

Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions. I have intentionally left a great deal of space for each problem. I do not expect each problem to take up all of the space provided!

**Part 0: Warmup. 4 points each**

1. The heat of solution of NaOH(s) in water is -41.6 kJ/mol NaOH. When NaOH is dissolved in water, the solution temperature

- a. increases.
- b. decreases.
- c. remains constant.
- d. either increases or decreases depending on the amount of NaOH dissolved.

Answer \_\_\_\_\_

2. A plausible final temperature when 75.0 mL of water at 80.0°C is added to 100.0 mL of water at 20.0°C is

- a. 28°C.
- b. 40°C.
- c. 46°C.
- d. 50°C.

Answer \_\_\_\_\_

3. For a process to occur spontaneously,

- a. the entropy of the system must increase.
- b. both the entropy of the system and surroundings must increase.
- c. the net change of the entropy of the system and surroundings must be a positive quantity.
- d. the entropy of the universe must remain constant.

Answer \_\_\_\_\_

4. Reactions with a positive  $\Delta H^\circ$  and a positive  $\Delta S^\circ$  are

- a. spontaneous at all temperatures.
- b. nonspontaneous at all temperatures.
- c. spontaneous at low temperatures but nonspontaneous at high temperatures.
- d. nonspontaneous at low temperatures but spontaneous at high temperatures.

Answer \_\_\_\_\_

5. Which of the processes below DOES NOT result in an increase in entropy?

- a.  $2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)$
- b.  $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(\ell)$  (The melting of ice.)
- c.  $\text{CO}_2(s) \rightarrow \text{CO}_2(g)$  (The sublimation of dry ice.)
- d.  $\text{NH}_4\text{NO}_3(s) \rightarrow \text{N}_2\text{O}(g) + 2 \text{H}_2\text{O}(\ell)$

Answer \_\_\_\_\_

**Part I: Complete all of problems 6-9.**

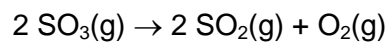
6. Concisely discuss the validity of each of the following statements. Clearly justify your reasoning. A few sentences should be sufficient. (12 points)
- Reactions with a positive  $\Delta H^\circ$  and a positive  $\Delta S^\circ$  can never be product-favored.
  
  
  
  
  
  
  
  
  
  
  - Free energy changes provide a good indication of which reactions are favorable and fast, as well as those that are unfavorable and slow.
7. An ice cube weighing 5.63 g originally at  $0.0^\circ\text{C}$  was dropped into an insulated cup. After a short period of time, the ice had all melted and the temperature of the remaining liquid water had reached  $25.2^\circ\text{C}$ . How much heat energy, in kJ, did the water lose to the surroundings as it melted and warmed? (For water,  $\Delta H^\circ_{\text{fusion}} = 333 \text{ J/g}$ ,  $\Delta H^\circ_{\text{vaporization}} = 2256 \text{ J/g}$ ) (12 points)

8. For the following processes, give the algebraic sign for  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$ . No calculations are necessary, use your common sense and briefly justify your decisions. A few sentences should be sufficient. (12 points)

a. The splitting of liquid water to give gaseous oxygen and gaseous hydrogen, a process that requires a considerable amount of energy.

b. The explosion of dynamite, a mixture of solid nitroglycerine and solid diatomaceous earth. The explosive decomposition gives gaseous products such as water,  $\text{CO}_2$  and others and much heat is evolved.

9. Answer the following questions regarding the decomposition of sulfur trioxide to sulfur dioxide and oxygen. (16 points)



Species	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol K)
O (g)	249.170	161.055
O <sub>2</sub> (g)	0	205.138
S (s)	0	31.80
S (g)	278.805	167.821
SO <sub>2</sub> (g)	-296.830	248.22
SO <sub>3</sub> (g)	-395.72	256.76

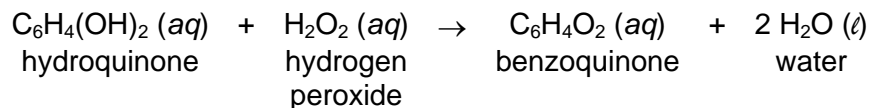
- a. Calculate the  $\Delta G^\circ$  for this reaction at 298K. (10 points)
- b. Calculate the minimum temperature required for the reaction to be product-favored. (6 points).

**Part II. Answer two (2) of problems 10-13. Clearly mark the problems you do not want graded. 14 points each.**

10. Solid ammonium nitrate can decompose to dinitrogen oxide gas and liquid water. What is the  $\Delta G^\circ$  at 298K? At what temperature, if any, does spontaneity of the reaction change? Is the reaction more or less spontaneous at high temperatures?

<b>Species</b>	<b><math>\Delta G^\circ_f</math> (kJ/mol)</b>	<b><math>\Delta H^\circ_f</math> (kJ/mol)</b>	<b><math>S^\circ_f</math> (J/mol)</b>
NH <sub>4</sub> NO <sub>3</sub> (s)	-183.9	-365.6	151.1
N <sub>2</sub> O (g)	+104.2	+82.05	219.9
H <sub>2</sub> O (l)	-237.1	-285.8	69.91

For problems 11-13, consider the Bombardier Beetle, who defends itself by spraying nearly boiling water on its predators. It has two glands on the tip of its abdomen, with each gland containing two compartments. The inner compartment holds an aqueous solution of hydroquinone and hydrogen peroxide. The outer compartment holds a mixture of enzymes that catalyze the following reaction:

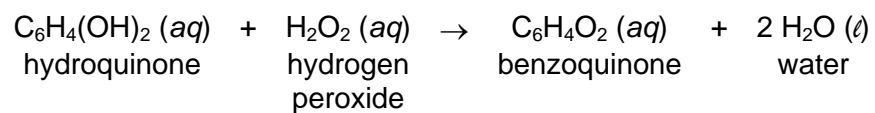


When threatened, the beetle squeezes some fluid from the inner compartment into the outer compartment, and sprays the mixture (which is near its boiling point) onto the predator.

11. Calculate the  $\Delta H^\circ$  for the Bombardier Beetle reaction using the following data:

Reaction	$\Delta H^\circ$
$\text{C}_6\text{H}_4(\text{OH})_2 (\text{aq}) \rightarrow \text{C}_6\text{H}_4\text{O}_2 (\text{aq}) + \text{H}_2 (\text{g})$	+177.4 kJ
$\text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O}_2 (\text{aq})$	-191.2 kJ
$2\text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2\text{H}_2\text{O} (\text{g})$	-483.6 kJ
$\text{H}_2\text{O} (\text{g}) \rightarrow \text{H}_2\text{O} (\ell)$	-43.8 kJ

12. Using the table of  $\Delta H_f^\circ$  below and your result from number 11, calculate the  $\Delta H_f^\circ$  of hydroquinone,  $C_6H_4(OH)_2$ , in kJ/mol. (Note: if you did not get an answer to number 11, you may use -200 kJ as a reasonable estimate for  $\Delta H_{rxn}^\circ$ ).



Species	$\Delta H_f^\circ$ (kJ/mol)	Species	$\Delta H_f^\circ$ (kJ/mol)
$H_2O_2 (aq)$	-191.2	$H_2O (g)$	-241.8
$H_2O_2 (\ell)$	-187.8	$H_2O (\ell)$	-285.8
$C_6H_4O_2 (aq)$	-50.4		

13. Assume a beetle emits 0.90 mL of 3.0 M hydroquinone and 1.10 mL of 3.0 M peroxide. If the initial temperature of this solution is 25.0°C, what will the solution temperature be after the reaction? Assume the specific heat of the solution is 4.184 J/gK and that the density of solution is 1.00 g/mL. (Note: if you did not get an answer to number 11, you may use -200 kJ as a reasonable estimate for  $\Delta H_{\text{rxn}}^{\circ}$ ).



### Possibly Useful Information

$\Delta G = \Delta H - T\Delta S$	$^{\circ}\text{C} = \text{K} - 273.15$
$q_{\text{rxn}} = n\Delta H_{\text{rxn}}$	$q = mc\Delta T$
henway = ~5-6 lbs	$q_{\text{released}} = -q_{\text{absorbed}}$

Compound	Molar Mass (g/mol)	Compound	Molar Mass (g/mol)
H <sub>2</sub> O	18.0153	SO <sub>2</sub>	64.065
H <sub>2</sub> O <sub>2</sub>	34.0147	SO <sub>3</sub>	80.064
C <sub>6</sub> H <sub>4</sub> O <sub>2</sub>	108.097	NH <sub>4</sub> NO <sub>3</sub>	80.0434
C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	110.112	N <sub>2</sub> O	44.0129
H <sub>2</sub>	2.01588	CO <sub>2</sub>	44.010
O <sub>2</sub>	31.9988		

Material	Specific Heat Capacity (J/gK)
H <sub>2</sub> O (s)	2.050
H <sub>2</sub> O (l)	4.184
H <sub>2</sub> O (g)	2.080

1 1A	2 2A											13	14	15	16	17	18 8A		
1 H 1.00794												3 Li 6.941	4 Be 9.01218						2 He 4.00260
11 Na 22.9898	12 Mg 24.3050	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 9B	10 10B	11 11B	12 12B	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948		
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9381	26 Fe 55.847	27 Co 58.9332	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80		
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 131.29		
55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)		
87 Fr (223)	88 Ra 226.025	89 †Ac 227.028	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Rg (272)									

*Lanthanide series	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	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 (262)

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