

*Thermochemistry & Thermodynamics*

Name ANSWER KEY

Slyter Box 007

Hour Examination 6

April 17, 2003

**General Chemistry (CHEM 122-01)**

*Thermochemistry & Thermodynamics*

*Dr. Bennett*

**Please do not open until instructed**

*Thermochemistry & Thermodynamics*Notes:

\* This exam consists of answering **3 questions on 6 pages** (the first question has five shorter questions). Please check to make sure that you have a complete copy of the exam.

\* *Please do not simply give me answers. Give me well-supported answers. Numerical answers that are not backed by supporting calculations will receive minimal credit.*

\* Please write clearly; if I can't read your answer, I can't give you credit for your answer.

\* Please note that different questions are worth different numbers of points. Plan your time accordingly.

\* Remember to include units and significant figures where appropriate.

\* No books or notes are to be used on this exam.

\* Please do NOT share calculators; if you need a calculator but do not have one, please let me know!

\* *If you feel that you would be better able to answer **any** question if you had additional information, please do not hesitate to ask for it. I will happily provide any information that I feel will help you answer the question without compromising the efficacy and fairness of the test.*

Question	Possible	Score
1	25	
2	20	
3	25	
<b>TOTAL</b>	70	
percent:		

$$R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$\Delta E = q + w$$

$$q = m \times s \times \Delta T$$

$$\Delta S = C_p \cdot \ln(T_2/T_1)$$

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

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

$$0^\circ\text{C} = 273.15 \text{ K}$$

$$w = -P_{\text{ex}}\Delta V$$

$$\Delta S = q_{\text{rev}}/T$$

$$S = k \cdot \ln(W)$$

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

$$k = 1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$$

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta S = \Delta H/T$$

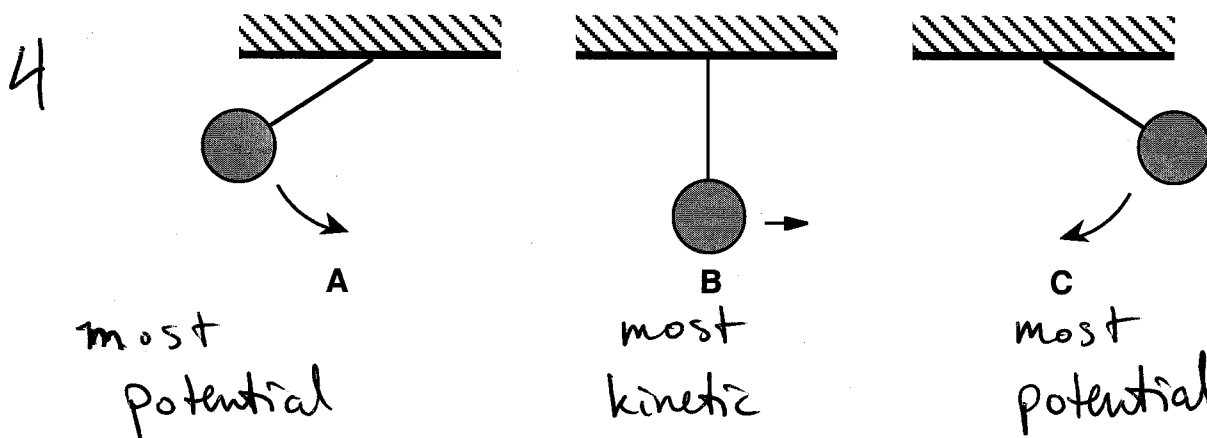
$$\Delta G = \Delta G^\circ + RT\ln Q$$

$$q = C_{\text{cal}}(\Delta T)$$

*The last page contains selected thermodynamic data*

1.

- (a) A pendulum swings back and forth as shown. Assume no energy is lost due to friction. At what point in its path does the pendulum have *the most potential energy*? At which point does it have *the most kinetic energy*?



- (b) You observe an eccentric professor combine some chemicals in a bottle, place a 1.0 kg mass on top of the bottle, and then use a spark to initiate a reaction.

There is a sudden loud bang, and the 1.0 kg mass is propelled to a position 15 meters away. Slightly dazed, the professor feels the reaction vessel and informs you that it has become very warm.

4  
Being a student of chemistry, you realize that a chemical reaction has taken place. Both heat ( $q$ ) and work ( $w$ ) were involved. Treating the reaction as the system, tell what the signs of  $q$  and  $w$  were for the reaction. Explain briefly.



the system

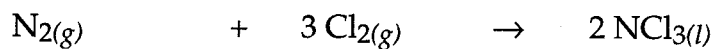
$$q_{\text{sys}} = \ominus$$

b/c it gave heat to its surroundings

$$w_{\text{sys}} = \ominus$$

b/c it did work on its surroundings

- 6  
(c) For each of the following reactions, predict whether the entropy change for the system is positive or negative. Give a brief explanation for each answer.



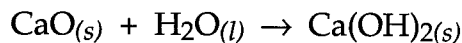
(-)

gases  $\rightarrow$  liq



(+)

1 gas  $\rightarrow$  2 gas

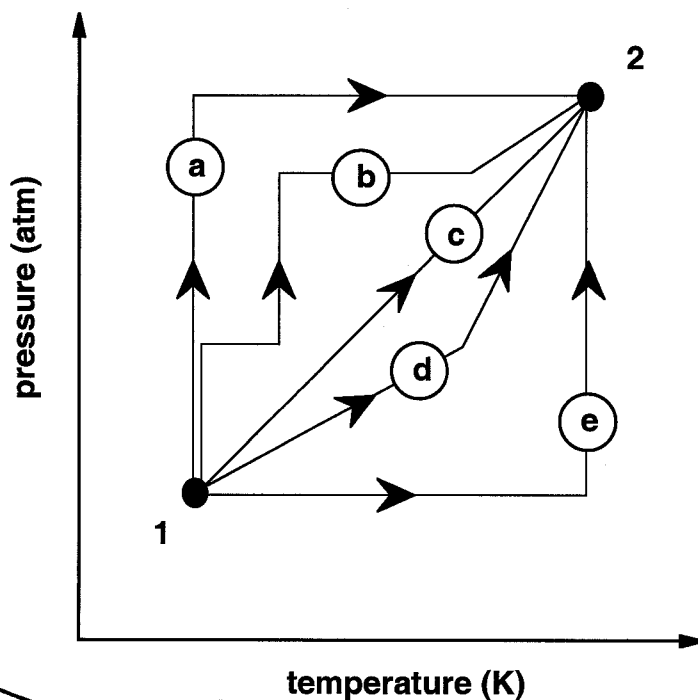


(-)

s & l  $\rightarrow$  just s

(d) Consider the following diagram for a gas changing from one temperature and pressure to another temperature and pressure. Complete this sentence by choosing one of the choices A — D:

3



A state function

"The change in entropy  $\Delta S$  in going from state 1 to state 2 is..."

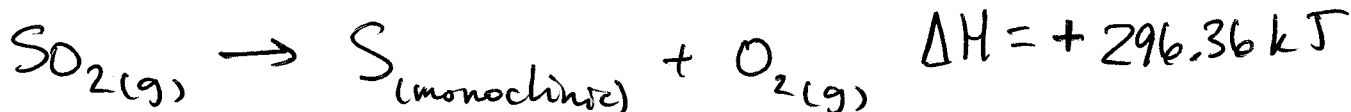
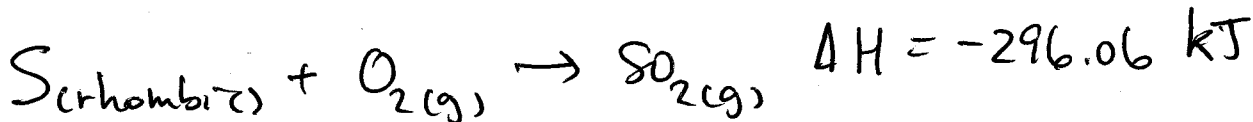
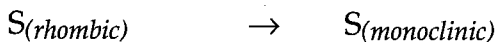
- (A) ...the same for paths (a) through (e)."
- (B) ...different for each of the paths."
- (C) ...smallest for path (c) because it is the shortest path."
- (D) ...the same for paths (a) and (e) but different for the other paths."

(e) Monoclinic and rhombic are different elemental forms of sulfur. From these data:



8

calculate the enthalpy change for the following transformation.



-3 pts for sign

-2 for units

2. A 7.51 g sample of  $\text{NH}_4\text{NO}_3$  (ammonium nitrate) is placed into 100.0 g of water in a calorimeter. The temperature of the water drops from 24.8 °C to 19.0 °C. Assume no heat is transferred to the calorimeter. The specific heat of water is  $s_{\text{H}_2\text{O}} = 4.184 \text{ J/g}\cdot^\circ\text{C}$ .

- (a) Calculate the heat released by the water ( $q_{\text{H}_2\text{O}}$ ).

$$\begin{aligned} \zeta \quad q_{\text{H}_2\text{O}} &= m_{\text{H}_2\text{O}} s_{\text{H}_2\text{O}} (T_{f,\text{H}_2\text{O}} - T_{i,\text{H}_2\text{O}}) \\ &= (100.0 \text{ g}) (4.184 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}}) (19.0 - 24.8)^\circ\text{C} \\ &= -2427 \text{ J} \end{aligned}$$

- (b) Calculate the heat absorbed by the reaction ( $q_{\text{rxn}}$ ).

$$\begin{aligned} \zeta \quad q_{\text{H}_2\text{O}} + q_{\text{rxn}} &= 0 \quad (\text{or}) \quad 2.427 \text{ kJ} \\ q_{\text{rxn}} &= -q_{\text{H}_2\text{O}} = \boxed{+2427 \text{ J}} \end{aligned}$$

- (c) What is  $\Delta H_{\text{rxn}}$  for  $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4\text{NO}_3(\text{aq})$  (in units of kJ/mol)?

$$\zeta \quad 7.51 \text{ g NH}_4\text{NO}_3 \left( \frac{1 \text{ mol NH}_4\text{NO}_3}{80 \text{ g NH}_4\text{NO}_3} \right) = 0.09387 \text{ mol NH}_4\text{NO}_3$$

$$\Delta H_{\text{rxn}} = \frac{2.427 \text{ kJ}}{0.09387 \text{ mol}} = \boxed{25.8 \text{ kJ/mol}}$$

- (d) This reaction is spontaneous. What is the sign of  $\Delta H_{\text{rxn}}$  that you found in (c)? Based on this, can you tell what the sign of  $\Delta S_{\text{rxn}}$  must be? If so, what is it?

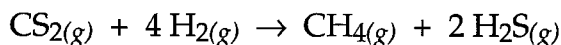
$\zeta$  spont means  $\Delta G_{\text{rxn}}$  must be  $\ominus$

to obtain  $\Delta G_{\text{rxn}} = \ominus$ , it must

be that  $\Delta S_{\text{rxn}} = \oplus$

b/c  $\Delta G = \Delta H - T\Delta S$

3. Carbon disulfide reacts with hydrogen at 25.0 °C to form methane gas and hydrogen sulfide vapor according to the following balanced equation.



- (a) Calculate the enthalpy change ( $\Delta H^\circ$ ) for this reaction.

7

$$\Delta H^\circ = [-74.9 + 2(-20.2)] - [117 + 4(0)]$$

$$= \underline{-232.3 \text{ kJ/mol}}$$

- (b) Calculate the entropy change ( $\Delta S^\circ$ ) for this reaction.

7

$$\Delta S^\circ = [186.1 + 2(205.6)] - [237.8 + 4(130.6)]$$

$$= -162.9 \text{ J/(mol}\cdot\text{K)}$$

- (c) Using the Gibbs Free Energy equation ( $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ) determine whether this reaction is spontaneous or not.

7

$$\Delta G^\circ = (-232.3 \text{ kJ/mol}) - [(298 \text{ K})(-0.1629 \frac{\text{kJ}}{\text{mol}\cdot\text{K}})]$$

$$= -184 \text{ kJ/mol} \quad \underline{\text{yes, spont}}$$

- (d) Which thermodynamic term ( $\Delta H^\circ$  or  $\Delta S^\circ$ ) would cause the reaction to tend to be spontaneous? Explain.

2  $\Delta H^\circ$ , not  $\Delta S^\circ \rightarrow \Delta H^\circ \ominus$  means increase in entropy (of surroundings)  
 $\Delta S^\circ \ominus$  means decrease in entropy (of system)

- (e) Estimate the temperature at which the spontaneity of this reaction changes.

2

$$\Delta G = 0 = -232 \frac{\text{kJ}}{\text{mol}} - (T)(-0.1629 \frac{\text{kJ}}{\text{mol}\cdot\text{K}})$$

$$T = 1424 \text{ K}$$

or 1152 °C

Table of selected thermodynamic data:

compound	$\Delta H^\circ_f$ (kJ/mol)	$S^\circ_f$ (J/mol·K)
$O_2(g)$	0	205.0
$H_2(g)$	0	130.6
$Cl_2(g)$	0	223
$HCl(g)$	-92.3	186.8
$HCl(aq)$	-167.5	55.1
$H_2S(g)$	-20.2	205.6
$H_2O(g)$	-241.8	188.7
$H_2O(l)$	-285.8	69.9
$CO_2(g)$	-393.5	213.7
$CS_2(g)$	117	237.8
$CH_4(g)$	-74.9	186.1
$C_2H_6(g)$	-84.7	229.5
$C_2H_5OH(l)$	-277.6	161

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$$\Delta S = C_p \cdot \ln(T_2/T_1)$$

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

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

$$0^\circ\text{C} = 273.15 \text{ K}$$

$$w = -P_{\text{ex}}\Delta V$$

$$\Delta S = q_{\text{rev}}/T$$

$$S = k \cdot \ln(W)$$

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

$$k = 1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$$

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta S = \Delta H/T$$

$$\Delta G = \Delta G^\circ + RT\ln Q$$

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