. Also, since $\Delta U = q + w$ and both ΔU and w are 0, $q = 0$ as well.

	w	q	ΔU	ΔH	ΔS
Part (a)	-3874 J	+3974 J	0	0	9.93 J/K
Part (b)	0	0	0	0	9.93 J/K

3. (20 points) Superheated water is water heated above 100°C without boiling. Much like supercooled water, superheated water is thermodynamically unstable.

Suppose 1.5 moles of superheated liquid water are converted to gaseous water (steam) at 110°C and a constant pressure of 1 atm.

The enthalpy of vaporization of water at its boiling point of 100°C is 40.79 kJ/mol. The molar heat capacity of liquid water is $75.5 \frac{J}{K \cdot mol}$ and of gaseous water (steam) is $34.4 \frac{J}{K \cdot mol}$.

- (a) Without doing any calculations predict whether ΔH_{system} , ΔS_{system} , $\Delta S_{surroundings}$, and $\Delta S_{universe}$ will be positive (+), negative (-), or equal to zero (0) for the process described above. Enter your predictions in the table below and briefly justify your answer. (6)

ΔH_{system}	ΔS_{system}	$\Delta S_{surroundings}$	$\Delta S_{universe}$
+	+	-	+

ΔH for the system is positive because heat is absorbed by the system to transform a liquid into a gas. ΔS_{system} must be positive because you are transforming a liquid to a gas and the entropy of the gas phase is greater than that of the liquid phase. The entropy change for the surroundings must be negative since heat is flowing into the system and out of the surroundings. Finally, $\Delta S_{universe}$ must be positive because the conversion of a liquid to gas at a temperature above its boiling point is spontaneous.

- (b) Using the data supplied above, determine ΔH_{system} for the process. You may assume that the heat capacities are independent of temperature. Show your work and enter your numerical result in the table below. Be sure to include the appropriate units. (4)

ΔH_{system}
60568 J or 60.57 kJ

We want the enthalpy of the system (vaporization) at 383 K. Since we know the enthalpy of vaporization at the boiling point of 373 K and the heat capacities of the liquid & we can construct a path along which we can actually solve for the enthalpy change at 383 K.

$$\Delta H_{system} = \int_{383}^{373} n C_p^{liquid} dT + n \Delta H_{vap} + \int_{373}^{383} n C_p^{gas} dT$$

$$\Delta H_{system} = n [C_p^{liquid} (373 - 383) + \Delta H_{vap} + C_p^{gas} (383 - 373)]$$

$$\Delta H_{system} = 1.5 (40379 \text{ J/mol}) = 60568 \text{ J}$$

- (c) Using the data supplied, calculate ΔS_{system} , $\Delta S_{surroundings}$, and $\Delta S_{universe}$. You may assume that the heat capacities are independent of temperature. Show your work and enter your numerical results in the table below. Be sure to include the appropriate units. (10)

ΔS_{system}	$\Delta S_{surroundings}$	$\Delta S_{universe}$
162.4 J/K	-158.14 J/K	+4.26 J/K

For ΔS_{system} we can use a similar approach as we did for solving for the enthalpy change, but use $dS = \frac{\partial q}{T}$:

$$\Delta S_{system} = \int_{383}^{373} \frac{nC_p^{liquid} dT}{T} + \frac{n\Delta H_{vap}}{T_{boiling}} + \int_{373}^{383} \frac{nC_p^{gas} dT}{T}$$

$$\Delta S_{system} = n \left[C_p^{liquid} \ln \frac{373}{383} + \frac{\Delta H_{vap}}{373 \text{ K}} + C_p^{gas} \frac{383}{373} \right]$$

$$\Delta S_{system} = 162.4 \text{ J/K}$$

For $\Delta S_{surroundings}$ we need to use the actual heat flow into or out of the surroundings. In part (b) you calculated that 60658 J of heat will be absorbed by the system during this process. Therefore, since $q_{system} = -q_{surroundings}$, the surroundings lost heat or the heat flow out of the surroundings was -60658 J.

$$\Delta S_{surroundings} = \frac{q_{surr}}{T_{surr}} = \frac{-\Delta H_{sys}}{T_{surr}} = \frac{-60568 \text{ J}}{383 \text{ K}} = -158.14 \text{ J/K}$$

Finally, $\Delta S_{universe}$ is the sum of the entropy change of the system and the surroundings:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 162.4 \text{ J/K} + -158.14 \text{ J/K} = +4.26 \text{ J/K}$$

4. (20 points) Please identify each of the following statements as true or false. Give a brief justification for each answer.

(a) The entropy of a *system* must always increase for a spontaneous process.. (5)

FALSE. ΔS of the universe must always increase for a spontaneous process. ΔS_{system} will always increase for an isolated spontaneous process since there is no contact with the surroundings.

(b) For a reversible, cyclic process $w = q = 0$. (5)

FALSE. We have a counter example, namely the Carnot cycle, where there is cyclic process and there is work and heat flow. It is true that w and q are not state functions and thus are not always zero for a cyclic process, but this does not mean they couldn't be zero. So saying that w and q are not state functions does not fully explain why this statement is false.

(c) In the reversible adiabatic expansion of a gas, the internal energy always decreases. (5)

TRUE. In an adiabatic expansion there is no heat flow ($q = 0$) and work is done by the expanding gas ($w < 0$). Since $q = 0$, $\Delta U = w$ and since w is less than zero the change internal energy is also negative (decreases).

(d) To determine the work done in a process all you need to know are the initial and final states of the system. (5)

FALSE. Work is NOT a state function, therefore in order to determine the work done you need to know the path taken, i.e. how the process is done (constant volume, constant pressure, adiabatic, isothermal, etc.)

Potentially useful information

$$R = 0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K} = 8.314 \text{ J}/\text{mol}\cdot\text{K}$$

$$PV = nRT \text{ for an ideal gas}$$

$$q_{\text{system}} = -q_{\text{surroundings}}$$

PERIODIC TABLE OF THE ELEMENTS

<http://www.periodict.com/en/>

GROUP		PERIOD															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIB	VIB	VIB	VIB	IB	IIB	IIIA	IVA	VA	VIA	VIA	VIIA
1 H 1.0079 HYDROGEN	2 He 4.0026 HELIUM	3 Li 6.941 LITHIUM	4 Be 9.0122 BERYLLIUM	5 B 10.811 BORON	6 C 12.011 CARBON	7 N 14.007 NITROGEN	8 O 15.999 OXYGEN	9 F 18.998 FLUORINE	10 Ne 20.180 NEON	11 Na 22.990 SODIUM	12 Mg 24.305 MAGNESIUM	13 Al 26.982 ALUMINIUM	14 Si 28.086 SILICON	15 P 30.974 PHOSPHORUS	16 S 32.065 SULFUR	17 Cl 35.453 CHLORINE	18 Ar 39.948 ARGON
19 K 39.098 POTASSIUM	20 Ca 40.078 CALCIUM	21 Sc 44.956 SCANDIUM	22 Ti 47.867 TITANIUM	23 V 50.942 VANADIUM	24 Cr 51.996 CHROMIUM	25 Mn 54.938 MANGANESE	26 Fe 55.845 IRON	27 Co 58.933 COBALT	28 Ni 58.693 NICKEL	29 Cu 63.546 COPPER	30 Zn 65.409 ZINC	31 Ga 69.723 GALLIUM	32 Ge 72.64 GERMANIUM	33 As 74.922 ARSENIC	34 Se 78.96 SELENIUM	35 Br 79.904 BROMINE	36 Kr 83.798 KRYPTON
37 Rb 85.468 RUBIDIUM	38 Sr 87.62 STRONTIUM	39 Y 88.906 YTRITIUM	40 Zr 91.224 ZIRCONIUM	41 Nb 92.906 NIOBIUM	42 Mo 95.94 MOLYBDENUM	43 Tc (98) TECHNETIUM	44 Ru 101.07 RUTHENIUM	45 Rh 102.91 RHODIUM	46 Pd 106.42 PALLADIUM	47 Ag 107.87 SILVER	48 Cd 112.41 CADMIUM	49 In 114.82 INDIUM	50 Sn 118.71 TIN	51 Sb 121.76 ANTIMONY	52 Te 127.60 TELLURUM	53 I 126.90 IODINE	54 Xe 131.29 XENON
55 Cs 132.91 CAESIUM	56 Ba 137.33 BARIUM	57-71 La-Lu Lanthanide	72 Hf 178.49 HAFNIUM	73 Ta 180.95 TANTALUM	74 W 183.84 WOLYBDENUM	75 Re 186.21 RHENIUM	76 Os 190.23 OSMIUM	77 Ir 192.22 IRIDIUM	78 Pt 195.08 PLATINUM	79 Au 196.97 GOLD	80 Hg 200.59 MERCURY	81 Tl 204.38 THALLIUM	82 Pb 207.2 LEAD	83 Bi 208.98 BISMUTH	84 Po (209) POLONIUM	85 At (210) ASTATINE	86 Rn (222) RADON
87 Fr (223) FRANCIUM	88 Ra (226) RADIUM	89-103 Ac-Lr Actinide	104 Rf (267) RUFBERGDIUM	105 Db (268) DUBNIUM	106 Sg (271) SEABORGIUM	107 Bh (272) BOHRNIUM	108 Hs (277) HASSIUM	109 Mt (276) MEITNERIUM	110 Ds (281) DARMSTADTIUM	111 Rg (280) ROSENBERGIUM	112 Cn (285) COCHIN	113 Nh (286) NIHONIUM	114 Fl (289) FLEROVIUM	115 Mc (290) MOSCOWIUM	116 Lv (293) LIVERMORIUM	117 Ts (294) TENNESSIUM	118 Og (294) OGANESSIUM

(1) Pure Appl. Chem., 78, No. 11, 2091-2096 (2006)
 Relative atomic mass is shown with five significant figures. For elements with no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element. However, three such elements (Tl, Po, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

LANTHANIDE		ACTINIDE	
57 La 138.91 LANTHANUM	58 Ce 140.12 CERMIUM	89 Ac (227) ACTINIUM	90 Th 232.04 THORIUM
59 Pr 140.91 PRASEODYMIUM	60 Nd 144.24 NEODYMIUM	91 Pa 231.04 PROCTINIUM	92 U 238.03 URANIUM
61 Pm (145) PROMETHIUM	62 Sm 150.36 SAMARIUM	93 Np (237) NEPTUNIUM	94 Pu (244) PLUTONIUM
63 Eu 151.96 EUROPIUM	64 Gd 157.25 GADOLINIUM	95 Am (243) AMERICIUM	96 Cm (247) CURIUM
65 Tb 158.93 TERBIUM	66 Dy 162.50 DYSPROSIUM	97 Bk (247) BERKELIUM	98 Cf (251) CALIFORNIUM
67 Ho 164.93 HOLIUM	68 Er 167.26 ERBIUM	99 Es (252) EINSTEINIUM	100 Fm (257) FERMIUM
69 Tm 168.93 THULIUM	70 Yb 173.04 YTERBIUM	101 Md (258) MIRZAPURIUM	102 No (259) NOBELIUM
71 Lu 174.97 LUTETIUM		103 Lr (262) LAWRENCIUM	