

# Chapter 6- Thermochemistry Study Guide

## 6.1 The Nature of Energy

Your textbook describes a number of terms for you. The terms, along with brief definitions, are given:

- **Thermodynamics:** The study of energy and its interconversions.
- **Energy:** The capacity to produce work or heat.
- **Kinetic Energy:** The energy of motion. Kinetic Energy =  $\frac{1}{2}$  mass x (velocity)<sup>2</sup>  
Measured in Joules. (1 J = 1 kg m<sup>2</sup>/s<sup>2</sup>).
- **Potential Energy:** Energy that can be converted into useful work. Measured in Joules.  
(1 J = 1 kg m<sup>2</sup>/s<sup>2</sup>).  $PE = mgh$   $g = 9.8 \text{ m/s}^2$
- **Heat:** Involves transfer of energy between 2 objects. Measured in Joules. Symbolized by the letter **q**.
- **Work:** Force x distance. Measured in Joules (1 J = 1 Nm = 1 kg m<sup>2</sup>/s<sup>2</sup>). Symbolized by the letter **w**.
- **State Function:** A property that is independent of pathway. That is, it does not matter how you get there, the difference in the value is the same. For example, you can drive from New York to Los Angeles via many different routes. No matter which one you take, you are still going from NY to LA. The actual difference between the two cities is the same. **Energy** is a state function, **work** and **heat** are not.

Four more definitions will set the stage for thermodynamics. The **universe** is composed into the **system** and the **surroundings**.

- **System:** That which we are focusing on.
- **Surroundings:** Everything else in the universe.
- **Exothermic:** Energy (as heat) flows **out of the system**.
- **Endothermic:** Energy (as heat) flows **into the system**.

**Work:** We will take a different approach to this topic than your textbook does. Let's look from the point of view of **units**.

$$\text{Force} = \text{mass} \times \text{acceleration} = \text{kg} \times \text{m/s}^2 = \text{Newton (N)}$$

$$\text{Work} = \text{force} \times \text{distance} = \text{kg m/s}^2 \times \text{m} = \text{kg m}^2/\text{s}^2 = \text{Nm} = \text{Joule (J)}$$

### Example 6.1A The units of work

If pressure = force/area, what are the units of pressure x volume?

$$P = \frac{\text{Force}}{\text{Area}} = \frac{\text{kg} \cdot \text{m/s}^2}{\text{m}^2} = \frac{\text{kg}}{\text{m} \cdot \text{s}^2} = 1 \text{ Pa}$$

$$P \times V = \frac{\text{kg}}{\text{m} \cdot \text{s}^2} \times \text{m}^3 = \frac{\text{kg m}^2}{\text{s}^2} = 1 \text{ J}$$

Therefore, P x V has the same units as force x distance (work), and both are measures of **energy**.

### Conclusion

For an ideal gas, **Work** = PΔV

This equation holds at constant pressure.

The sign conversions for work are as follows:

- When the system expands, it is doing positive work on the surroundings. Therefore, it is doing *negative work on the system*.
- When the system contracts, the surroundings have done work on the system, therefore there is *positive work done on the system*.

From the point of view of the system, then:  $w = -(P\Delta V)$

### Example 6.1B Work

Calculate the work (with the proper sign) associated with the contraction of a gas from 75 L to 30 L (work is done "on the system") at a constant external pressure of 6.0 atm in:

- L·atm
- Joules (1 L·atm = 101.3 J)

**Helpful hint:** Keep in mind that system compression is positive work and system expansion is negative work.

a) The work is positive (compression)

$$\Delta V = V_f - V_i = 30\text{ L} - 75\text{ L} = -45\text{ L}$$

$$w = P\Delta V = (-6.0\text{ atm})(-45\text{ L}) = +270\text{ L}\cdot\text{atm}$$

$$b) 270\text{ L}\cdot\text{atm} \left( \frac{101.3\text{ J}}{1\text{ L}\cdot\text{atm}} \right) = +2.7 \times 10^4\text{ J}$$

### The First Law of Thermodynamics

The law of conservation of energy also called the first law of thermodynamics is described in your book. It states that energy can be converted from one form to another, but can neither be created nor destroyed. Another way of stating the first law is that:

**THE ENERGY OF THE UNIVERSE IS CONSTANT**

We know that energy can be changed through work. As chemical bonds are made and broken, energy is converted between the potential energy (stored within chemical bonds) and thermal energy (kinetic energy) as heat.

The change in the internal energy of the system, which is equal in size but opposite in sign to that of the surroundings is equal to the sum of the heat and work.

$$\Delta E = q + w \quad \text{or} \quad \Delta E = Q - P\Delta V$$

Your textbook points out that the SIGN of the energy change must be viewed from the point of view of the SYSTEM.

$\Delta E = -$  means the system LOSES energy

$\Delta E = +$  means the system GAINS energy

### Example 6.1C The First Law

Calculate the change in energy of the system if 38.9 J of work is done by the system with an associated heat loss of 16.2 J.

**Strategy:** The most important part of a problem involving thermodynamics is getting the signs correct.

$q = (-)$  because the heat is lost

$w = (-)$  because work is done by the system

**Solution:**  $\Delta E = q + w = -16.2\text{ J} + (-38.9\text{ J}) = -55.1\text{ J}$ . The system has lost 55.1 J of energy.

### Example 6.1D Practice with Heat and Work

A piston is compressed from a volume of 8.3 L to 2.8 L against a constant pressure of 1.9 atm. In the process, there is a heat gain by the system of 350 J. Calculate the change in energy of the system.

**Solution:**

$$w = -P\Delta V = -1.9 \text{ atm} (-5.5 \text{ L}) = +10.45 \text{ L}\cdot\text{atm}$$
$$+10.45 \text{ L}\cdot\text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L}\cdot\text{atm}} = +1059 \text{ J}$$
$$q = +350 \text{ J}$$
$$\Delta E = q + w = +1059 \text{ J} + 350 \text{ J} = 1409 \text{ J} = 1400 \text{ J} \text{ (2 sig figs)}$$

### Problems:

1. Calculate:

a. Q when a system does 72 J of work and its internal energy decreases by 90 J.

$$W = -72 \text{ J} \quad \Delta E = Q + W$$
$$\Delta E = -90 \text{ J} \quad Q = \Delta E - W = -90 \text{ J} - (-72 \text{ J}) = -18 \text{ J}$$

Losing 18 J of heat

b.  $\Delta E$  for a gas that releases 35 J of heat and has 128 J of work done on it.

$$Q = -35 \text{ J} \quad \Delta E = Q + W = (-35 \text{ J}) + 128 \text{ J} = 93 \text{ J}$$
$$W = +128 \text{ J}$$

internal energy going up by 93 J

2. Find:

a.  $\Delta E$  when a gas absorbs 45 J of heat and has 32 J of work done on it.

$$Q = +45 \text{ J} \quad \Delta E = Q + W = 45 \text{ J} + 32 \text{ J} = \boxed{77 \text{ J}}$$
$$W = +32 \text{ J}$$

b. Q when 62 J of work are done on a system and its internal energy is increased by 84 J.

$$W = +62 \text{ J} \quad Q = \Delta E - W = 84 \text{ J} - 62 \text{ J} = \boxed{+22 \text{ J}}$$
$$\Delta E = +84 \text{ J}$$

3. A gas expands from 10 L to 20 L against a constant pressure of 5 atm. During this time, it absorbs 2 kJ of heat. Calculate the work done in kJ.

$$P = 5 \text{ atm}$$
$$V_i = 10 \text{ L}$$
$$V_f = 20 \text{ L}$$
$$Q = 2 \text{ kJ} = 2000 \text{ J}$$
$$\text{WORK} = -P(\Delta V) = -(5 \text{ atm})(20 \text{ L} - 10 \text{ L}) =$$
$$\text{work} = -50 \text{ L}\cdot\text{atm} \left( \frac{101.3 \text{ J}}{1 \text{ L}\cdot\text{atm}} \right) \leftarrow \text{conversion from Example 6.1B}$$
$$\text{work} = -5065 \text{ J} = -5.1 \text{ kJ}$$

$$\boxed{1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}}$$

4. A piston expands against 1.00 atm of pressure, from 11.2 L to 29.1 L. This is done without any transfer of heat.
- a. Calculate the change in energy of the system.

$$\Delta E = Q + W = -P(\Delta V) = -(1 \text{ atm})(29.1 \text{ L} - 11.2 \text{ L}) = -17.9 \text{ L atm} \left( \frac{101.3 \text{ J}}{1 \text{ L atm}} \right) = -1813.27 \text{ J} = -1.81 \times 10^3 \text{ J}$$

- b. Calculate the change in energy for the above change if, in addition, the system absorbs 1,037 J of heat from the surroundings.

$$Q = +1037 \text{ J}$$

$$\Delta E = Q + W = +1037 \text{ J} + (-1813.27 \text{ J}) = -776.27 \text{ J} = \boxed{-776 \text{ J}}$$

5. If the internal energy of a thermodynamic system is decreased by 300 J when 75 J of work is done on the system, how much heat was transferred, and in which direction, to or from the system?

$$\Delta E = -300 \text{ J}$$

$$Q = \Delta E - W = -300 \text{ J} - (75 \text{ J}) = -375 \text{ J}$$

$$W = +75 \text{ J}$$

Exothermic - heat is leaving the system (Q is negative)

6. A gas is compressed against a constant pressure of 3.4 atm from 27.9 L to 16.3 L. During this process, there is a heat gain by the system of 122 J. Calculate the change in energy of the system.

$$P = 3.4 \text{ atm}$$

$$V_i = 27.9 \text{ L}$$

$$V_f = 16.3 \text{ L}$$

$$Q = 122 \text{ J}$$

$$\Delta E = Q + W = Q + (P(\Delta V))$$

$$\Delta E = 122 \text{ J} + 3995.3 \text{ J}$$

$$\Delta E = 4117 \text{ J} = \boxed{4.1 \text{ kJ}}$$

$$W = -P(\Delta V) = -3.4(16.3 - 27.9)$$

$$W = +39.44 \text{ L atm} = +3995.3 \text{ J}$$

## 6.2 Enthalpy and Calorimetry

**Enthalpy** Your textbook derives and defines a term called **enthalpy** (H), or the flow of heat. It is a **state function**, so that the change in H is independent of pathway. That is,

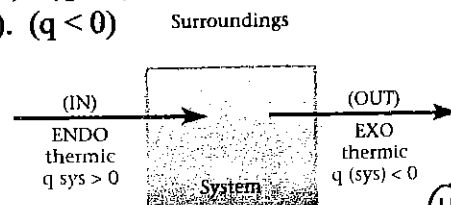
$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

$$\Delta H = E + PV$$

The change in enthalpy ( $\Delta H$ ) of the system is equal to the energy flow as heat **at constant pressure**.  $\Delta H = q_p$

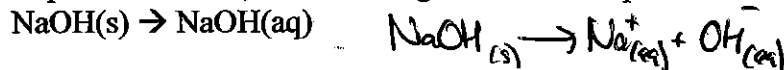
If  $\Delta H > 0$ , the reaction is **endothermic** (Heat is absorbed by the system). ( $q > 0$ )

If  $\Delta H < 0$ , the reaction is **exothermic** (Heat is given off by the system). ( $q < 0$ )



### Example 6.2 A *Enthalpy*

Upon adding solid potassium hydroxide pellets to water, the following reaction takes place:



For this reaction at constant pressure,  $\Delta H = -43 \text{ kJ/mole}$ . Answer the following questions regarding the addition of 14 g of NaOH to water:

- Does the beaker get warmer or colder?
- Is the reaction exo- or endothermic?
- What is the enthalpy change for the dissolution?

#### Solution:

- If  $\Delta H < 0$ , then heat is given off by the system. The beaker therefore gets warmer. ← Surroundings
- If heat is given off by the system, the reaction is **exothermic**.
- $14 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.0 \text{ grams}} \times \frac{-43 \text{ kJ}}{\text{mole}} = -15 \text{ kJ} = \Delta H$

**Calorimetry** Calorimetry is the experimental technique used to determine the heat exchange (q) associated with a reaction.

At constant pressure,  $q = \Delta H$

At constant volume,  $q = \Delta E$

In both cases, however, **heat gain or loss** is being determined. The amount of heat exchanged in a reaction depends upon:

- The net temperature change** during the reaction.
- The amount of substance**. The more you have, the more heat can be exchanged.
- The heat capacity (C)** of a substance.

$$C = \frac{\text{heat absorbed}}{\text{Increase in temperature}} = \text{J}^\circ\text{C}$$

Some substances can absorb more heat than others for a given temperature change. There are three ways of expressing heat capacity:

- Heat capacity** (as above) =  $\text{J}^\circ\text{C}$
- Specific Heat Capacity** = heat capacity per gram of a substance ( $\text{j/g}^\circ\text{C}$ )
- Molar heat capacity** = heat capacity per mole of substance ( $\text{j/mol}^\circ\text{C}$  or  $\text{j/mol}^\circ\text{K}$ )

You can solve calorimetry problems very well using dimensional analysis. Before we solve numerical problems, let's do a problem involving interpretation of specific heat capacities.

### Example 6.2 B *Specific Heat Capacity*

Look at Table 6.1 in your textbook. Based on the values for specific heat capacity, which conducts heat better, water or aluminum? Why is this important in cooking?

#### Solution:

The heat capacity of water is  $4.18 \text{ J/g}^\circ\text{C}$ . This means that it takes 4.18 J of energy to raise the temperature of one gram of water  $1^\circ\text{C}$ .

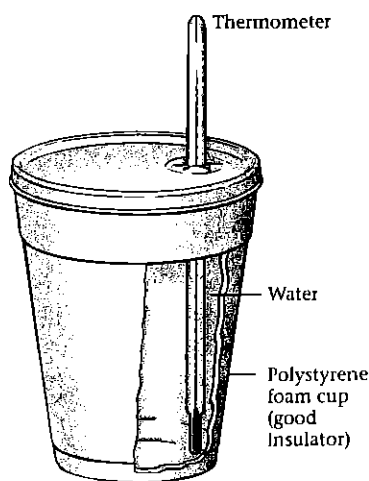
The heat capacity of aluminum is  $0.89 \text{ j/g}^\circ\text{C}$ . This means that it takes 0.89 J of energy to raise the temperature of one gram of aluminum  $1^\circ\text{C}$ .

In other words, it takes almost 5 times as much energy (4.18/0.89) to raise the temperature of an equivalent amount of water by 1 °C. Therefore, **aluminum conducts heat better** because less heat causes an equal rise in temperature. This is important in cooking because pots made of aluminum transfer heat very well to food. Note that iron pots conduct heat even more readily than aluminum (but they are more difficult to take care of).

Your textbook discusses doing **constant pressure calorimetry** using a “coffee cup calorimeter.” In this case,  $\Delta H = q_p$  in units of joules. Remember that you may use dimensional analysis to solve calorimetry problems.

### Coffee-Cup Calorimeter

To measure the heat flow in a reaction, it is carried out in a device known as a **calorimeter**. The apparatus contains water,



$$q_{\text{reaction}} = -q_{\text{calorimeter}}$$

$$q_{\text{reaction}} = -m_{\text{water}} \times 4.18 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \times \Delta t$$

**Figure 8.2**

Coffee-cup calorimeter. The heat given off by a reaction is absorbed by the water. If you know the mass of the water, its specific heat (4.18 J/g · °C), and the temperature change as read on the thermometer, you can calculate the heat flow,  $q$ , for the reaction.

### Example 6.2 C Constant Pressure Calorimetry (Coffee Cup Calorimetry)

Recall from Example 6.2 A that the  $\Delta H$  of NaOH is -43 kJ/mole when  $\text{NaOH (s)} \rightarrow \text{NaOH(aq)}$ . If 10.0 grams of solid NaOH is added to 1.0 L of water (specific heat capacity = 4.18 J/g°C) at 25.0 °C in a constant pressure calorimeter, what will be the final temperature of the solution? (Assume the density of the final solution is 1.05 g/mL)

**Strategy:** We need to know 3 things.

1. Mass of the solution = 1000 mL x 1.05 g/mL = 1050 grams
2. Heat capacity of the solution = 4.18 j/g°C
3. The enthalpy of the solution =

$$10.0 \text{ g NaOH} \left( \frac{1 \text{ mole}}{40.0 \text{ g}} \right) \left( \frac{-43 \text{ kJ}}{\text{mole}} \right) \left( \frac{1000 \text{ J}}{1 \text{ kJ}} \right) = -10,750 \text{ J}$$

We want to know the change in temperature ( $\Delta T$ ). We can solve using  $Q = mc\Delta T$ . Keep in mind the temperature will rise because heat is evolved, or absorbed.

Solution:

$$\Delta t = \frac{10,750 \cancel{\text{J}}}{(1050 \cancel{\text{g}})(4.18 \cancel{\text{J}}/\cancel{\text{g}} \cdot \text{C})} = \boxed{2.4^\circ\text{C}}$$

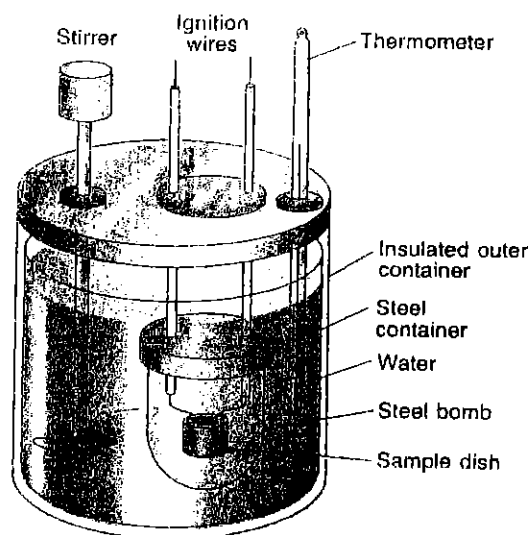
$$\Delta t = \frac{Q}{mc}$$

The final temperature will equal  $25.0^\circ\text{C} + 2.4^\circ\text{C} = 27.4^\circ\text{C}$ .

Constant Volume calorimetry is discussed in your book. The **bomb calorimeter** is used for this application. In this case, because  $\Delta V = 0$ , no work is done, and  $\Delta E = q$ , in units of joules. Here as well, dimensional analysis works well. Each bomb calorimeter is different. The **heat capacity ( $\text{J}^\circ\text{C}$ )** of the bomb and its parts must be determined using a known substance before the energy (or heat) of combustion can be determined.

#### Bomb Calorimeter

A coffee-cup calorimeter is suitable for measuring heat flows for reactions in solution. However, it cannot be used for reactions involving gases, which would escape from the cup; nor would it be appropriate for reactions in which the products reach high temperatures. The bomb calorimeter, shown in Figure 5.7, is a more versatile instrument. This type of calorimeter was used to determine most of the enthalpy changes that we have referred to in this chapter.



The bomb calorimeter is usually used with combustion reactions.

**FIGURE 5.7** Bomb calorimeter. To determine  $q$  for a reaction carried out in this apparatus, we must consider the heat absorbed by the metal parts of the calorimeter as well as by the water. To find  $q_{\text{bomb}}$ , a reaction is carried out for which  $q$  is known and  $\Delta t$  is measured.

#### Example 6.2 D Constant Volume Calorimetry (bomb calorimeter)

The heat of combustion of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$  is  $2500 \text{ kJ/mole}$ . A sample of glucose weighing  $5.00 \text{ g}$  was burned with excess oxygen in a bomb calorimeter. The temperature of the bomb rose  $2.4^\circ\text{C}$ . What is the heat capacity of the calorimeter?

A  $4.40 \text{ g}$  sample of propane ( $\text{C}_3\text{H}_8$ ) was then burned with excess oxygen in the same bomb calorimeter. The temperature of the bomb increased  $6.85^\circ\text{C}$ . Calculate  $\Delta E_{\text{combustion}}$  of propane.

$$Q_{\text{Bomb}} = C_{\text{Bomb}} \cdot \Delta t$$

**Strategy:** There are two parts to this problem. First, we must calculate the heat capacity of the bomb calorimeter using the data for glucose. Second, we can use this heat capacity to determine the energy (heat) of combustion of propane.

Remember that the energy of combustion is expressed in **kJ/mole**. A useful beginning is to convert grams of substance to moles of substance.

**Solution:**

**A. Heat Capacity of the calorimeter**

$$\text{Moles } C_6H_{12}O_6 = 5.00 \text{ g} \times \frac{1 \text{ mole}}{180.0 \text{ g}} = 2.78 \times 10^{-2} \text{ moles glucose}$$

$$\text{Heat capacity (kJ/}^\circ\text{C)} = 2.78 \times 10^{-2} \text{ moles glucose} \times \frac{2800 \text{ kJ}}{\text{Mole}} = 77.84 \text{ kJ}$$

5 g Glucose  
2800 kJ/mole  
2.4°C temp ↑

$$\frac{77.84 \text{ kJ}}{2.4 \text{ }^\circ\text{C}} = 32.4 \text{ kJ/}^\circ\text{C}$$

**B. Energy of Combustion of Propane**

4.4 g C<sub>3</sub>H<sub>8</sub>     Δt = 6.85°C

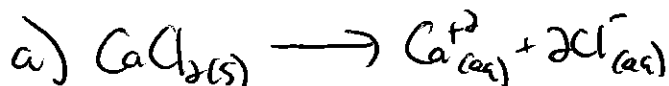
$$\text{Moles } C_3H_8 = 4.40 \text{ g propane} \times \frac{1 \text{ mole}}{44.0 \text{ g}} = 0.100 \text{ moles propane}$$

$$\Delta E_{\text{combustion}} = 32.4 \text{ kJ/}^\circ\text{C} \times 6.85 \text{ }^\circ\text{C} = 22.2 \text{ kJ}$$

$$\frac{22.2 \text{ kJ}}{0.100 \text{ moles}} = -2200 \text{ kJ/mole (note: We add negative sign because heat is evolved.)}$$

**Problems:**

7. Calcium chloride is a compound frequently found in first-aid hot packs. It gives off heat when dissolved in water. When 1.50 g of CaCl<sub>2</sub> is dissolved in 150.0 g of water, the temperature of the water rises from 20.50 °C to 22.25 °C. Assume that all the heat is absorbed by the water (specific heat = 4.18 J/g°C).
  - a. Write a balanced equation for the solution process.
  - b. What is q for the solution process?
  - c. Is the solution exo- or endothermic?
  - d. How much heat is absorbed by the water if one mole of calcium chloride is dissolved?



b)  $Q_{\text{water}} = -Q_{\text{rxn}} = -(150 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(22.25^\circ\text{C} - 20.50^\circ\text{C}) = \underline{-1098.3 \text{ J}}$

c) Exothermic

d)  $\frac{1098.3 \text{ J}}{1.50 \text{ g } CaCl_2} \left( \frac{111 \text{ g}}{1 \text{ mole } CaCl_2} \right) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) = \boxed{81.3 \text{ kJ/mole } CaCl_2}$



8. A 5.037 g piece of iron is heated to 100. °C and placed in a coffee-cup calorimeter that initially contains 27.3 g of water at 21.2 °C. If the final temperature is 22.7 °C, what is the specific heat capacity of the iron (J/g°C)?

$$Q_w = -Q_{Fe}$$

$$m_w c_w \Delta t_w = -(m_{Fe} c_{Fe} \Delta t_{Fe})$$

$$(27.3g)(4.184 \text{ J/g}^\circ\text{C})(22.7 - 21.2) = -(5.037g)(c_{Fe})(22.7 - 100)$$

$$c_{Fe} = 0.440 \text{ J/g}^\circ\text{C}$$

$m_w = 27.3g$        $m_{Fe} = 5.037g$   
 $c_w = 4.184 \text{ J/g}^\circ\text{C}$        $c_{Fe} = ?$   
 $t_f = 22.7^\circ\text{C}$        $t_f = 22.7^\circ\text{C}$   
 $t_i = 21.2^\circ\text{C}$        $t_i = 100^\circ\text{C}$

9. The specific heat of aluminum is 0.89 J/g°C. How much energy is required to raise the temperature of a 15.0 gram aluminum can 18 °C?

$$Q = mc\Delta t = (15.0g)(0.89 \text{ J/g}^\circ\text{C})(18^\circ\text{C}) = \boxed{240.3 \text{ J}} = 240 \text{ J}$$

10. The heat capacity of a bomb calorimeter was determined by burning 6.79 g of methane (heat of combustion = 802 kJ/mole) in the bomb. The temperature changed by 10.8 °C.

a. What is the heat capacity of the bomb?

$$6.79g \text{ CH}_4 \left( \frac{1 \text{ mole}}{16g \text{ CH}_4} \right) \left( \frac{802 \text{ kJ}}{\text{mole}} \right) = 340.3 \text{ kJ}$$

$$C_{\text{Bomb}} = \frac{\text{kJ}}{^\circ\text{C}} = \frac{340.3 \text{ kJ}}{10.8^\circ\text{C}} = \boxed{31.5 \text{ kJ/}^\circ\text{C}}$$

- b. A 12.6 g sample of acetylene, C<sub>2</sub>H<sub>2</sub>, produced a temperature increase of 16.9 °C in the same calorimeter. What is the heat of combustion of acetylene (kJ/mole)?

$$12.6g \text{ C}_2\text{H}_2 \left( \frac{1 \text{ mole}}{26g} \right) = .485 \text{ mol C}_2\text{H}_2$$

$$Q_{\text{Bomb}} = -Q_{\text{rxn}}$$

$$Q_{\text{Bomb}} = C_{\text{Bomb}} \cdot \Delta t = 31.5 \frac{\text{kJ}}{^\circ\text{C}} (16.9^\circ\text{C}) = 532.58 \text{ kJ}$$

-532.58 kJ released (by bomb)  
 =  $\frac{532.58 \text{ kJ}}{.485 \text{ mol C}_2\text{H}_2} = \boxed{-1098.9 \text{ kJ/mole}}$

11. A sample of C<sub>6</sub>H<sub>5</sub>COOH (benzoic acid) weighing 1.221 g was placed in a bomb calorimeter and ignited in a pure O<sub>2</sub> atmosphere. A temperature rise from 25.24 °C to 31.67 °C was noted. The heat capacity of the calorimeter was 5.020 kJ/°C and the combustion products were CO<sub>2</sub> and H<sub>2</sub>O. Calculate the ΔH in kJ/mole for the reaction.

$$1.221g \text{ B.A.} \left( \frac{1 \text{ mole}}{122g} \right) = .010008 \text{ mol B.A.}$$

$$\Delta t = 31.67 - 25.24 = 6.43^\circ\text{C}$$

$$C_{\text{Bomb}} = 5.020 \text{ kJ/}^\circ\text{C}$$

$$Q_{\text{Bomb}} = -Q_{\text{rxn}}$$

$$C_{\text{Bomb}} \cdot \Delta t = -Q_{\text{rxn}}$$

$$(5.020 \text{ kJ/}^\circ\text{C})(6.43^\circ\text{C}) = -32.28 \text{ kJ}$$

$$\Delta H = \frac{Q_{\text{rxn}}}{\text{moles}} = \frac{-32.28 \text{ kJ}}{.010008 \text{ mol}} = -3225 \text{ kJ/mole} = \boxed{-3.225 \text{ kJ/mole}} \quad (9)$$

12. Methanol,  $\text{CH}_3\text{OH}$ , is used as a fuel in some cars. When one mole of methanol burns, 726 kJ of heat is evolved. Five mL of methanol ( $d = 0.796 \text{ g/mL}$ ) is burned in a bomb calorimeter; heat capacity =  $8342 \text{ J/}^\circ\text{C}$ . If the bomb is initially at  $22.73^\circ\text{C}$ , what is the final temperature?

$$5 \text{ mL} \left( \frac{0.796 \text{ g CH}_3\text{OH}}{\text{mL}} \right) \left( \frac{1 \text{ mole}}{32 \text{ g}} \right) = 0.124 \text{ mol CH}_3\text{OH}$$

$$C_{\text{bomb}} = 8342 \text{ J/}^\circ\text{C} = 8.342 \text{ kJ/}^\circ\text{C}$$

$$t_i = 22.73^\circ\text{C}$$

$$t_f = ?$$

6.3 Hess's Law

$$Q = 726 \frac{\text{kJ}}{\text{mol}} \times 0.124 \text{ mol} =$$

$$Q_{\text{rxn}} = 90.3 \text{ kJ}$$

$$Q_{\text{bomb}} = -Q_{\text{rxn}}$$

$$Q_{\text{rxn}} = C_{\text{bomb}} \cdot \Delta T$$

$$Q_{\text{rxn}} = 90.3 \text{ kJ}$$

$$\Delta T = \frac{Q_{\text{rxn}}}{C_{\text{bomb}}} = \frac{90.3 \text{ kJ}}{8.342} = 10.8^\circ\text{C}$$

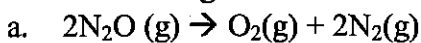
$$t_f = \Delta T + t_i = 10.8^\circ\text{C} + 22.73^\circ\text{C} = 33.53^\circ\text{C}$$

The critical point that is made in this section is that **enthalpy changes are state functions**. The implication is that **it does not matter if  $\Delta H$  for a reaction is calculated in one step or a series of steps. This idea is called Hess's Law.**

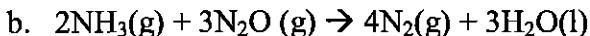
By using values of  $\Delta H$  of known reactions, we can use Hess's Law to solve for enthalpies of reactions whose values we do not know.

### Example 6.3 A Hess's Law

Given the following reactions and  $\Delta H$  values,



$$\Delta H = -164 \text{ kJ}$$



$$\Delta H = -1012 \text{ kJ}$$

Calculate  $\Delta H$  for:  $4\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$

**Strategy:** The idea is to manipulate equations a and b so that they add up to the desired equation. There are 3 ways we can manipulate equations.

1. We can reverse the entire equations. By doing this, the products become the reactants and vice-versa.
2. We can multiply the entire equation by a factor such as 3, 2,  $\frac{1}{2}$  or  $\frac{1}{3}$ .
3. We can do both #1 and #2.

The most important thing to keep in mind is that **WHEN YOU MANIPULATE AN EQUATION, YOU MUST MANIPULATE THE  $\Delta H$  VALUE EXACTLY THE SAME WAY!**

**Solution:** In my experience, the best way to solve Hess's Law problems is to **find a substance that only appears once in the reactants**. Modify that reaction so that the substance appears where it should be, and in the correct amount, as in the final reaction. The entire substance equation must therefore be correct. In our example,  $\text{NH}_3$  appears only once in the reactants. ( $\text{N}_2\text{O}$  appears in both equations....STAY AWAY FROM  $\text{N}_2\text{O}$ !)

We have  $2\text{NH}_3$  on the left hand side. We want  $4\text{NH}_3$  on that side. Therefore we must multiply equation b and its  $\Delta H$  by +2, which gives:

