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Chapter 6- Thermochemistry Study Guide

Key

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)²
Measured in Joules. (1 J = 1 kg m²/s²).
- **Potential Energy:** Energy that can be converted into useful work. Measured in Joules.
(1 J = 1 kg m²/s²). $PE = mgh$ $g = 9.8 \text{ m/s}^2$
- **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 m²/s²). 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.

①

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. ΔE 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. ΔE 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,

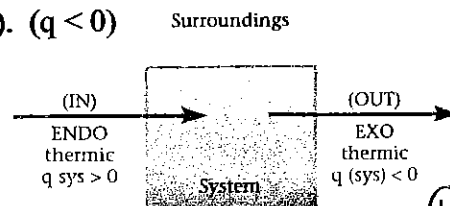
$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

$$\Delta H = E + PV$$

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

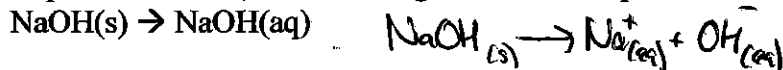
If $\Delta H > 0$, the reaction is **endothermic** (Heat is absorbed by the system). ($q > 0$)

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, $\Delta H = -43$ 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) = J°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°C .

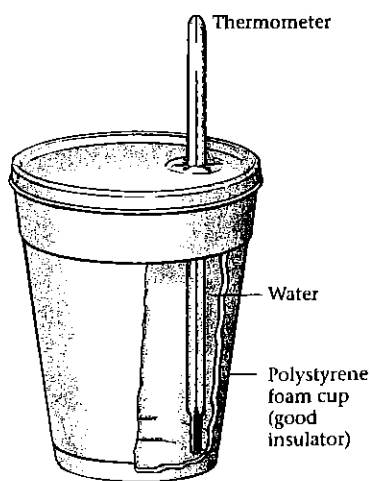
The heat capacity of aluminum is $0.89 \text{ j/g}^\circ\text{C}$. This means that it takes 0.89 J of energy to raise the temperature of one gram of aluminum 1°C .

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

Solution:

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

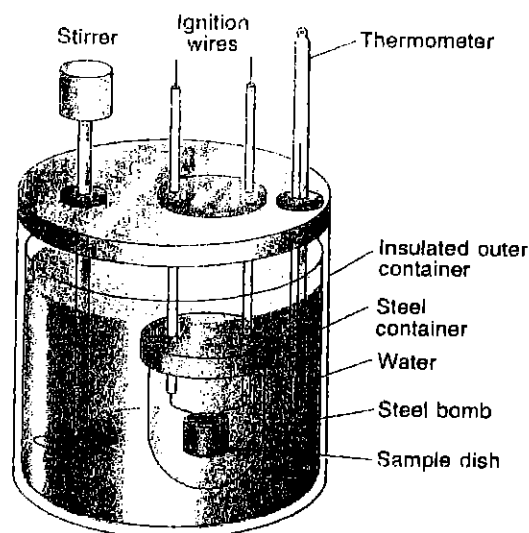
$$\Delta t = \frac{Q}{mc}$$

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 (J°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_{bomb} , a reaction is carried out for which q is known and Δt 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 kJ/mole . A sample of glucose weighing 5.00 g was burned with excess oxygen in a bomb calorimeter. The temperature of the bomb rose 2.4°C . **What is the heat capacity of the calorimeter?**

A 4.40 g sample of propane (C_3H_8) was then burned with excess oxygen in the same bomb calorimeter. The temperature of the bomb increased 6.85°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

5 g Glucose
2800 kJ/mole
2.4°C temp ↑

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

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

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

B. Energy of Combustion of Propane

4.4 g C₃H₈ Δt = 6.85°C

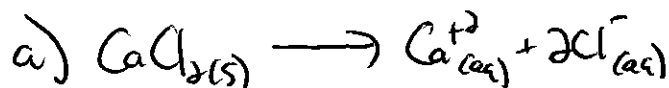
$$\text{Moles } C_3H_8 = 4.40 \text{ g propane} \times \frac{1 \text{ mole}}{44.0 \text{ g}} = 0.100 \text{ moles propane}$$

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

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

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 CaCl₂ 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) $Q_{\text{water}} = -Q_{\text{rxn}} = -(150 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(22.25^\circ\text{C} - 20.50^\circ\text{C}) = \underline{-1098.3 \text{ J}}$

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)?

$$Q_w = -Q_{Fe}$$

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

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

$$m_w = 27.3g \quad m_{Fe} = 5.037g$$

$$c_w = 4.184 \frac{J}{g^\circ C} \quad c_{Fe} = ?$$

$$t_f = 22.7^\circ C \quad t_f = 22.7^\circ C$$

$$t_i = 21.2^\circ C \quad t_i = 100^\circ C$$

$$\boxed{c_{Fe} = 0.440 \frac{J}{g^\circ C}}$$

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?

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

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?

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

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

- b. A 12.6 g sample of acetylene, C₂H₂, produced a temperature increase of 16.9 °C in the same calorimeter. What is the heat of combustion of acetylene (kJ/mole)?

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

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

$$-532.58 \text{ kJ released (kJ)}$$

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

absorbed 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 C₆H₅COOH (benzoic acid) weighing 1.221 g was placed in a bomb calorimeter and ignited in a pure O₂ 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 CO₂ and H₂O. Calculate the ΔH in kJ/mole for the reaction.

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

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

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

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

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

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

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

12. Methanol, CH_3OH , 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°C , what is the final temperature?

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

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

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

$$t_f = ?$$

6.3 Hess's Law

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

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

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

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

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

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

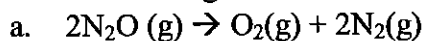
$$t_f = \Delta t + t_i = 10.8^\circ\text{C} + 22.73^\circ\text{C} = 33.53^\circ\text{C}$$

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 ΔH for a reaction is calculated in one step or a series of steps**. This idea is called **Hess's Law**.

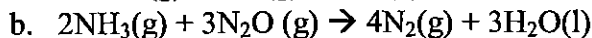
By using values of ΔH of known reactions, we can use Hess's Law to solve for enthalpies of reactions whose values we do not know.

Example 6.3 A Hess's Law

Given the following reactions and ΔH values,



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



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

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

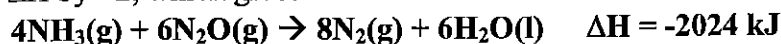
Strategy: The idea is to manipulate equations a and b so that they add up to the desired equation. There are 3 ways we can manipulate equations.

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 ΔH 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, NH_3 appears only once in the reactants. (N_2O appears in both equations....STAY AWAY FROM N_2O !)

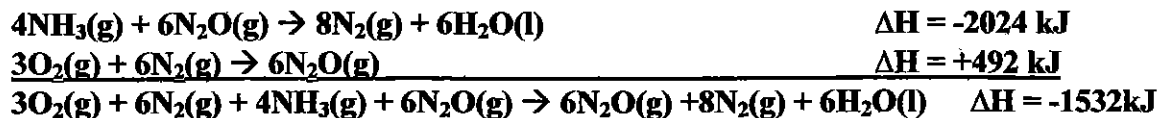
We have 2NH_3 on the left hand side. We want 4NH_3 on that side. Therefore we must multiply equation b and its ΔH by +2, which gives:



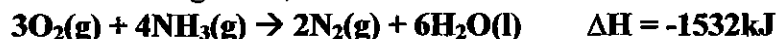
Oxygen appears only once in the reactants. Therefore, if we modify equation a to get the correct amount of O₂ in the proper place, we should be done. (We have modified both equations.) We need to *reverse* equation a and *multiply* it by 3 to get 3O₂ on the left side. This will agree with the desired reaction. Remember to multiply equation a's ΔH by -3 as well! This gives:



Let's get the final ΔH by adding our "modified" equations,



And cancelling terms,

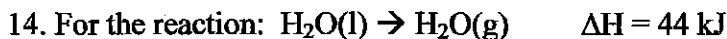
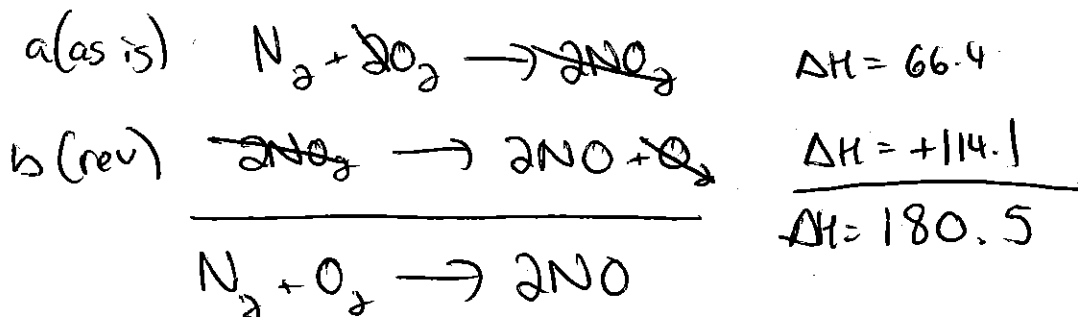
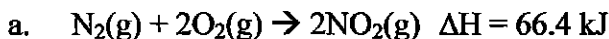


Getting the final reaction serves as your check of correctness.

Problems:



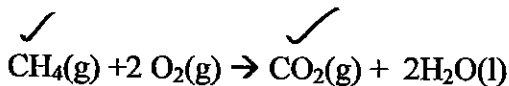
Given:



How much heat is evolved when 9.0 grams of water vapor is condensed to liquid water?

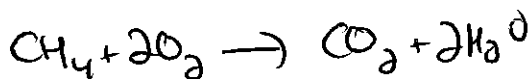
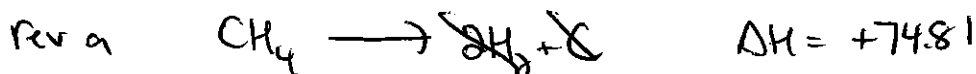
$$\Delta\text{H}_{\text{condensed}} = -44 \frac{\text{kJ}}{\text{mole}} \times \frac{1 \text{ mole H}_2\text{O}}{18 \text{ g}} \times 9 \text{ g H}_2\text{O} = \boxed{-22 \text{ kJ}}$$

15. Calculate ΔH for:



Given:

- a. $2\text{H}_2(\text{g}) + \text{C}(\text{s}) \rightarrow \text{CH}_4(\text{g}) \quad \Delta H = -74.81 \text{ kJ}$
b. $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) \quad \Delta H = -571.66 \text{ kJ}$
c. $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H = -393.52 \text{ kJ}$



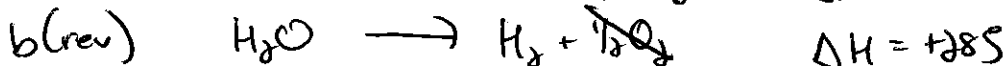
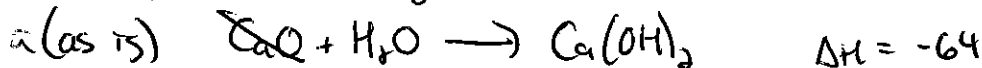
$$\Delta H = -890.37 \text{ kJ}$$

16. Calculate ΔH for:



Given:

- a. $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s}) \quad \Delta H = -64 \text{ kJ}$
b. $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H = -285 \text{ kJ}$
c. $\text{Ca}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s}) \quad \Delta H = -635 \text{ kJ}$



$$\Delta H = -414 \text{ kJ}$$

6.4 Standard Enthalpies of Formation

Look at your textbook, where the **standard enthalpy of formation** (ΔH_f°) of a compound is defined. There are some important points that are worth going over.

1. ΔH_f° is always given **per mole** if compound formed.
2. ΔH_f° involves formation of a compound from its elements with the substances in their **standard states**.
3. Your textbook lists the following standard state conditions.

For an element:

- It is the form which the element exists in at 25 °C and 1 atmosphere.

For a compound:

- For a gas it is a pressure of exactly 1 atmosphere.
- For a substance in solution, it is a concentration of exactly 1 M.
- For a pure solid or liquid, it is the pure solid or liquid.

4. ΔH_f° for an element in its standard state (such as Ba(s) or N₂(g)) equals 0.

Example 6.4A *Standard Enthalpies of Formation*

By consulting Appendix 4 of your textbook, and from your knowledge of standard states, list the standard enthalpy of formation for each of the following substances.

- | | |
|---------------------------------------|---|
| a. Al ₂ O ₃ (s) | -1676 kJ |
| b. Ti(s) | 0 kJ (solid is the standard state of titanium) |
| c. P ₄ (g) | 59 kJ |
| d. SO ₄ ²⁻ (aq) | -909 kJ |
| e. F ₂ (g) | 0 kJ (The gaseous diatom is the standard state of fluorine) |

The key to calculating standard enthalpy changes is to remember “products minus reactants.” More correctly, $\Delta H_{\text{reaction}}^\circ = \sum n_p \Delta H_f^\circ \text{ products} - \sum n_r \Delta H_f^\circ \text{ reactants}$

This reads “the sum of the ΔH_f° for n moles of each of the products minus the sum of the ΔH_f° for n moles of each of the reactants.”

Keep in mind that just as in Hess’s Law problems, when you multiply the substance by an integer coefficient in a balanced equation, you must multiply the ΔH_f° value by that integer as well!

Example 6.4B *Calculating Standard Enthalpies of Formation*

Using your data in Appendix 4 of your textbook, calculate ΔH_f° for the following reaction:



Solution: $\Delta H_{\text{reaction}}^\circ = \sum n_p \Delta H_f^\circ \text{ products} - \sum n_r \Delta H_f^\circ \text{ reactants}$

$$\begin{aligned} \sum n_p \Delta H_f^\circ \text{ products} &= 6 \times \Delta H_f^\circ \text{H}_2\text{O}(\text{l}) + 6 \times \Delta H_f^\circ \text{CO}_2(\text{g}) = (6 \text{ mol} \times -286 \text{ kJ/mol}) + (6 \text{ mol} \times -393.5 \text{ kJ/mol}) \\ &= -4077 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \sum n_r \Delta H_f^\circ \text{ reactants} &= 2 \times \Delta H_f^\circ \text{C}_3\text{H}_6(\text{g}) + 9 \times \Delta H_f^\circ \text{O}_2(\text{g}) = (2 \text{ mol} \times 20.9 \text{ kJ/mol}) + (9 \text{ mol} \times 0 \text{ kJ/mol}) \\ &= +41.8 \text{ kJ} \end{aligned}$$

$$\text{Finally, } \Delta H = (-4077 \text{ kJ}) - (+41.8 \text{ kJ}) = \mathbf{-4119 \text{ kJ}}$$

Problems:

17. Using standard heats of formation (Appendix 4 in your book), calculate ΔH for the following reactions:

- a. $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ $\Delta H_f^\circ \text{H}_2\text{O}_2(\text{l}) = -187.8 \text{ kJ/mole}$
b. $\text{HCl}(\text{g}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
c. $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$
d. $\text{C}_2\text{H}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g})$
e. $2\text{NaOH}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{g})$

$$\text{a) } [2(\overset{-286}{\cancel{-187.8}}) + 0] - [2(-187.8)] = \underline{-196.4 \text{ kJ/mole}}$$

$$\text{b) } [0 + (-167)] - [(-92)] = \underline{-75 \text{ kJ/mole}}$$

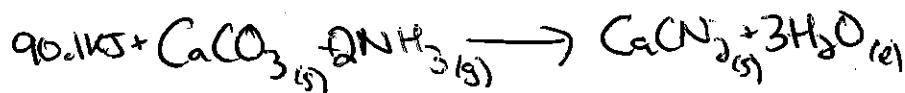
$$\text{c) } [82] - [2(34)] = \underline{14 \text{ kJ/mole}}$$

$$\text{d) } [52] - [227 + 0] = \underline{-175 \text{ kJ/mole}}$$

$$\text{e) } [-1131 + (-242)] - [2(-427) + (-393.5)] = -1373 - (-1247.5) = \underline{-125.5 \text{ kJ/mole}}$$

18. When one mole of calcium carbonate reacts with ammonia gas, solid calcium cyanamide, CaCN_2 and liquid water are formed. The reaction absorbs 90.1 kJ of heat.

a. Write a balanced equation for the reaction. Include the ΔH .



b. Using Appendix 4, calculate ΔH_f° for calcium cyanamide.

$$[\Delta H_f(\text{CaCN}_2) + 3(\Delta H_f(\text{H}_2\text{O}))] - [\Delta H_f(\text{CaCO}_3) + 2\Delta H_f(\text{NH}_3)] = 90.1 \text{ kJ}$$

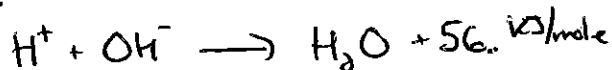
$$(X + 3(-286)) - (-1207 + 2(-46)) = 90.1$$

$$(X + (-858)) - (-1299) = 90.1$$

$$X - 85.8 + 1299 = 90.1$$

$$\boxed{X = -350.9 \text{ kJ}}$$

19. The heat released when HNO_3 reacts with NaOH is 56 kJ/mole of water produced. How much energy is released when 400.0 mL of 0.200 M HCl is mixed with 500.0 mL of 0.150 M NaOH ? How does this compare with the answer to **problem #78** in your textbook? Why?



$$(0.4 \text{ L})(0.2 \frac{\text{mol}}{\text{L}}) = 0.08 \text{ mol HCl} = 0.08 \text{ mol H}^+$$

$$(0.5 \text{ L})(0.15 \frac{\text{mol}}{\text{L}}) = 0.075 \text{ mol NaOH} \quad \boxed{0.075 \text{ mol OH}^-} \text{ - LR}$$

$$0.075 \text{ mol OH}^- \left(\frac{56 \text{ kJ}}{\text{mole}} \right) = \boxed{4.2 \text{ kJ}}$$

Strong Acid / Strong Base always releases 56 kJ/mole

Chapter 16- Spontaneity, Entropy & Free Energy Problems

- Choose the state that is more random, and thus is more probable.
 - A lawn before the leaves are raked or after they are raked. *before raked*
 - A house being built or after it is built. *being built*
 - A deck of cards before of after a successful game of "52 pickup?" *Before*
 - A football team at the huddle or after the huddle. *Before*
- Which of the following processes are spontaneous?
 - Glass shattering when it is dropped. *Spont.*
 - Outlining your chemistry notes. *non-spont*
 - Perfume aroma from an open bottle filling the air. *-spont.*

$\ominus \Delta S = \text{more organized}$
 $\oplus \Delta S = \text{less organized more random}$

- Predict the sign of ΔS for:
 - The freezing of water ~~(\oplus)~~ \ominus
 - Evaporation of a seawater sample to dryness $\oplus \Delta S$
 - ammonia vapor condensing $\ominus \Delta S$
 - weeding a garden $\oplus \Delta S$
- Predict the sign of ΔS for each of the following reactions:
 - $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ ~~(\oplus)~~ \ominus
 - $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$ ~~(\oplus)~~ \oplus
 - $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ ~~(\oplus)~~ \ominus
 - $S(s) + O_2(g) \rightarrow SO_2(l)$ ~~(\oplus)~~ \ominus

- Use the table of thermodynamic data to calculate the ΔS° for each of the following reactions:
 - $4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g)$

$$\Delta S = (4(240) + 6(189)) - (4(193) + 7(205)) = 2094 - 2207 = -113 \text{ J/mol}\cdot\text{K}$$

\ominus more organized

- $2H_2O_2(l) + N_2H_4(l) \rightarrow N_2(g) + 4H_2O(g)$

$$\Delta S = (192 + 4(189)) - ((2(90) + 121)) = 756 - 301 = +455 \text{ J/mol}\cdot\text{K}$$

\oplus more random

- $2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2SO_2(g)$

$$\Delta S = (2(189) + 2(248)) - (2(206) + 3(205)) = 437 - 1027 = -590 \text{ J/mol}\cdot\text{K}$$

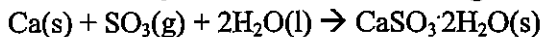
\ominus more organized

- $Ag(s) + 2H^+(g) + NO_3^-(aq) \rightarrow Ag^+(aq) + H_2O(l) + NO_2(g)$

$$\Delta S = (73 + 70 + 240) - (43 + 2(0) + 146) = 383 - 189 = +194 \text{ J/mol}\cdot\text{K}$$

\oplus more random

6. Calculate the ΔH_f° and S° for $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$ given the following information:



$$\Delta H^\circ = -795 \text{ kJ}; \Delta S^\circ = -235.5 \text{ J/K}$$

$$-795 = (x) - (0 + (-396) + 2(-286))$$

$$-795 = x - (-968)$$

$$\Delta H = x = -1763 \text{ kJ/mole}$$

$$-235.5 = (x) - (41 + 257 + 2(70))$$

$$-235.5 = x - 438$$

$$x = \Delta S_p = 673.5 \text{ J/mol K}$$

7. Calculate ΔG° at 25°C for reactions for which:

a. $\Delta H^\circ = +210 \text{ kJ}; \Delta S^\circ = +32.5 \text{ J/K}$

b. $\Delta H^\circ = +7.34 \text{ kJ}; \Delta S^\circ = +0.337 \text{ kJ/K}$

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

$$\Delta G = 210 \frac{\text{kJ}}{\text{mole}} - (298 \text{ K}) \left(\frac{0.0325 \text{ kJ}}{\text{mol K}} \right)$$

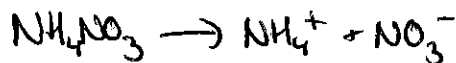
$$\Delta G = 200.3 \text{ kJ/mole}$$

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

$$= 7.34 \text{ kJ} - (298 \text{ K}) \left(\frac{0.337 \text{ kJ}}{\text{mol K}} \right)$$

$$\Delta G = -93.1 \text{ kJ/mole}$$

8. Show by calculation whether the dissolving of ammonium nitrate in water at 25°C .



a. Is exothermic or endothermic.

$$\Delta H = (-132 + (-205)) - (-366) = +29 \text{ kJ/mole} \text{ endothermic}$$

b. Increases or decreases in entropy.

$$\Delta S = (113 + 146) - 151 = 108 \text{ J/mol K} \text{ increasing in entropy}$$

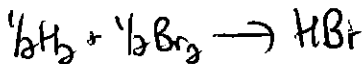
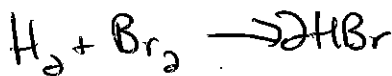
c. Is spontaneous.

$$\Delta G = (-79 + (-109)) - (-184) = -4 \text{ kJ/mole}$$

$$\text{or } \Delta G = \Delta H - T\Delta S = 29 - 298(0.108) = -3.184$$

$\Delta G = \text{spont!}$

9. Calculate the ΔH_f° , and ΔS_f° for the formation of 1 mole of HBr(g) from its elements. Calculate the temperature at which ΔG_f° is -60.0 kJ/mol .



$$\Delta H = (-36) - \left(\frac{1}{2}(0) + \frac{1}{2}(0) \right) = -36 \text{ kJ/mol}$$

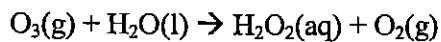
$$\Delta S = (199) - \left(\frac{1}{2}(131) + \frac{1}{2}(152) \right) = +57.5 \text{ J/mol K} = 0.0575 \text{ kJ/mol K}$$

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

$$T = \frac{\Delta G - \Delta H}{-\Delta S} = \frac{\Delta H - \Delta G}{\Delta S} = \frac{-36 \text{ kJ/mol} - (-60 \text{ kJ/mol})}{0.0575}$$

$$T = 417.4 \text{ K}$$

10. A student warned his friends not to swim in a river close to an electric plant. He claimed that the ozone produced by the plant turned the river water to hydrogen peroxide, which would bleach hair. The reaction is:



Show by calculation whether his claim is plausible (a spontaneous reaction would be "plausible"), assuming the river water is at 25°C, and all the species are at standard concentrations. Take ΔG_f° $\text{O}_3(\text{g})$ at 25°C to be +163.2 kJ/mol and ΔG_f° $\text{H}_2\text{O}_2(\text{aq})$ at 25°C to be -134.0 kJ/mol.

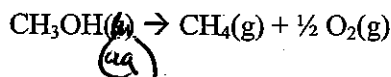
$$\Delta G = \sum G_f(\text{prod}) - \sum G_f(\text{react})$$

$$\Delta G = (-134 \text{ kJ/mole} + 0) - (163.2 \text{ kJ/mole} + (-237 \text{ kJ/mole}))$$

$$\Delta G = -134 - (-73.8) = -60.2 \text{ kJ/mole}$$

Reaction is spontaneous ($-\Delta G$), so it is plausible.

11. It has been proposed that wood alcohol, CH_3OH , a relatively inexpensive fuel to be produced, be decomposed to produce methane. Methane is a natural gas commonly used for heating homes. Is the decomposition of wood alcohol to methane and oxygen thermodynamically feasible at 25°C?



Calculate ΔH_f° , and ΔS_f° . Calculate ΔG using formula $\Delta G = \Delta H - T\Delta S$.

$$\Delta H = (-75 + \frac{1}{2}(0)) - (-239) = +164 \text{ kJ/mole}$$

$$\Delta S = (186 \text{ J/mol}\cdot\text{K} + \frac{1}{2}(205 \text{ J/mol}\cdot\text{K})) - (127) = +161.5 \text{ J/mol}\cdot\text{K} = .1615 \text{ kJ/mol}\cdot\text{K}$$

$$\Delta G = \Delta H - T\Delta S = 164 \text{ kJ/mole} - (298 \text{ K})(.1615 \text{ kJ/mol}\cdot\text{K})$$

$$\Delta G = +115.9 \text{ kJ/mole}$$

+ ΔG = spont. not feasible
 + ΔH = endothermic not feasible
 + ΔS = more random feasible

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

$$-\Delta G = \text{spontaneous}$$

$$+\Delta G = \text{non-spontaneous}$$

12. Discuss the effect of temperature change upon the spontaneity of the following reactions at 1 atm. Also, at what temperature does ΔG° become zero (reaches equilibrium) for each of the reactions.



@ 298 K $\Delta G = 851.5 \text{ kJ} - (298)(.0385) = +840 \text{ kJ}$ - NON-SPONTANEOUS

$\Delta G = 0$ $T = \frac{\Delta H - \Delta G}{\Delta S} = \frac{851.5 - 0}{.0385} = 22,117 \text{ K}$ - Temp for $\Delta G = 0$

Any temp higher than $2.21 \times 10^4 \text{ K}$ will be spontaneous



@ 298 K $\Delta G = -50.6 - (298)(.3315) = -149.4 \text{ kJ/mol}$ - SPONTANEOUS

$\Delta G = 0$ $T = \frac{\Delta H - \Delta G}{\Delta S} = \frac{-50.6}{.3315} = -153 \text{ K}$ (Impossible to have a \ominus Kelvin, so this reaction is always spont.)

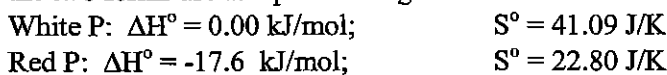


@ 298 K $\Delta G = 98.9 - (298)(.0939) = 70.9 \text{ kJ/mol}$ - non spontaneous

$\Delta G = 0$ $T = \frac{\Delta H - \Delta G}{\Delta S} = \frac{98.9}{.0939} = 1053 \text{ K}$

This reaction will be spontaneous at any temp above 1053 K

13. Red Phosphorus is formed when heating white phosphorus. Calculate the temperature at which the two forms are at equilibrium given:

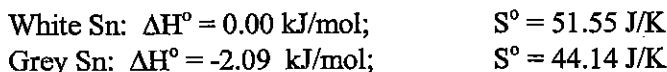
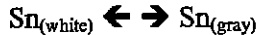


$\Delta H = H_{\text{prod}} - H_{\text{react}} = -17.6 - 0 = -17.6 \text{ kJ/mol}$

$\Delta S = S_{\text{prod}} - S_{\text{react}} = 22.8 - 41.09 = -18.29 \text{ J/mol K} = -.01829 \text{ kJ/mol K}$

$T = \frac{\Delta H - \Delta G^\circ}{\Delta S} = \frac{\Delta H}{\Delta S} = \frac{-17.6}{-.01829} = 962 \text{ K}$

14. Tin organ pipes in unheated churches develop tin "disease," in which white tin is converted to gray tin.



$\Delta H = -2.09 - 0 = -2.09 \text{ kJ/mol}$

$\Delta S = 44.14 - 51.55 = -7.41 \text{ J/mol K} = -.00741 \text{ kJ/mol K}$

$\Delta G = 0$ $T = \frac{\Delta H - \Delta G^\circ}{\Delta S} = \frac{\Delta H}{\Delta S} = \frac{-2.09 \text{ kJ/mol}}{-.00741} = 282 \text{ K}$

$\Delta H, \Delta S + \Delta G$ Chart

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

ΔH

ΔS

ΔG

ΔH	ΔS	ΔG
(+)	(-)	NON-SPONTANEOUS (+) Always at any temp
(-)	(+)	SPONTANEOUS (-) Always at any temp
(+)	(+)	(-) Spontaneous at <u>high</u> temp (+) Non-spont. at <u>low</u> temp
(-)	(-)	(-) Spontaneous at <u>low</u> temp (+) Non-spont. at <u>high</u> temp