CHAPTER 5 – THERMOCHEMISTRY

Section 5.1 – The Nature of Energy

1. (a) The study of energy and its transformations is known as thermodynamics. The study of the relationships between chemical reactions and energy changes that involve heat is known as ___________________________________.

   (b) Energy is commonly defined as the capacity to _________________________ or ____.

   (c) Work is the energy used to cause an object to ___________________________________

   (d) Heat is the energy used to cause the ____

2. Kinetic energy is the energy of ______________; all other kinds of energy are classified as _________________ energy.

3. When a ball rolls down a hill, we can talk about gravitational forces.

   Do gravitational forces play a significant role in the ways that atoms and molecules interact with one another? ____________

4. Write Equation 5.2 from page 161. Identify what each term in the equation represents.

5. As the distance (d) between two charged particles approaches infinity, the electrostatic potential energy (E_{el}) between the particles approaches what value? _________________

6. Suppose that you have two particles that have like charges (both positive or both negative.) As these charges are brought closer together, what happens to the electrostatic potential energy between them? Why?

7. Suppose that you have two particles that have opposite charges. As these charges are brought closer together, what happens to the electrostatic potential energy between them? Why?

8. The SI unit of energy is the __________ .

9. When analyzing energy changes, we need to focus on and distinguish between two regions. The portion we single out for study is called the _________________, and everything else is called the ____________________________.

10. An ______________ system is one in which matter and energy can be exchanged with the surroundings. A ________________ system can exchange energy but not matter with its surroundings. Figure 5.4 is an example of a(n) __________________ system.

11. For each of the following, determine if the surroundings is doing work on the system or if the system is doing work on the surroundings. We will define the baseball as the system in each example.
    (a) A person throws a baseball: ____
    (b) The baseball breaks a window: ____

12. Write the mathematical equation for work (Equation 5.3) ______________________________

13. Heat is the energy transferred from a ______________ object to a ____________ one.

14. In chemistry, we normally define the substances involved in a chemical reaction as the _________________ and everything else as the ________________________.

Section 5.2 – The First Law of Thermodynamics

1. What is the first law of thermodynamics? ____
____

2. We define the internal energy (E) of a system as the sum of ___________________________
____

3. We generally can't determine the actual values of E_{final} and $E_{initial}$ for any system of practical interest. We need only the value of _______ in order to apply the first law.

4. It is important to know that ΔE has both a number and a unit. Together these values tell us the ____________________ of the energy change. ΔE also has a ____________, which tells us the direction of the energy change.

5. When $E_{final} > E_{initial}$, the sign of ΔE is ________________, indicating that the system has

____

6. When $E_{final} < E_{initial}$, the sign of ΔE is ________________, indicating that the system has

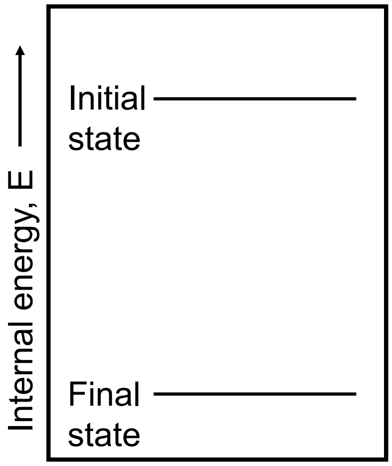
____

7. In a chemical reaction, the initial state refers to the __________________, and

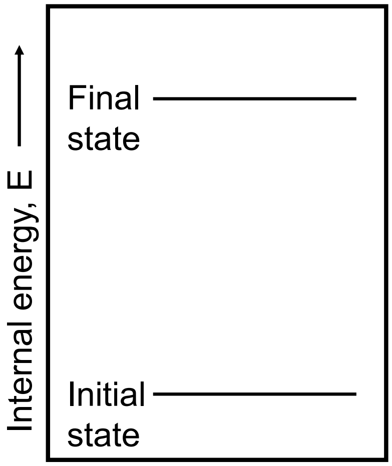
the final state refers to the _____________________.

8. Use the information in Figure 5.6 to help you label the reactants, products, and ΔE values for each reaction shown below. Draw an arrow from the initial state toward the final state on each diagram. Indicate if the value of ΔE is positive or negative for each reaction.

Synthesis of water



Decomposition of water



9. In a closed system, the system may exchange energy with its surroundings in two general

ways: as ____________ or as _______________

10. Write the equation for the change in ΔE ____________________ (Equation 5.5)

11. In each box in the table below, describe what is happening with respect to the system.

q is positive	*q* is negative
w is positive	*w* is negative
ΔE is positive	ΔE is negative

12. Suppose that a piece of dry ice (solid CO_2) is confined in a cylinder-and-piston arrangement similar to the diagram in Figure 5.4 on page 162. If this cylinder is warmed, the dry ice will undergo sublimation, causing the piston to move upward. The atmospheric pressure outside the cylinder remains constant. The system is defined as the contents of the cylinder.

    (a) The sign of *q* for the system is _____ because the system ______________________ heat.

    (b) The sign of *w* for the system is _____ because work is done ___________ the system.

13. Suppose that a system absorbs 250 J of heat from the surroundings, and it also does 90 J of work on the surroundings. What is the value of ΔE for this process? Include the sign of ΔE in your answer. ______________________

14. During an endothermic process, such as the melting of ice, heat flows from the

    _______________________ into the ______________________.

    During an exothermic process, such as the combustion of gasoline, heat flows from the

    _______________________ into the ______________________.

Consider the following situations.

(a) A beaker of water is placed on a hot plate, and it is heated until the water boils. The temperature of the water <u>increases</u> and the water changes from a liquid to a gas.

(b) Water, in the form of perspiration is produced on our skin during exercise. The surface temperature of our skin <u>decreases</u> as the water changes from a liquid to a gas.

15. Both of these situations involve the evaporation of water. Is evaporation classified as an endothermic process or an exothermic process? _________________________________

16. Explain how situation (a) resulted in an increase in temperature, whereas situation (b) resulted in a decrease in temperature. Discuss the system and the surroundings in order to help you explain what is going on in each situation.

Section 5.3 – Enthalpy

1. Write the mathematical equation for enthalpy. _________________________ (Equation 5.6)

2. The work involved in the expansion or compression of gases is called pressure-volume work.

   When pressure is constant in a process, the equation for this type of work becomes

   ________________________________ (Equation 5.8)

3. Most of the chemical processes that we are interested in studying occur at constant pressure.

   Therefore the change in enthalpy equals the change in _____________ at constant pressure.

In chemistry, the change in enthalpy (ΔH) becomes more useful to us than the change in internal energy (ΔE). For most reactions, the value of PΔV is small. Therefore, ΔH and ΔE are very close in value. In AP Chemistry, the terms "enthalpy" and "internal energy" will not be distinguished.
You can think of the change in enthalpy as the change in heat.

4. Determine the sign of ΔH (in terms of the system) for each of the following processes.

   (a) Liquid water freezes: _________

   (b) Solid silver melts: ________

   (c) Propane gas burns in air to produce carbon dioxide and water: ________

   (d) Solid mercury(II) oxide decomposes into mercury and oxygen: ________

Section 5.4 – Enthalpies of Reaction

1. Write the mathematical equation for the enthalpy change (Equation 5.16).

2. When you see the symbol ΔH_{rxn}, the letters "rxn" are an abbreviation for _________________

3. It is important that the value of ΔH_{rxn} has a sign. A positive sign means that the reaction is

   ___________________; a negative sign means the reaction is ________________________

Balanced chemical equations that show the associated enthalpy change are called thermochemical equations. The guidelines on page 174 are helpful when using thermochemical equations and energy diagrams.

4. Enthalpy is an extensive property. The magnitude of ΔH is proportional to the ____________

   of reactant consumed in the process.

5. The enthalpy change for a certain chemical reaction is equal in magnitude, but

   ___________________ in sign, to the ΔH for the reverse reaction.

6. The enthalpy change for a reaction depends on the _____________ for the reactants and products, such as (*s*), (*l*), and (*g*).

7. This is problem 5.39, found on page 199.

   The complete combustion of ethanol, $C_2H_5OH(l)$, to form $H_2O(g)$ and $CO_2(g)$ at constant pressure releases 1235 kJ of heat per mole of C_2H_5OH. (a) Write a balanced thermochemical equation for this reaction. (b) Draw an enthalpy diagram for the reaction (similar to Figure 5.6 or Figure 5.14)

8. This is problem 5.40, found on page 199.

   The decomposition of slaked lime, $Ca(OH)_2(s)$, into lime, $CaO(s)$, and $H_2O(g)$ at constant pressure requires the addition of 109 kJ of heat per mole of $Ca(OH)_2$. (a) Write a balanced thermochemical equation for this reaction. (b) Draw an enthalpy diagram for the reaction.

9. The thermite reaction is shown in Figure 5.8 on page 168. Aluminum reacts with iron(**III**) oxide to produce aluminum oxide and iron. Write a balanced chemical equation for this reaction.

10. Based on the information in Figure 5.8, what is the sign of ΔH for this reaction? ___________

11. The thermite reaction releases 848 kJ of heat for every 1 mole of iron(III) oxide that reacts.

    (a) How much heat is released when 1.00 gram of iron(III) oxide reacts with excess aluminum? Show the setup for this calculation, which involves two conversion factors.

    (b) If 1750 kJ of heat are released in this reaction, how many grams of iron metal are produced? Show the setup for this calculation, which involves three conversion factors.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H = -890\text{ kJ}$$

12. Based on the information in the thermochemical equation above, determine the value of ΔH for the following reactions.

    (a) $2\,CH_4(g) + 4\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(l)$ $\Delta H =$ ____________ kJ

    (b) $CO_2(g) + 2\,H_2O(l) \longrightarrow CH_4(g) + 2\,O_2(g)$ $\Delta H =$ ____________ kJ

13. The value of ΔH for the following reaction is not equal to –890 kJ. Explain.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

14. Decide if the magnitude of ΔH for the reaction shown in #13 should be larger than 890 kJ or smaller than 890 kJ. Draw an enthalpy diagram to justify your answer.

15. Hydrogen peroxide decomposes to produce water and oxygen gas. When 5.00 g of $H_2O_2(l)$ decomposes at constant pressure, 14.4 kJ of heat is released.

(a) Write a balanced chemical equation for the decomposition of hydrogen peroxide. Include the phases of matter for each substance.

(b) Calculate the value of ΔH for the reaction written in part (a).

16. This is problem 5.48, found on page 199.

Consider the decomposition of liquid benzene, $C_6H_6(l)$, to gaseous acetylene, $C_2H_2(g)$:

$$C_6H_6(l) \longrightarrow 3\ C_2H_2(g) \qquad \Delta H = +630\ \text{kJ}$$

(a) What is the enthalpy change for the reverse reaction? ________________

(b) What is ΔH for the formation of 1 mol of acetylene? __________________

(c) Which is more likely to be thermodynamically favored, the forward reaction or the reverse \

reaction? ___________________________________

(d) If $C_6H_6(g)$ were consumed in this reaction instead of $C_6H_6(l)$, would you expect the magnitude of ΔH to be less than 630 kJ, greater than 630 kJ, or equal to 630 kJ? Draw an enthalpy diagram to justify your answer.

Section 5.5 – Calorimetry

1. Calorimetry is defined as the measurement of heat flow. In the laboratory, we don't measure heat directly. Instead, we measure the magnitude of the ______________________________ that is caused by heat flow. A calorimeter is a device used to measure the heat flow.

2. Define the term **specific heat capacity** (also called specific heat).

3. Write Equation 5.22 on page 176. Identify each term in the equation and the units that are normally associated with them.

4. Calculate the amount of heat (in kJ) required to raise the temperature of 25.0 g $H_2O(l)$ from 20.0°C to 80.0°C.

5. Suppose that 5.00 g Al(*s*) and 5.00 g $H_2O(l)$ are both at an initial temperature of 25°C. Each sample of matter absorbs 100. J of heat. Calculate the final temperature for each substance.

6. Based on the answer to #5, fill in the blanks in the following sentences.

   Substance A and Substance B have the same mass and are at the same temperature. Each substance absorbs the same quantity of heat. After the heat has been absorbed by both substances, it was determined that Substance A is at a higher temperature.

   Substance A experienced a _____________ value of ΔT in this experiment. Therefore,

   Substance A must have a _______________ specific heat capacity than Substance B.

7. Suppose that you have 10.0 g of pure magnesium (c = 1.02 J/g-°C) and 10.0 g of pure lead (c = 0.160 J/g-°C). Each sample is at room temperature (25°C). Heat is slowly added to each substance. Which substance will reach 50°C first? Justify your answer.

8. A piece of copper with a mass of 100.0 grams was sitting in a boiling water bath at 100.0°C. The copper was removed from the boiling water and quickly added to a sample of water in a Styrofoam coffee cup. The water in the coffee cup had a mass of 100.0 g and was at an initial temperature of 22.0°C.

   (a) What will happen to the temperature of the copper metal? ______________________

   (b) What will happen to the temperature of the water in the cup? ____________________

   (c) At some point, the copper-water mixture reaches thermal equilibrium at a temperature of 28.7°C. Calculate ΔT for the copper and ΔT for the water in this experiment.

9. Based on the information in #8, which of the following statements do you agree with? Assume that the Styrofoam cup was perfectly insulated and no thermal energy was lost to the surroundings.

   (a) The amount of thermal energy lost by the copper is greater than the amount of thermal energy gained by the water.

   (b) The amount of thermal energy lost by the copper is equal to the amount of thermal energy gained by the water.

   (c) The specific heat capacity of the copper is greater than the specific heat capacity of the water.

   (d) The specific heat capacity of the copper is equal to the specific heat capacity of the water.

10. Use the information from #8 to calculate the specific heat capacity of copper. Include units in your answer.

11. Is there an important difference between expressing the units of specific heat as J/g-°C or J/g-K ? Explain.

12. Aluminum has a specific heat capacity of 0.91 J/g-°C. A piece of aluminum with a mass of 100.0 grams was sitting in a boiling water bath at 100.0°C. The aluminum was removed from the boiling water and quickly added to a sample of water in a Styrofoam coffee cup. The water in the coffee cup had a mass of 100.0 g and was at an initial temperature of 22.0°C. Calculate the final temperature of the water-aluminum mixture. Assume that no thermal energy is lost to the surroundings.

13. In a coffee-cup calorimeter, water is usually the solvent when two solutions are mixed together. There is no physical boundary between the system and the surroundings. In a certain experiment, a student mixed 25 mL of 2.0 *M* HCl with 25 mL of 2.0 *M* NaOH in a coffee-cup calorimeter. The temperature of the solution increased from 22.0°C to 35.3°C. The total volume of the solution is 50. mL. Assume that the density of the solution is 1.0 g/mL. Assume that the specific heat of the solution is 4.18 J g^{-1} $°C^{-1}$

(a) What is the balanced molecular equation for this chemical reaction?

____

(b) What represents the system? ____

(c) What represents the surroundings? ____________________________________

(d) What is the value of ΔT from this experiment? ______________

(e) What is the total mass of the solution in this experiment? ____________

(f) What is the total amount of heat (q) transferred to the water? ____________

(g) Should the sign of ΔH for this reaction be positive or negative? ___________

13. (h) What is the number of moles of HCl used in this experiment? ____________

    (i) Calculate the value of ΔH for this reaction in units of kJ/mol.
    Include the sign of ΔH in your answer.

14. Suppose that the experiment described in #13 were repeated. But instead of mixing 25 mL of 2.0 *M* HCl with 25 mL of 2.0 *M* NaOH, the experiment used 25 mL of 1.0 *M* HCl and 25 mL of 1.0 *M* NaOH.

    (a) Do you predict that the magnitude of ΔT from this experiment should be lower than, higher than, or equal to the ΔT value you calculated in 13(d)? Justify your answer.

    (b) Do you predict that the magnitude of q from this experiment should be lower than, higher than, or equal to the q value you calculated in 13(f)? Justify your answer.

    (c) Do you predict that the magnitude of ΔH from this experiment should be lower than, higher than, or equal to the magnitude of the ΔH value you calculated in 13(i)? Justify your answer.

15. See Figure 5.19 on page 179. A "bomb" calorimeter is not an explosive device. It is merely a precise instrument for doing calorimetry experiments. It is a container designed to withstand high pressures. A substance is placed inside the bomb (reaction chamber) and allowed to undergo a chemical reaction. In a certain experiment, the combustion of benzene (C_6H_6) was performed in a bomb calorimeter. The heat capacity of the calorimeter was determined to be 8.25 kJ/°C. When 5.00 g of benzene was burned completely, the temperature of the calorimeter increased from 25.0°C to 50.4°C.

    (a) What is the value for ΔT in this experiment? __________

15. (b) Calculate how much heat (q) was transferred from the combustion reaction to the bomb calorimeter.

(c) Calculate the number of moles of benzene used in this experiment.

(d) Calculate the value of ΔH for the combustion reaction in units of kJ/mol. Include the sign of ΔH in your answer.

Section 5.6 – Hess's Law

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

(2) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$ $\Delta H = -283.0$ kJ

(3) $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ $\Delta H = ?$

1. Show how equations (1) and (2) can be manipulated in such a way that they will be equal to equation (3) when they are combined together.

2. What is the value of ΔH for the reaction $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$? ____________________

3. Hess's Law states that if a reaction is carried out in a series of steps, ΔH for the overall reaction equals ____

4. If you reverse a chemical reaction, what effect does this have on the ΔH for that reaction?

5. If you multiply all of the coefficients in a balanced chemical equation by 2, what effect does this have on the ΔH for that reaction?

(1) $C_2H_2(g) + \frac{5}{2}\,O_2(g) \rightarrow 2\,CO_2(g) + H_2O(l)$ $\Delta H = -1299.6$ kJ

(2) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

(3) $H_2(g) + \frac{1}{2}\,O_2(g) \rightarrow H_2O(l)$ $\Delta H = -285.8$ kJ

(4) $2\,C(s) + H_2(g) \rightarrow C_2H_2(g)$ $\Delta H = ?$

6. Show how equations (1), (2), and (3) can be manipulated in such a way that they will be equal to equation (4) when they are combined together. Calculate ΔH for Equation 4.

7. Answer problems 5.65 and 5.66 on pp. 200-201 in order to confirm your understanding of the concept of Hess's Law.

(5.65) $H_2(g) + F_2(g) \rightarrow 2\ HF(g)$ $\Delta H = -537\ \text{kJ}$

$C(s) + 2\ F_2(g) \rightarrow CF_4(g)$ $\Delta H = -680\ \text{kJ}$

$2\ C(s) + 2\ H_2(g) \rightarrow C_2H_4(g)$ $\Delta H = +52.3\ \text{kJ}$

Target Equation: $C_2H_4(g) + 6\ F_2(g) \rightarrow 2\ CF_4(g) + 4\ HF(g)$

(5.66) $N_2(g) + O_2(g) \rightarrow 2\ NO(g)$ $\Delta H = +180.7\ \text{kJ}$

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$ $\Delta H = -113.1\ \text{kJ}$

$2\ N_2O(g) \rightarrow 2\ N_2(g) + O_2(g)$ $\Delta H = -163.2\ \text{kJ}$

Target Equation: $N_2O(g) + NO_2(g) \rightarrow 3\ NO(g)$

Section 5.7 – Enthalpies of Formation

1. (a) Enthalpy of vaporization (ΔH_{vap}) is the enthalpy change associated with converting a

   _____________ into a ___________.

   (b) Enthalpy of fusion (ΔH_{fus}) is the enthalpy change associated with converting a

   _____________ into a ___________.

   (c) Enthalpy of combustion (ΔH_{comb}) is the enthalpy change associated with combusting a

   substance in the presence of ________________.

   (d) Enthalpy of formation (ΔH_f) is the enthalpy change associated with the _______________

   ____

2. Standard conditions for ΔH are defined at a temperature of ________ and a pressure of 1 atm.

3. For each of the following substances, write the chemical symbol or formula of the stable form of that substance under standard conditions. Include the phase of matter (*s*), (*l*), (*g*) for each substance.

   (a) hydrogen

   (b) lithium

   (c) carbon

   (d) nitrogen

   (e) oxygen

   (f) fluorine

   (g) sodium

   (h) water

   (i) carbon dioxide

   (j) hydrogen chloride

   (k) methane

   (l) methanol

   (m) benzene

   (n) sucrose

4. By definition, the standard enthalpy of formation of the most stable form of any element is

   equal to ________________.

5. For each of the following substances, write the equation corresponding to the standard enthalpy of formation. Include phases of matter for all substances.

   (a) sodium oxide

   (b) potassium chloride

   (c) glucose

   (d) iron(III) bromide

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

6. Use the equation above and the information in Table 5.3 on page 184 to calculate the standard enthalpy change for each of the following reactions.

   (a) $C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(l)$

   (b) $C_6H_6(g) + 7.5\ O_2(g) \longrightarrow 6\ CO_2(g) + 3\ H_2O(l)$

   (c) $2\ NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$

   (d) $CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3\ H_2(g)$

7. Use the data in Table 5.3 on page 184 and the information below to answer the following questions.

    (a) $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$ $\Delta H = -129.7$ kJ

    What is the standard enthalpy of formation for $CuO(s)$?

    (b) $C_4H_{10}O(l) + 6\ O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(l)$ $\Delta H = -2723.7$ kJ

    What is the standard enthalpy of formation for $C_4H_{10}O(l)$?

    (c) $2\ C_4H_{10}(g) + 13\ O_2(g) \rightarrow 8\ CO_2(g) + 10\ H_2O(l)$ $\Delta H = -5754$ kJ

    What is the standard enthalpy of formation for $C_4H_{10}(g)$?

8. Use the data in Appendix C on page 1059 and the information below to answer the following question.

    $CaC_2(s) + 2\ H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$ $\Delta H = -127.2$ kJ

    What is the standard enthalpy of formation for $CaC_2(s)$?