

Name: \_\_\_\_\_

KEY

**Chemistry 112**  
**Test 3**  
**March 29, 2006**

Instructions before starting the test:

1. Your exam booklet should have **eight** pages total, with questions on Pages 2-5, and a periodic table and other reference data on Pages 6-8. Check to see you have eight pages now. If you do not, ask for another copy of the exam.
2. Write your name in the space above and on the backs of Pages 2-5.
3. This exam is closed-everything.
4. You may use programmable calculators, but chemical data should not be stored in them.
5. You have up to **90 minutes** to work on this exam, if you start work at 8:00 a.m.

<u>Question (Possible Points)</u>	<u>Your Score</u>
Question 1 (24)	
Question 2 (40)	
Question 3 (16)	
Question 4 (20)	
Total (100)	

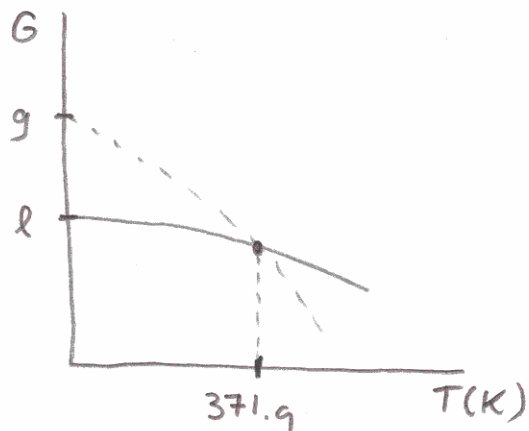
mean 77

Average after Three Tests	
<b>Estimated Grade</b>	

1. (24 points total) Junior chemistry majors typically perform an experiment studying the evaporation of heptane ( $C_7H_{16}$ ). Last fall, one lab team obtained the following data:



(a) (12 points) On the same graph, draw  $G$ - $T$  curves for both  $C_7H_{16}(l)$  and  $C_7H_{16}(g)$  at 1 bar pressure. Calculate the standard (that is, the 1-bar) boiling point (in K) of  $C_7H_{16}(l)$ , and label this point on your graph.



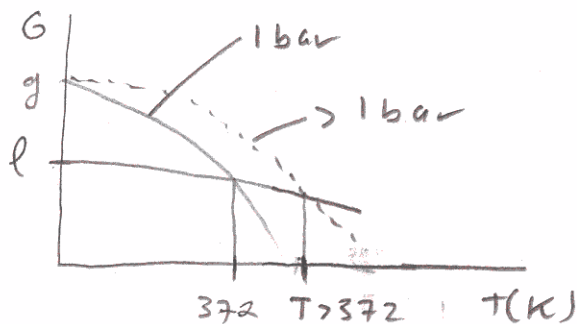
$$\Delta G = \Delta H - T\Delta S = 0 \text{ at equil}$$

$$T = \frac{\Delta H}{\Delta S} = \frac{\Delta_r H^\circ}{\Delta_r S^\circ}$$

$$T = \frac{31800 \text{ J mol}^{-1}}{85.5 \text{ J mol}^{-1} \text{ K}^{-1}} = 371.9 \text{ K}$$

-2 sig figs error

(b) (12 points) Propose one way to raise the boiling point of heptane above its standard value. Justify your proposal clearly using words and  $G$ - $T$  curves.

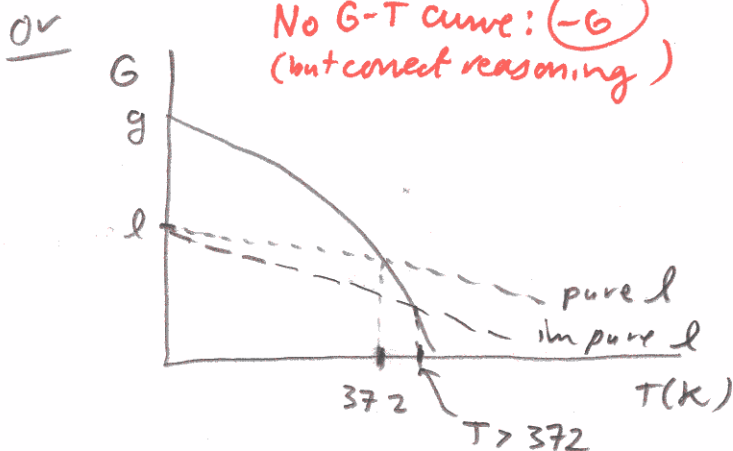


Increase  $P$  in system  $\Rightarrow \downarrow S$  of  $g$   
 $\Rightarrow G$ - $T$  curve of gas falls less steeply  $\Rightarrow$  intersects  $l$   $G$ - $T$  curve at a higher  $T$

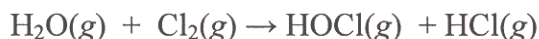
(-4) major misstatement / vague  
 (-9) invalid proposal  
 (-9) invalid explanation  
 (-11) something

Dissolve a solute in  $l \Rightarrow \uparrow S$  of  $l$   
 $\Rightarrow G$ - $T$  curve of  $l$  falls more steeply  $\Rightarrow$  intersects gas'  $G$ - $T$  curve at a higher  $T$

(-6) no explanation



2. (40 points total) In the 1990's, a hapless graduate student at the California Institute of Technology was told by his advisor to generate 0.250 mol of gaseous hypochlorous acid (HOCl(g)) for an experiment. The student's lab partner suggested the following reaction:



In the system, the partial pressure of each reactant and product was exactly 1 bar.

- (a) (12 points) Calculate the entropy change in the system (in  $\text{J K}^{-1}$ ) if the above reaction forms 0.250 mol of HOCl(g).

$$\Delta_r S^\circ = S^\circ(\text{HOCl}(g)) + S^\circ(\text{HCl}(g)) - S^\circ(\text{H}_2\text{O}(g)) - S^\circ(\text{Cl}_2(g))$$

$$\Delta_r S^\circ = [236 + 187 - 189 - 223] \text{ J mol}^{-1} \text{ K}^{-1} = 11 \text{ J mol}^{-1} \text{ K}^{-1} \leftarrow \text{known to the one's place}$$

$$\text{so } \Delta S_{\text{sys}} = (0.250 \text{ mol})(11 \text{ J mol}^{-1} \text{ K}^{-1}) = \boxed{2.75 \text{ J K}^{-1}} \quad \leftarrow \text{is } \approx \text{ sig figs!}$$

(-2) 3 sig figs

(-5) Didn't mult by 0.250 mol

(-2) unit error/math error

(-5) sign error

(-5) multiplied only  $S^\circ(\text{HOCl})$  by 0.250 mol

(-9) fundamentally wrong approach

- (b) (18 points) Calculate the entropy change in the surroundings (in  $\text{J K}^{-1}$ ) at  $150.^\circ\text{C}$  if the above reaction forms 0.250 mol of HOCl(g).

$$\Delta S_{\text{surv}} = \frac{q_{\text{surv}}}{T} = \frac{-q_{\text{sys}}}{T} = \frac{-\Delta H}{T}$$

$$\Delta_r H^\circ = \Delta_f H^\circ(\text{HOCl}(g)) + \Delta_f H^\circ(\text{HCl}(g)) - \Delta_f H^\circ(\text{H}_2\text{O}(g)) - \Delta_f H^\circ(\text{Cl}_2(g))$$

$$\Delta_r H^\circ = [-74.48 - 92.31 + 241.8 - 0] \text{ kJ mol}^{-1} = +75.01 \text{ kJ mol}^{-1}$$

$$\text{so } \Delta H = (0.250 \text{ mol}) \left( \frac{75.01 \text{ kJ}}{\text{mol}} \right) \left( \frac{10^3 \text{ J}}{\text{kJ}} \right) = 1.87525 \times 10^4 \text{ J}$$

$$\text{and } T = 150. + 273.15 = 423.15 \text{ K}$$

$$\therefore \Delta S_{\text{surv}} = \frac{-1.87525 \times 10^4 \text{ J}}{423.15 \text{ K}} = \boxed{-44.32 \text{ J K}^{-1}}$$

(-2) sig fig error

(-13) assumes  $\Delta S_{\text{univ}} = 0$  or other wrong approach

(-2) unit error

(-2) sign error (if dropped)

(-13) wrong way to calc  $\Delta H$

(-3) sign error (if never written)

(-4) math error/wrong T

(-4) wrong  $\Delta_f H^\circ$

[Question 2 continues on the next page.]

- (c) (10 points) Is the above reaction an effective way of generating HOCl(g) at 150.°C? Justify your answer with a calculation.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = (2.75 - 44.32) \text{ J K}^{-1} = -41.57 \text{ J K}^{-1} < 0$$

or  $\Delta G = \Delta H - T \Delta S = 1.87_{525} \times 10^4 \text{ J} - (423.15 \text{ K})(2.75 \text{ J K}^{-1}) \therefore \text{NOT EFFECTIVE}$

$$= 187_{520.5} \text{ J} - 1163.7 \text{ J} = +175_{89} \text{ J} > 0 \quad \uparrow$$

( $\Delta G^\circ = 703_{55} \text{ J mol}^{-1}$ )

(-2) missing units

(-3) math error

(-5) significant mis-statement

(-7) wrong calc erroneous

(-9) wrong or vague approach (usually no calculation)

3. (16 points) At 8:46 a.m. on March 23, the National Weather Service reported that the current temperature at the MSP Airport was 34°F, the current humidity was 81%, and the dew point was 28°F. Say the Weather Service's humidity measurement was wrong—it was actually 96%. If this had been the case, the dew point would have been

less than 28°F

equal to 28°F

greater than 28°F

Circle the correct answer above and justify it with a  $G$ - $T$  graph and words below. Make sure all temperatures in the problem—both the current temperature and the dew point(s)—are correctly labeled on the  $G$ - $T$  graph. *Calculation not necessary.*

(-3) no  $G$ - $T$  curve for 34°F

(-5) no explicit discussion of entropy

(-8) Dew point at 96% humidity > 34°F

(-6) missing or invalid discussion

(+1) something

(+2)

(-5) missing either the 81% or 96%  $G$ - $T$  curve (but explained)

(-5) Changing humidity  $\Rightarrow$  (substantial) change in air  $P$  or  $P_{\text{H}_2\text{O}} = 1 \text{ bar}$  at 100% humidity

(-5) 34°F not labeled at all

(-10) crossing pts mislabeled

(-3) minor labeling error

4. (20 points total) Since March 10, you have witnessed demonstrations of (i) the boiling of acetone at room temperature, (ii) liquid water (not at equilibrium) supercooled to  $-7^{\circ}\text{C}$  that suddenly freezes upon agitation, (iii)  $\text{CO}_2(\text{s})$  forming  $\text{CO}_2(\text{l})$  instead of  $\text{CO}_2(\text{g})$  at 5 bar, and (iv) a cooled supersaturated solution of sodium acetate (not at equilibrium) suddenly and exothermically precipitating solid sodium acetate. Explain one of these demos in detail using  $G$ - $T$  curves, words, and the relevant equation(s) from p. 6. Your discussion of any equation you invoke should remain qualitative; do not calculate any actual numbers.

(i) (12 responses)

(-5) system was open in demo

(-7) wrong eqn invoked

(-4)  $T > T_{\text{bp}}$  to boil

(-4) eqn for  $\Delta S$ , not  $S$

(-2) minor misstatement

(-3)  $\downarrow P \Rightarrow \uparrow$  amount of  $E_{\text{translational}}$

(+2) something

(ii) (10 responses)

If correct  $G$ - $T$  curves...

(-5) no mention ~~text~~ of  $T \uparrow$  to  $273 \text{ K}$  at end

(-6) " " of transition fr.  $l$  to  $s$   $G$ - $T$  curve at  $T < 273 \text{ K}$

If interpreted as freezing pt depression (-10) (-7) wrong eqn invoked

(-5)  $S_{\text{liq}} = S^{\circ}_{\text{liq}} - R \ln x_{\text{H}_2\text{O}}$  not interpreted

(-7) no eqn invoked

Interpreted as pressure changing  $S(l)$  (-12)

(-5)  $G = H - TS$  not applied to demo

(iii) (23 responses)

(-5) no explanation of  $H(g)$  being not much higher than  $H(l)$  and  $H(s)$

(-4) eqn for  $\Delta S$ , not  $S$

(-6) valid eqn cited, but not explained/applied properly to demo

(-2) minor mis-statement

(-7) Valid  $G$ - $T$  curves not used to interpret demo precisely

(-10) Wrong  $G$ - $T$  curves (or missing)

(a): Supercooling  
(b): Crashing out of soln

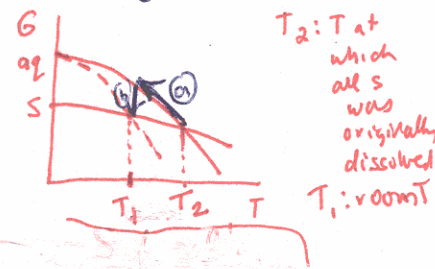
(iv) (9 responses)

(-7) no eqn invoked or explained

(-6) no discussion of entropy

(-7) ~~mass~~ only 1  $G$ - $T$  curve for aqueous phase

(-7)  $G$ - $T$  curve for pure water



(-6) eqn cited not applied precisely to what happened in demo

(-6) no transition fr. higher  $x$  to lower  $x$  curve

(-2) minor error

**Possibly Useful Information**

$$\frac{n_j}{n_i} = e^{-(E_j - E_i)/kT} = e^{-\Delta E_{ij}/kT} \quad PV = nRT \quad P\Delta V = (\Delta n)RT$$

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15 \quad T(^{\circ}\text{F}) = 1.800T(^{\circ}\text{C}) + 32.00$$

$$\Delta S = nR \ln \frac{V_2}{V_1} \quad \Delta S = -nR \ln \frac{P_2}{P_1} \quad \Delta S = -nR \ln \frac{[X]_2}{[X]_1}$$

$$S_x = S_x^{\circ} - R \ln P_x / \text{bar} \quad S_x = S_x^{\circ} - R \ln [X] / \text{M} \quad S_{\text{liq}} = S_{\text{liq}}^{\circ} - R \ln x_{\text{H}_2\text{O}}$$

$$\Delta_r S = \Delta_r S^{\circ} - R \ln Q \quad q_{\text{sys}} = -q_{\text{surr}} \quad \Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0 \quad H = U + PV \quad \Delta H = \Delta U + P\Delta V = q_{\text{sys}}$$

$$G = H - TS \quad \Delta G = \Delta H - T\Delta S \leq 0$$

$$k = 1.381 \times 10^{-23} \text{ J K}^{-1} \quad R = 0.08315 \text{ L bar mol}^{-1} \text{ K}^{-1} = 8.315 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \quad 1 \text{ kJ} = 10^3 \text{ J}$$

Table 7.1. Standard Molar Entropies (J/mol·K) at 298 K ( $S_{298}^{\circ}$ )							
Solids		Liquids		Gases			
C(d)	2.4	H <sub>2</sub> O(l)	70	He(g)	126	HCN(g)	202
C(gr)	5.7	Hg(l)	76	H <sub>2</sub> (g)	131	F <sub>2</sub> (g)	203
P(red)	23	CH <sub>3</sub> OH(l)	127	HD(g)	143	O <sub>2</sub> (g)	205
P(black)	23	Br <sub>2</sub> (l)	152	D <sub>2</sub> (g)	145	PH <sub>3</sub> (g)	210
Fe(s)	27	HNO <sub>3</sub> (l)	156	Ne(g)	146	NO(g)	211
Mn(s)	32	H <sub>2</sub> SO <sub>4</sub> (l)	157	Ar(g)	155	CO <sub>2</sub> (g)	214
Mg(s)	33	N <sub>2</sub> O <sub>4</sub> (l)	209	Xe(g)	170	Cl <sub>2</sub> (g)	223
LiF(s)	36	CCl <sub>4</sub> (l)	216	HF(g)	174	C <sub>2</sub> H <sub>6</sub> (g)	230
P(white)	41			Hg(g)	175	O <sub>3</sub> (g)	239
SiO <sub>2</sub> (q)	42			CH <sub>4</sub> (g)	186	NO <sub>2</sub> (g)	240
Sn(gray)	44			HCl(g)	187	Br <sub>2</sub> (g)	245
Sn(white)	52			H <sub>2</sub> O(g)	189	I <sub>2</sub> (g)	261
LiCl(s)	58			N <sub>2</sub> (g)	192	C <sub>3</sub> H <sub>10</sub> (g)	293
NaCl(s)	72			NH <sub>3</sub> (g)	193	N <sub>2</sub> O <sub>4</sub> (g)	304
KCl(s)	83			CO(g)	198	PCl <sub>3</sub> (g)	312
KI(s)	106			HBr(g)	199	PCl <sub>5</sub> (g)	361
I <sub>2</sub> (s)	116			HOCl(g)		N <sub>2</sub> O(g)	220

Table 9.1. Standard Molar Enthalpies of Formation (kJ/mol) at 298 K ( $\Delta H_{298}^{\circ}$ )							
Solids		Liquids		Gases			
C(d)	1.895	Br <sub>2</sub> (l)	0	Br <sub>2</sub> (g)	30.91	HCl(g)	-92.31
C(gr)	0	CH <sub>3</sub> OH(l)	-238.66	CH <sub>4</sub> (g)	-74.81	Hg(g)	60.83
Fe(s)	0	Hg(l)	0	C <sub>2</sub> H <sub>6</sub> (g)	-85.68	H <sub>2</sub> O(g)	-241.8
I <sub>2</sub> (s)	0	HNO <sub>3</sub> (l)	-174.10	CO(g)	-110.53	I <sub>2</sub> (g)	62.44
LiCl(s)	-408.71	H <sub>2</sub> O(l)	-285.83	CO <sub>2</sub> (g)	-393.51	N <sub>2</sub> (g)	0
NaCl(s)	-410.9	H <sub>2</sub> O <sub>2</sub> (l)	-187.78	Cl <sub>2</sub> (g)	0	NH <sub>3</sub> (g)	-46.11
P(red)	-17.6	H <sub>2</sub> SO <sub>4</sub> (l)	-813.99	F <sub>2</sub> (g)	0	NO(g)	90.25
P(white)	0			H(g)	217.97	NO <sub>2</sub> (g)	33.18
SiO <sub>2</sub> (q)	-910.94			H <sub>2</sub> (g)	0	N <sub>2</sub> O <sub>4</sub> (g)	9.16
Sn(gray)	-2.09			HF(g)	-271.1	O(g)	249.17
Sn(white)	0			HBr(g)	199	O <sub>2</sub> (g)	0
				HOCl(g)	-74.48	O <sub>3</sub> (g)	142.7

## PERIODIC TABLE OF THE ELEMENTS

1A												8A					
1 H 1.0079	2A										5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179	
3 Li 6.941	4 Be 9.0122											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
11 Na 22.990	12 Mg 24.305	3B	4B	5B	6B	7B	—8B—			1B	2B						
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 †Ac 227.03															

*58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
†90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)