

AP Chemistry: Calorimetry CW

1. While running, a typical adult expends 5.0×10^5 J/mi. If this amount of energy could be transferred as heat to water, how many grams of water could be raised from room temperature (25°C) to the boiling point (100°C)? (1600g)

$$5.0 \times 10^5 \text{ J/mi} = x (4.184 \text{ J/g}^\circ\text{C}) (100 - 25)$$

$$x = 1600 \text{ g}$$

2. The heat capacity of $\text{NH}_3(\text{l})$ is $4.381 \text{ J/g}^\circ\text{C}$. Calculate the heat required to raise the temperature of $1.50 \text{ g NH}_3(\text{l})$ from -60.0°C to -55.0°C . (33 J)

$$q = (1.50 \text{ g}) (4.381 \text{ J/g}^\circ\text{C}) (-55.0 - -60.0)$$

$$q = 32.9 \text{ J}$$

3. A piece of unknown metal with mass = 5.19 g is heated to 100.0°C and dropped in 10.0 mL of water at 22.00°C . The final temperature of the system is 23.83°C . What is the specific heat capacity of the metal? (0.463 cal/goC or 0.194 J/goC)

water	metal
m $10.0 \text{ mL} = 10.0 \text{ g}$	m 5.19 g
C 4.184	C x
T_f 23.83°C	T_f 23.83°C
T_i 22.00°C	T_i 100.0°C
ΔT 1.83°C	ΔT -76.17°C

$$-(5.19 \cdot x \cdot -76.17) = (10.0 \cdot 4.184 \cdot 1.83)$$

$$x = 0.194 \text{ J/g}^\circ\text{C}$$

4. If a piece of Cd with a mass = 37.6 g and initial temperature of 100.0°C is dropped in 25.0 mL of water at 23°C , what is the final temperature of the system? specific heat of Cd = $0.232 \text{ J/g}^\circ\text{C}$; specific heat of water = $4.184 \text{ J/g}^\circ\text{C}$. (28.9°C)

water	metal
m $25.0 \text{ mL} = 25.0 \text{ g}$	m 37.6 g
C $4.184 \text{ J/g}^\circ\text{C}$	C $0.232 \text{ J/g}^\circ\text{C}$
T_f x	T_f x
T_i 23°C	T_i 100.0°C
ΔT	ΔT

$$-(37.6 \cdot 0.232 \cdot (x - 100)) = (25 \cdot 4.184 \cdot (x - 23))$$

$$-8.7232x + 872.32 = 104.6x - 2405.8$$

$$+8.7232x \qquad \qquad \qquad +2405.8$$

$$3278.12 = 113.3x$$

$$28.9^\circ\text{C} = x$$

The combustion of 0.80 g of sulfur to form SO_3 yields sufficient heat to raise the temperature of 100.0 g of water by 17.8°C . Calculate the heat of combustion of 1 mol of sulfur. (-300 kJ/mole)

$$q_{\text{water}} = (100.0 \text{ g}) (4.184) (17.8^\circ\text{C})$$

$$q = \frac{7447.52 \text{ J}}{1000 \text{ J}} = 7.45 \text{ kJ}$$

$$\frac{0.80 \text{ g S}}{32.07 \text{ g S}} = 0.0249 \text{ mol S}$$

$$\frac{7.45 \text{ kJ}}{0.0249 \text{ mol}} = 299 \text{ kJ/mol} = -3.0 \times 10^2 \text{ kJ/mol}$$

6. The burning of 1.010 g sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, in a bomb calorimeter cause the water temperature to rise from 24.92 to 28.33°C . The calorimeter contains 980.0 g water, and the heat capacity of the calorimeter is $785 \text{ J}/^\circ\text{C}$. a) What is the heat of combustion of sucrose, expressed in kJ/mol? b) Verify the claim of sugar manufacturers that one teaspoon of sugar (about 4.8 g) "contains only 18 Cal." (-5640 kJ/mol, -19 kcal)

$$a) q_{\text{rxn}} = q_w + q_{\text{cal}}$$

$$= ((980.0 \text{ g}) (4.184) (28.33 - 24.92)) + (785 \text{ J}/^\circ\text{C}) (28.33 - 24.92)$$

$$q = \frac{16658.9 \text{ J}}{1000 \text{ J}} = 16.66 \text{ kJ} \quad \left(\frac{1.010 \text{ g sucrose}}{342.3 \text{ g}} \right) = 5650 \text{ kJ/mol}$$

$$b) \frac{4.8 \text{ g}}{342.3 \text{ g}} = 0.0140 \text{ mol} \quad \frac{5650 \text{ kJ}}{\text{mol}} = 79.23 \text{ kJ} \quad \frac{79.23 \text{ kJ}}{4.184 \text{ kJ}} = 19 \text{ kcal}$$

7. The combustion of benzoic acid is often used in the laboratory to determine the heat capacity of a bomb calorimeter assembly. If the combustion of a 1.000 g sample of benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$) causes a temperature increase of 4.96°C when a bomb calorimeter contains 1085 g of water, what is the heat capacity of the calorimeter? (A handbook lists the heat of combustion of benzoic acid as -26.42 kJ/g .) ($787.0 \text{ J}/^\circ\text{C}$)

$$q_{\text{rxn}} = q_w + q_{\text{cal}} \rightarrow \text{J}$$

$$26420 \text{ J} = ((1085 \text{ g}) (4.184) (4.96)) + (x \cdot 4.96)$$

$$C_{\text{cal}} = 787.0 \text{ J}/^\circ\text{C}$$

8. When one mole of $\text{CH}_4(\text{g})$ burns in a bomb calorimeter (heat capacity = $1.20 \text{ kcal}/^\circ\text{C}$) containing 21.00 kg of water, the temperature rises 9.53°C . Calculate: a) q for the combustion of one mole of $\text{CH}_4(\text{g})$. b) q per gram of methane burned. (-212 kcal/mol -13.2 kcal/g)

$$a) q_{\text{rxn}} = q_w + q_{\text{cal}}$$

$$= (21000 \text{ g}) (4.184 \text{ J/g}^\circ\text{C}) (9.53) + \left(\frac{1.20 \text{ kcal}}{4.184 \text{ kJ}} \cdot \frac{1000 \text{ J}}{1 \text{ kcal}} \right) (9.53^\circ\text{C})$$

$$q_{\text{rxn}} = \frac{885192 \text{ J}}{4.184 \text{ J}} \cdot \frac{1 \text{ kcal}}{1000 \text{ J}} = -212 \text{ kcal/mol}$$

$$b) \frac{212 \text{ kcal}}{\text{mol}} \cdot \frac{1 \text{ mol}}{16.042 \text{ g}} = -13.2 \text{ kcal/g}$$

9. To determine the heat capacity of a bomb calorimeter, a student adds 150 g of water at 50.0 to the bomb, which is initially at 25.0°C. The final temperature is 33.0°C. What is the heat capacity of the bomb in cal/°C? (319 cal/°C)

$$q_B = -q_w$$

$$q_w = (150 \text{ g}) (4.184) (33 - 50)$$

$$q_w = -10669.2 \text{ J}$$

$$q_B = C_B (\Delta T)$$

$$10669.2 = X (33 - 25)$$

$$X = \frac{10669.2 \text{ J}}{8} = 1333.65 \text{ J/}^\circ\text{C}$$

$$\frac{1 \text{ cal}}{4.184 \text{ J}} = 0.239 \text{ cal/J}$$

$$1333.65 \text{ J/}^\circ\text{C} \times 0.239 \text{ cal/J} = 319 \text{ cal/}^\circ\text{C}$$

10. When 1.50 g of the rocket fuel dimethylhydrazine, $(\text{CH}_3)_2\text{N}_2\text{H}_2$, is burned in a bomb calorimeter (heat capacity = 440 cal/°C) containing 5.00 kg of water, the temperature rises from 22.05 to 24.13°C. Calculate the amount of heat that would be evolved in the combustion of one mole of dimethylhydrazine. (452 kcal)

$$q_{\text{rxn}} = q_w + q_{\text{cal}}$$

$$q_{\text{rxn}} = \left((5000 \text{ g}) (4.184) (24.13 - 22.05) \right) + \left((440 \text{ cal/}^\circ\text{C}) (24.13^\circ\text{C} - 22.05^\circ\text{C}) \right)$$

$$43513.6 \text{ J} + 3829.2 \text{ J} = 47342.8 \text{ J}$$

$$47342.8 \text{ J} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 11315.2 \text{ cal} = 11.3152 \text{ kcal}$$

11. When one gram of benzoic acid is burned in a bomb calorimeter containing 2.95 kg of water, the temperature rises from 24.33 to 26.25°C. The heat of combustion of benzoic acid under these conditions is 6.315 kcal/g. What is the heat capacity of the bomb in cal/°C? (339 cal/°C)

$$6315 \text{ cal/g} = \left((2950 \text{ g}) (4.184) (26.25 - 24.33) \right) + \left(X (26.25 - 24.33) \right)$$

$$X = 339 \text{ cal/}^\circ\text{C}$$

$$11.3152 \text{ kcal}$$

$$\frac{1.50 \text{ g } (\text{CH}_3)_2\text{N}_2\text{H}_2}{60.104 \text{ g/mol}} = 0.02495 \text{ mol}$$

$$\frac{11.3152 \text{ kcal}}{0.02495 \text{ mol}} = 453 \text{ kcal/mol}$$

Chapter 19: Entropy

How does the organization of atoms and molecules affect chemical states?

Model I: The Deck of Cards analogy

Imagine a brand new deck of cards sitting by itself in a large room. The deck has never been used, except that it has been removed from its box. It has not been shuffled, but is still in the factory shipped order, which is:

Hearts, Clubs, Diamonds, Spades
Ace to King within each suit

Definition: The *state* of a deck of cards refers to the order of cards within the deck. We will call the factory order an *ordered state*, that is, the cards from each suit are all together and in order from ace to king.

Questions

1. In card games, what is the purpose of shuffling the deck before playing?
to have randomness
2. In a randomly shuffled deck of cards
 - (a) Are there a large number or small number of ordered states?
Small
 - (b) Are there a large number or small number of disordered states?
large
3. After shuffling, is the observed order (or *state*) more likely to be an ordered state, or a disordered state?
disordered
4. Form this into a generalization – why does the order of cards in a shuffled deck always come out disordered? Use a complete sentence.
the odds of it being disordered are greater than it being ordered.
5. Are you more or less likely to have ordered states in a blackjack dealer's "shoe" – a device that can contain six or more decks of cards, all shuffled together? *less likely*

Information

Entropy (abbreviated "S") is a measure of the number of states a system can have. However, because the more states a system can have means that it is more like to be found in a disordered state we often just say that entropy is a measure of disorder. (Notice that entropy is related to disorder, not order).

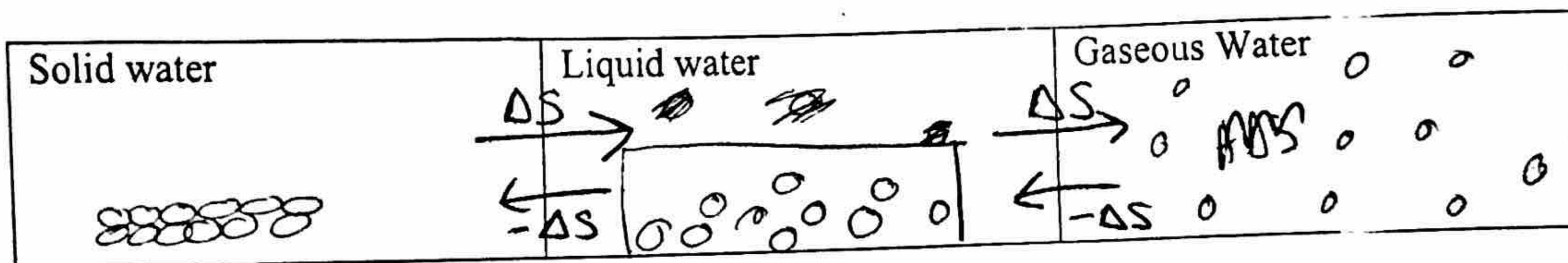
Entropy: **S** for "SPREADIQUITNESS"

If a change occurs which leads to a more disordered system, the change in entropy (ΔS) is positive. If the system becomes more ordered, the ΔS is negative.

Questions

6. Which of these has the highest entropy: an ordered deck or a shuffled deck? shuffled deck
7. Rank the following from least to greatest entropy.
- (a) Legos scattered on the floor, legos mixed together in a bucket, legos assembled together
3 2 1
- (b) A bag of marbles, the same marbles spilled on a floor, the same marbles sitting in a straight line, the same marbles in a straight line organized by color
3 2 1 a
8. If a person spills a bag of marbles, is this a positive or negative change in entropy (ΔS)?
 $+\Delta S$
9. If a person organizes a desk, is this a positive or a negative ΔS (change in entropy) for the desk?
 $-\Delta S$

Model II: Predicting the Sign of ΔS



Definition: For any substance, its *state* is a description of the position and speeds of the atoms in that substance.

Questions

10. Draw in representations for the solid, liquid and gaseous water.
11. What do you know about how molecules of H_2O can move in a solid versus a liquid versus a gas?
 H_2O molecules only vibrate in the solid form (slow) versus in a liquid form they slide past each other (faster) and gases where there is random motion (fastest)
12. In which state of matter, solid, liquid, or gas can the molecules have the most numbers of possible positions and speeds, in other words, which phase can water have the most chemical states?
13. In terms of entropy, write the phases of matter in proper order from most to least entropic.
gas > liquid > solid
14. In the transition from liquid to gas, is the system increasing or decreasing entropy? Is this a positive or a negative change?
 $+\Delta S$
15. In the transition from solid to liquid, is the system increasing or decreasing in entropy? Is this a positive or a negative change?
 $+\Delta S$
16. Is sublimation (solid to gas) a positive or negative change in entropy?
 $+\Delta S$
17. If you increase the temperature of a solid, does its entropy increase, decrease or remain the same? Justify your answer in terms of the definition of chemical state given above.
 $+\Delta S$ b/c the average kinetic energy will increase

18. If you have a reaction that changes one mole of gas into two moles of gas, will the entropy of the system increase, decrease or remain the same? Justify your answer in terms of the definition of chemical state given above.

increase

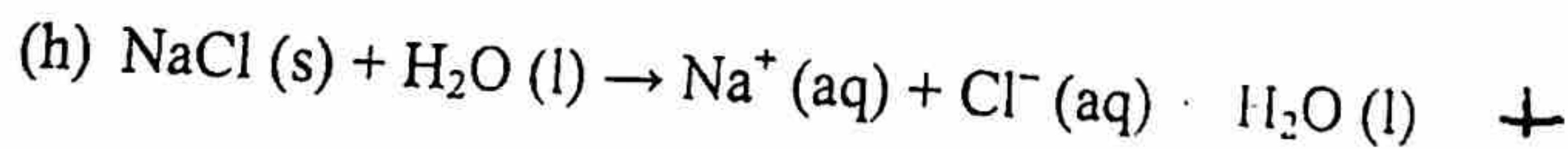
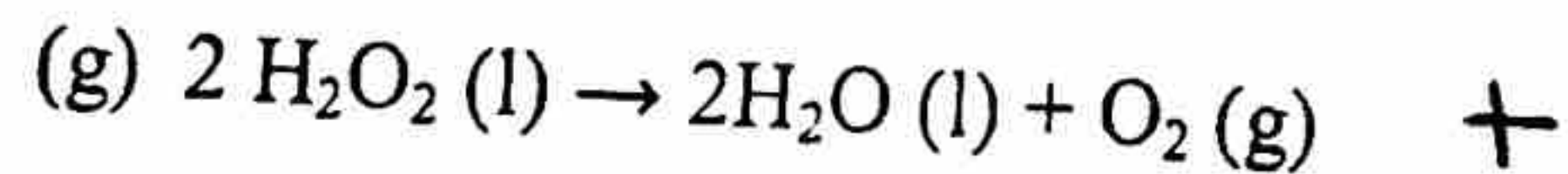
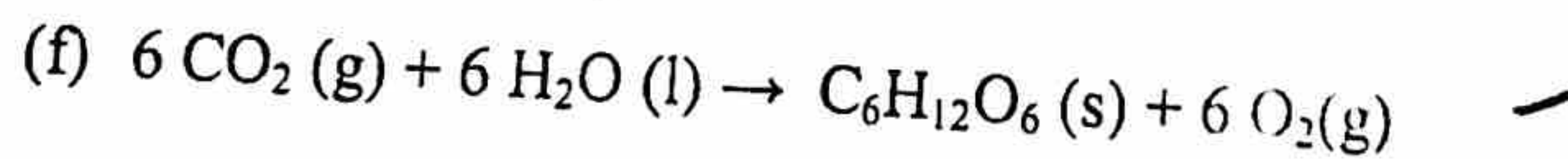
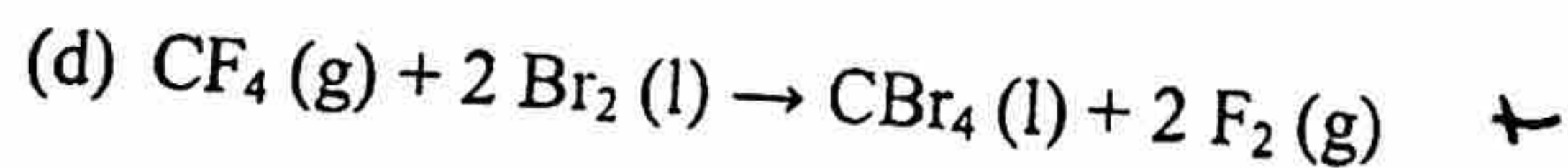
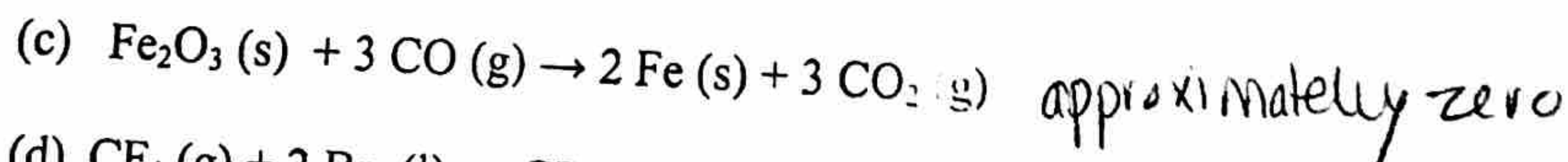
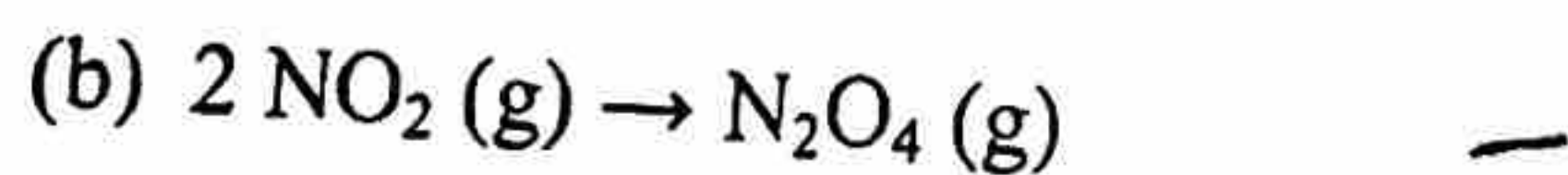
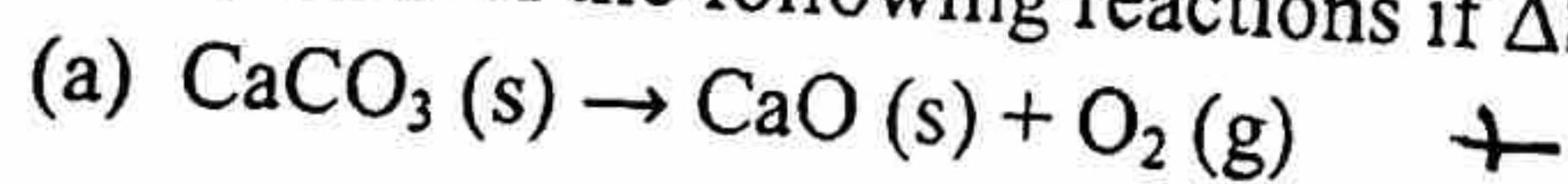
Exercises

1. Fill in the chart below:

Change	Sign of ΔS	Sign of ΔH
Evaporation $l \rightarrow g$	+	+ + +
Condensation $g \rightarrow l$	-	- -
Sublimation (solid to gas)	+	+ + +
Deposition (gas to solid)	-	- -
Melting $s \rightarrow l$	+	+ + +
Freezing $l \rightarrow s$	+ -	- -
Decomposition to atoms	+	+
Formation of a compound from atoms	-	-

2. A hot piece of metal is dropped into a cool glass of water. What is the sign of ΔS for the water? + What is the sign of ΔS for the metal? -

3. Determine for each of the following reactions if ΔS is positive, negative, or approximately zero.



(Solid sodium chloride dissolves in water)

AP Chemistry: Entropy Classwork

1. Predict whether the entropy change of the system is positive or negative. (+, +, -, ?, -)

- a) $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$ +
- b) $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}(g)$ +
- c) $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$ -
- d) $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g)$ -
- e) $\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$ -

2. Predict whether the entropy change of the system is positive or negative:

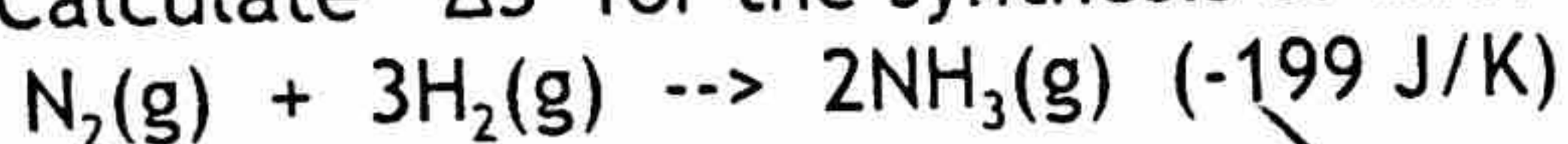
(+, +, -, +, +, -)

- a) $\text{CaH}_2(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(s) + \text{H}_2(g)$ +
- b) $\text{Ag}_2\text{O}(s) \rightarrow 2\text{Ag}(s) + 1/2\text{O}_2(g)$ +
- c) $2\text{Fe}(s) + 3/2\text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s)$ -
- d) $\text{Cl}_2(g) \rightarrow 2\text{Cl}(g)$ +
- e) $\text{NaCl}(s) \rightarrow \text{NaCl}(aq)$ +
- f) $\text{HCl}(aq, 1M) \rightarrow \text{HCl}(aq, 0.1M)$ -

3. Under what conditions would you expect the following reactions to occur spontaneously?

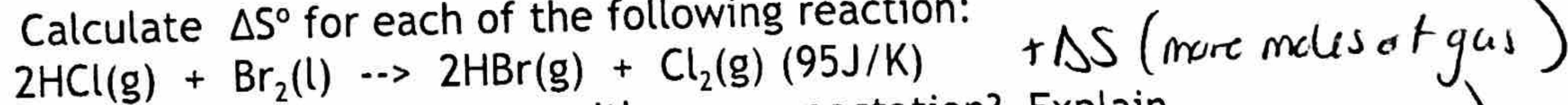
- a) $2\text{NH}_4\text{NO}_3(s) \rightarrow 2\text{N}_2(g) + 4\text{H}_2\text{O}(g) + \text{O}_2(g)$ $\Delta H = -236\text{kJ}$ (all temps) + ΔS always
- b) $\text{I}_2(g) \rightarrow 2\text{I}(g)$ (high temp) + ΔH + ΔS

4. Calculate ΔS° for the synthesis of ammonia from $\text{N}_2(g)$ and $\text{H}_2(g)$:



$$(2 \cdot 193) - (192 + (3 \cdot 131)) = -199 \text{ J/K}$$

5. Calculate ΔS° for each of the following reaction:



Does the sign of ΔS° agree with your expectation? Explain.

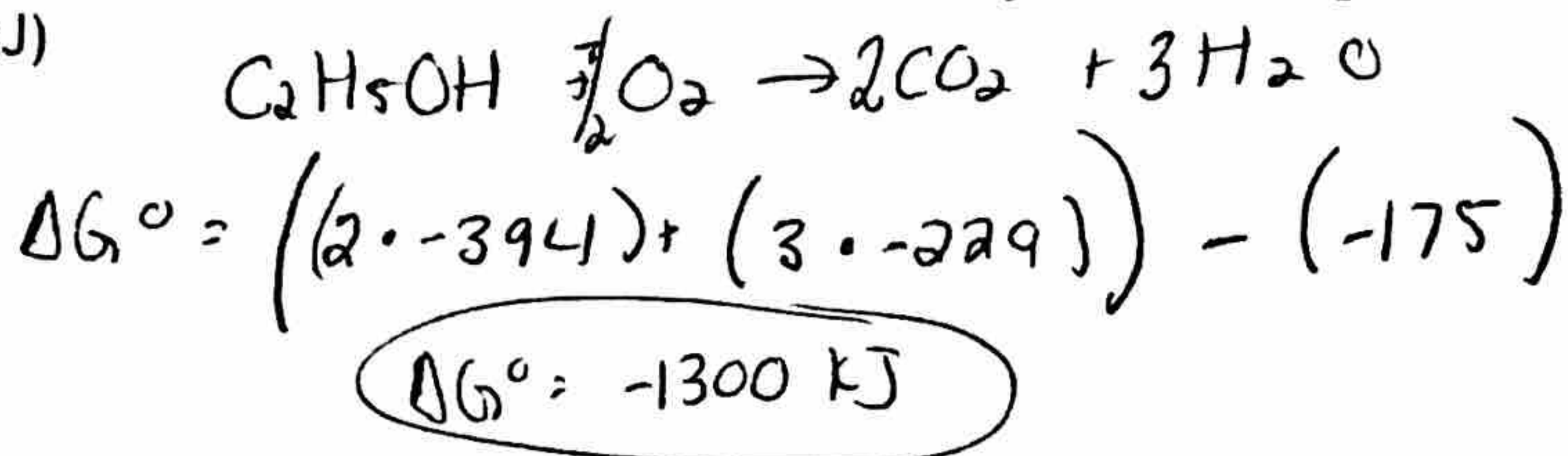
$$\Delta S^\circ = \sum (\Delta S^\circ_f \text{ Cl}_2 + 2(\Delta S^\circ_f \text{ HBr})) - (2(\Delta S^\circ_f \text{ HCl}) + 1(\Delta S^\circ_f \text{ Br}_2))$$

$$(223 + 2(199)) - ((2 \cdot 187) + (152))$$

$$\Delta S^\circ = 95 \text{ J/K}$$

AP Chemistry: Free Energy Classwork

1. What is ΔG° for the combustion of ethyl alcohol (C_2H_5OH) to give $CO_2(g)$ and $H_2O(g)$? (-1300 kJ)



2. Calculate ΔG°_{298} for: $H_2O_2(g) \rightarrow H_2O(g) + 1/2O_2(g)$ given that $\Delta H^\circ_{298} = -106 \text{ kJ}$ and $\Delta S^\circ_{298} = 58 \text{ J/K}$ for this process. Would you expect $H_2O_2(g)$ to be very stable at 298 K? Explain briefly. (-120 kJ)

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

$$\Delta G^\circ = -106 \text{ kJ} - (298 \text{ K})(0.058 \text{ kJ/K})$$

$$\Delta G^\circ = -123 \text{ kJ}$$

*spontaneous since $-\Delta G^\circ$
→ not stable

3. Classify each of the following as belonging to one of the four possible types summarized in your notes:

a) $N_2(g) + 3F_2(g) \rightarrow 2NF_3(g)$:	$\Delta H^\circ = -249 \text{ kJ}$ S	$\Delta S^\circ = -278 \text{ J/K}$ NS	low temp
b) $N_2(g) + 3Cl_2(g) \rightarrow 2NCl_3(g)$:	$\Delta H^\circ = +460 \text{ kJ}$ NS	$\Delta S^\circ = -275 \text{ J/K}$ NS	never
c) $N_2F_4(g) \rightarrow 2NF_2(g)$:	$\Delta H^\circ = +85 \text{ kJ}$ NS	$\Delta S^\circ = +198 \text{ J/K}$ S	high temp
d) $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$:	$\Delta H^\circ = +572 \text{ kJ}$ NS	$\Delta S^\circ = +329 \text{ J/K}$ S	high temp

4. a) Calculate ΔG° at 25°C for the following process: $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$

$$\Delta G^\circ = \sum -163 - (-137)$$

$$\Delta G^\circ = -26 \text{ kJ/mol}$$

- b) Calculate ΔG° at 500°C assuming that ΔH° and ΔS° do not change with temperature.

$$\Delta H^\circ = (-201) - (-110.5) = -90.5 \text{ kJ/mol}$$

$$\Delta S^\circ = (240) - (198 + (2 \cdot 131)) = -220 \text{ J/mol}$$

$$\Delta G^\circ = -90.5 \text{ kJ/mol} - (773 \text{ K})(-0.220 \text{ kJ/mol}) = 79.6 \text{ kJ}$$

- c) Explain the change in values from a to b. (-26 kJ, 79.6 kJ)

Since ΔH and ΔS are both -, in order for ΔG to be spontaneous there needs to be a low temp. 79.6 kJ * don't forget to switch to K

*need to solve for ΔH° and ΔS° first

5. The following reaction is employed in the metallurgy of iron to obtain iron metal from its oxide: $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 2\text{Fe}(\text{s})$. At what temperature does this reaction become spontaneous under standard conditions?

$$\Delta H = (3 \cdot -393.5) - ((3 \cdot -110.5) + -826) = -23 \text{ kJ} \quad 0 = -23 \text{ kJ} - T(0.012)$$

$$\Delta S = (2 \cdot 27) + (3 \cdot 214) - (90 + 3(198)) = 12 \text{ J} \quad 23 = -T(0.012)$$

1917 K

6. For the "reaction," $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$, $\Delta H^\circ = +31.0 \text{ kJ/mol}$ and $\Delta S^\circ = 92.9 \text{ J/molK}$. Assuming that H and S are nearly temperature independent, calculate the approximate temperature at which $\text{Br}_2(\text{l})$ will be in equilibrium with $\text{Br}_2(\text{g})$ at 1 atm. (334 K)

$$0 = (31.0 \text{ kJ/mol}) - T(0.0929 \text{ J/mol K})$$

T = 334 K

7. ~~2~~. What is the standard molar entropy of vaporization of water at 100.00°C , given that the standard molar enthalpy of vaporization is 40.7 kJ/mol ? (0.109 kJ/mol K)

** phase change so $\Delta G^\circ = 0$*

$$0 = (40.7 \text{ kJ/mol}) - (373)(x)$$

$\Delta S = 0.109 \text{ kJ/mol K}$

8. ~~3~~. Calculate ΔG at 298 K for the following reaction if the reaction mixture consists of 1.0 atm N_2 , 3.0 atm H_2 , and 1.0 atm NH_3 : $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ ~~1477 J~~

$$K_p = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{1^2}{(1)(3)^3} \quad \Delta G = -RT \ln(K)$$

$$\Delta G = (-8.314)(298)(\ln(0.037))$$

$\Delta G = 8.2 \text{ kJ}$

9. ~~4~~. a) Explain qualitatively how ΔG changes for the following reaction as the partial pressure of N_2 is increased: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

$K \downarrow \quad \Delta G \uparrow$

- b) Calculate ΔG for this reaction if $P_{\text{N}_2} = 5.0 \text{ atm}$, $P_{\text{NH}_3} = 0.10 \text{ atm}$, and $P_{\text{H}_2} = 2.0 \text{ atm}$.

~~(more negative, 55 kJ)~~

$$K_p = \frac{(0.10)^2}{(5)(2)^3} \quad \Delta G = (-8.314)(298)(\ln(2.5 \times 10^{-4}))$$

$$K_p = 2.5 \times 10^{-4} \quad \Delta G = -20549 \text{ J} \rightarrow \text{20.6 kJ}$$

10. Calculate ΔG at 298 K for the following reaction if the reaction mixture consists of 2.0 atm of $\text{CO}(\text{g})$, 2.0 atm of $\text{O}_2(\text{g})$, and 10.0 atm of $\text{CO}_2(\text{g})$: $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$

$$K_p = \frac{(10)^2}{(2)^2(2)} = 12.5 \quad \Delta G = (-8.314)(298)(\ln(12.5))$$

$$\Delta G = -6258 \text{ J} \rightarrow \text{6.3 kJ}$$

29