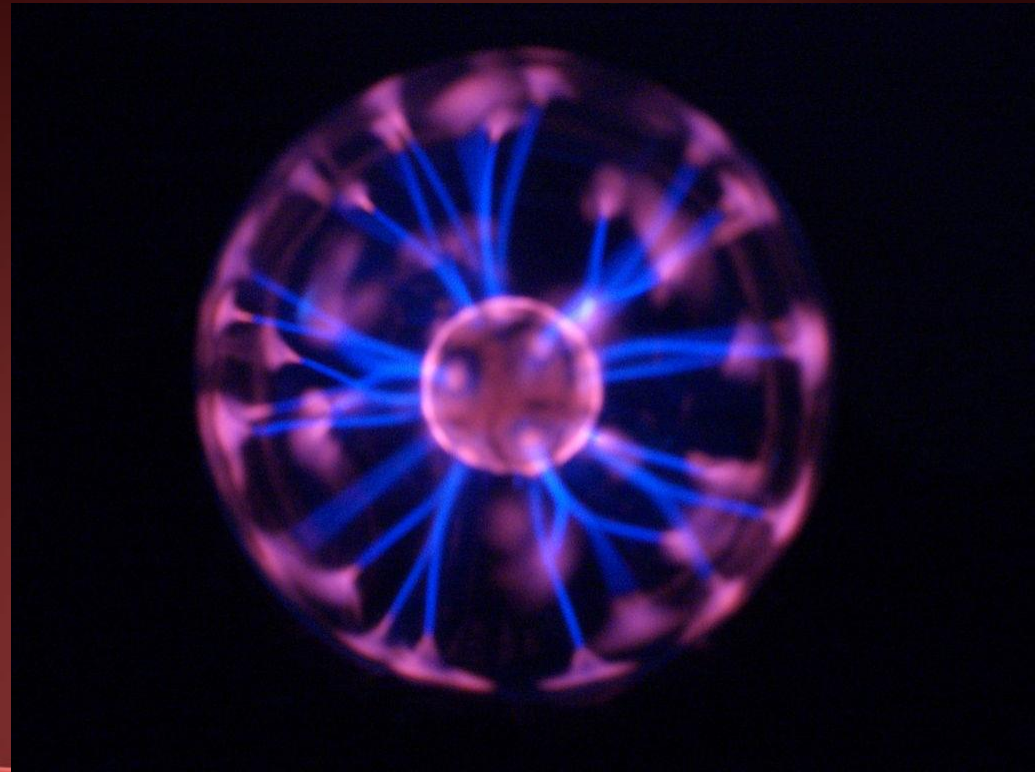




USDOE



Thermochemistry

Chemistry, Karl Steffin, 2006, 8/30/2024

By end of this unit I can...

- CT1: identify and describe the phase states and transitions between phases.**
- CT2: identify both an exothermic and endothermic process.**
- CT3: describe the differences in an exothermic and endothermic process.**
- CT4: solve the enthalpy of an equation, based on step equations, using Hess' Law.**
- CT5: identify and describe the components of the equation for heat.**
- CT6: calculate the enthalpy of a compound using calorimetry.**

- **This chapter will be a crossover into the realm of Physics.**
- **Thermodynamics (Gr: Heat Power)**
 - The study of fluid motion, and transformations.
- **Chemical reactions change the electron configurations**
 - Normally this results in a more efficient configuration so left-over energy is released (to the surroundings).
 - If the result is less efficient the reaction may need energy.



- **The SI unit of energy is the Joule.**
 - Prescott Joule (1818-1889)
- **1 Joule is actually a very small amount of Energy (even in chemistry).**
 - 1 kiloJoule (kJ) = 1000-J
- **calorie:** The amount of energy used to raise 1-g of H_2O 1°C is called a calorie (lower case).
 - 1 cal = 4.184 J
 - 1,000 cal = 1kcal = 1 Calorie (Nutritional label)

Sample Problem

Convert 2.0-kJ to calories.

1. Convert to Joules (x 1000)

2. Dimensional Analysis

– (Want on top/Remove on bottom)

$$2.0 \text{ - } \cancel{\text{kJ}} \times \frac{1000}{\cancel{\text{k}}} \times \frac{1 \text{ - } \text{cal}}{4.184 \text{ - } \cancel{\text{J}}} = 478.01 \text{ - } \text{cal}$$

478.0-cal

Systems Versus Surroundings

- Take a look at the following:



- This reaction has an excess of Energy.
 - The bonds of the product(s) requires less energy than the reactant(s). **Exothermic** (out).
- Reactions can also need energy from the surroundings, although not as common.
 - This is an **Endothermic** (into) reaction.

Endothermic versus Exothermic



- Excess energy is released by the reaction.
- The surroundings heat up...Exothermic.



- Energy is needed for the reaction to happen.
- The surroundings cool down...Endothermic.

- It is not common to place the amount of energy in a chemical equation.

- **H stands for the Enthalpy of the system.**
 - Enthalpy takes into account pressure and volume of the substance.
 - Also shows a return to the starting point.
- **Take a look at the following:**
$$\text{C}_3\text{H}_{8(g)} + 5\text{O}_2 \rightarrow 3\text{CO}_{2(g)} + 4\text{H}_2\text{O}_{(g)} + 2043\text{-kJ}$$
 - The combustion of propane produces 2043-kJ of energy (exothermic).
 - After heat is liberated what would the surrounding increase be? (**2043-kJ higher**)
 - What would it take to get back to the original condition? (**remove the heat or -2043-kJ**)

- **Chemistry Formulas show how to get back to the original conditions.**



$$\Delta H^\circ = -2043 \text{ kJ}$$

Using Enthalpy

- How much heat will be released if 1.0-g of Hydrogen Peroxide decomposes?



$$\Delta H^\circ = -190 \text{ kJ}$$

?-kJ

$$1 - \cancel{g} \text{H}_2\text{O}_2 \times \frac{1 - \cancel{\text{mol}}}{34 - \cancel{g}} \times \frac{190 - \cancel{\text{kJ}}}{2 - \cancel{\text{mol}} \text{H}_2\text{O}_2} =$$

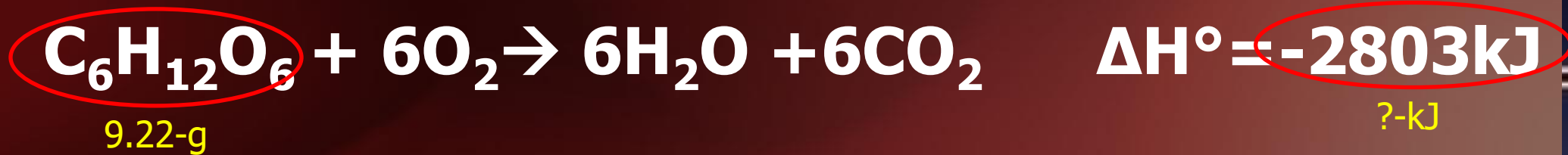
$$\frac{190 - \cancel{\text{kJ}}}{68} = 2.79$$

2.8-kJ



Using Enthalpy

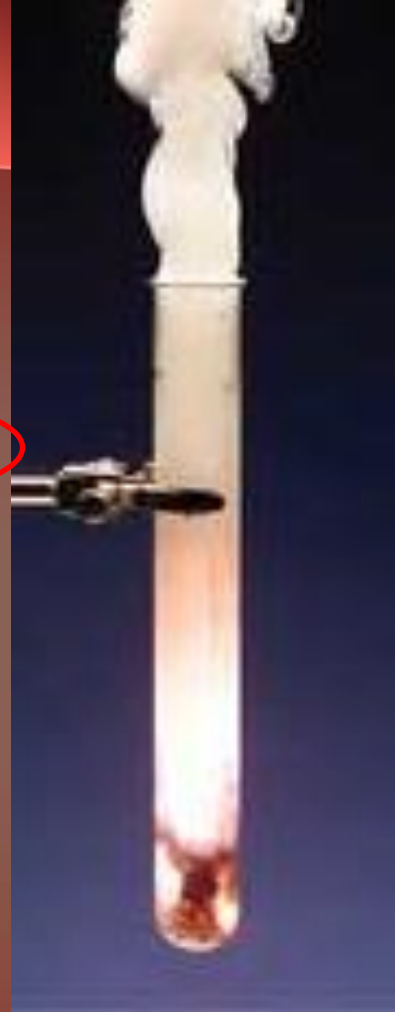
- How much heat is transferred when 9.22-g of Glucose reacts with O₂?



$$9.22 - \cancel{g \text{ Glu}} \times \frac{1 - \cancel{mol}}{180 - \cancel{g}} \times \frac{2803 - \cancel{kJ}}{1 - \cancel{mol \text{ Glu}}} =$$

$$\frac{25843 - \cancel{kJ}}{180} = 143.57$$

143.6-kJ



Non Chemical Look at Hess' Law

- **Imagine making a chocolate cake with icing. The nutritional info is desired.**
- **Two recipes are needed: the cake and icing.**
- **To find the nutritional value:**
 - **Can the icing be found before the cake?**
 - **Can all separate ingredients (sugar, egg, chocolate, flour...) be found and then added together?**
 - **Can the calories of the cake and then the icing be found and then added together?**
- **Hess' Law states that it does not matter whether all are mixed together or added up separately; the result is the same each time.**

Hess's Law (Germain Henri Hess 1802-1850)



- From the following reactions:
 - $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO} \quad \Delta H^\circ = 181 \text{ kJ}$
 - $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \quad \Delta H^\circ = -113 \text{ kJ}$
- If combined the reaction is:
 - $\text{N}_2 + 2\text{O}_2 + 2\text{NO} \rightarrow 2\text{NO} + 2\text{NO}_2$
 - Simplified $\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2$ (not natural)
- While not natural it is the end result.
- Rather than always calculating separate reactions Hess's Law says to sum the component parts together... (181kJ-113kJ=68kJ) and treat them as one.

Two Rules for Hess's Law



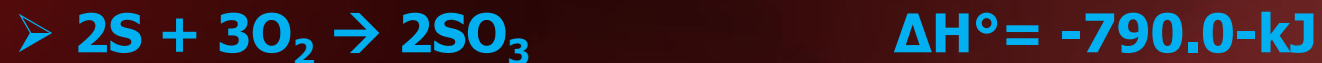
- What if the reaction was doubled?
- $2\text{C} + 2\text{H}_2\text{O} \rightarrow 2\text{CO} + 2\text{H}_2$ $\Delta\text{H}^\circ = +226 \text{ kJ}$



- What if the reaction was reversed?
- $\text{H}_2 + \text{CO} \rightarrow \text{C} + \text{H}_2\text{O}$ $\Delta\text{H}^\circ = -113 \text{ kJ}$

Samples of Hess's Law

- Take the following:



- What is ΔH° for $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$?

- Reverse first reaction:



- Combine:



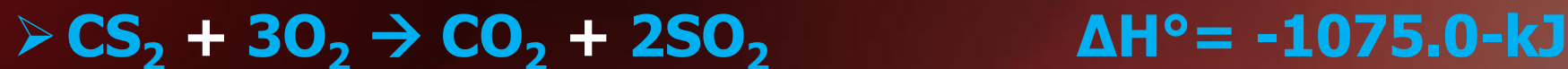
$$\Delta H^\circ = 196\text{-kJ} + -790\text{-kJ} = -594\text{-kJ}$$

- Simplify:



Samples of Hess's Law

- Take the following:



- What is ΔH° for $\text{CS}_2 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}_2\text{S}$?

- Reverse and double the first reaction:



- Combine:



$$\Delta\text{H}^\circ = 1126\text{-kJ} + -1075\text{-kJ} = 51\text{-kJ}$$

- Simplify:



- **Calorimetry is the study of heat flow and measurement.**
- **Heat Capacity: The amount of heat needed to raise the temperature of an object 1°-C .**
 - **Depends on the size and composition of the object:**
 - **It takes more Energy to boil a pot of water than a cup of water.**
 - **Metals (conductors) heat and cool faster than glass/plastics (insulators).**

- **A formula for calculating heat:**
 - **$Q_{\text{system}} = Cm\Delta T$**
 - **Q = heat transfer in the reaction (J or kJ)**
 - **C = Specific Heat of material (J/g·°C)**
 - **m = mass of material (g)**
 - **ΔT = change in Temperature of material (°C).**
- **Waters Specific Heat (C) is 4.184-J/g·°C.**
 - **This means that it will take 4.184-J of energy to raise a gram of water 1-°C.**
- **This formula can also be used to solve for the Specific Heat of a material.**

Specific Heat Example

- What is the Specific Heat if 4500.0-J are needed to raise 85.0-g of a material 45.0-°C?

$$Q = cm\Delta T$$

$$4500.0 - J = 85 - g \cdot c \cdot 45 - ^\circ C$$

$$4500.0 - J = 3825 - g^\circ C \cdot c$$

$$1.17 - \frac{J}{g^\circ C} = c$$

$$c = 1.2 - \frac{J}{g^\circ C}$$

$$Q = 4500.0 - J$$

$$m = 85.0 - g$$

$$c = x$$

$$\Delta T = 45.0 - ^\circ C$$

Calorimetry Example I (Partial)

- **5.75-g** of K_2CO_3 dissolves in 80.0-g of water. The temperature drops from 21.0-°C to 16.9-°C. Calculate ΔH° .
 - This shows H_2O 's ΔT , not K_2CO_3 so ignore its mass for now.
 - 1. Solve for the Q of the water first (system).

$$Q_{Water} = Cm\Delta T$$

$$Q_W = 80 - g \cdot 4.184 - \frac{J}{g^\circ C} \cdot -4.1 - ^\circ C$$

$$Q_W = -1372.35 - J$$

$$Q_W = \boxed{-1372.4 - J}$$

$$Q = ?$$

$$m = 80.0 - g$$

$$C = 4.184 - J/g^\circ C$$

$$\Delta T = 16.9 - 21.0 \dots$$

$$\Delta T = -4.1 - ^\circ C$$

This is the first part of the process.

Calorimetry From Partial to Full Solve

- Not fully discussed yet is that when a salt is added to water, it splits into ions:



- This causes the water to heat up or cool down (normally by a small amount).
- To solve for the ΔH° of any salt:
 1. Use $Q=Cm\Delta T$ to solve for the Q water (unit will be in J)
 2. The Q water will equal - the Q salt. /1000 to get kJ.
 3. Find out how many moles of salt you have.
 4. Set up a ratio and solve.

Calorimetry Example II

- 4.25-g of NH_4NO_3 dissolves in 20.0-g of water. The temperature drops from 20.3-°C to 8.0-°C. Calculate the ΔH° .

$$Q_{\text{Water}} = Cm\Delta T$$

$$Q_W = 20.0 \text{ g} \cdot 4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \cdot -12.3 \text{ }^\circ\text{C}$$

$$Q_W = -1029.264 \text{ J}$$

$$Q_{\text{Water}} = ?$$

$$m = 20.0\text{-g}$$

$$C = 4.184\text{-J/g}^\circ\text{C}$$

$$\Delta T = -12.3\text{-}^\circ\text{C}$$

The water temp went down so the reaction is Endothermic (ΔH is '+')

Calorimetry Example II

- If the water lost 1029.26-J it had to be from the NH_4NO_3 absorbing it.

2. Solve for the Q of the chemical (reaction).

Since ΔH is given in units of kJ now would also be a good time to convert. (divide by 1000)

$$Q_{\text{Water}} = -1029.264 - J$$

$$Q_{\text{Water}} + Q_{\text{Salt}} = 0 - J \quad (\text{Conservation of Energy})$$

$$Q_{\text{Salt}} = -Q_{\text{Water}}$$

$$Q_{\text{Salt}} = -(-1029.264 - J) \times \frac{k}{1000}$$

$$Q_{\text{Salt}} = 1.029264 - kJ$$

Calorimetry Example II

- $Q_{\text{Salt}} = 1.029\text{-kJ}$ is the heat absorbed due to 4.25-g of NH_4NO_3 . ΔH° assumes the chemical is equal to one mole.

3. Convert to moles.

4. Set up a ratio.

$$4.25 \text{ - g } \text{NH}_4\text{NO}_3 \times \frac{1 \text{ - mol}}{80.0 \text{ - g}} = .0531 \text{ - mol}$$

$$\Delta H^\circ = \frac{Q_{\text{Salt}}}{n_{\text{Salt}}}$$

$$\Delta H^\circ = \frac{1.029264 \text{ - kJ}}{.0531 \text{ - mol}} = 19.37$$

$$\Delta H^\circ = \boxed{19.4\text{-kJ/mol}}$$

Calorimetry Example III

- 56.0-g of H_3BO_3 dissolves in 50.0-g of water. The temperature rises from 15.0-°C to 33.4-°C. Calculate ΔH° .

$$Q_{\text{Water}} = Cm\Delta T$$

$$Q_W = 50 - g \cdot 4.184 - \frac{J}{g^\circ C} \cdot 18.4 - ^\circ C$$

$$Q_W = 3849.28 - J$$

$$Q = ?$$

$$m = 50.0 - g$$

$$C = 4.184 - J/g^\circ C$$

$$\Delta T = 18.4 - ^\circ C$$

The water temp went up so the reaction is Exothermic (ΔH is '-')

$$Q_{\text{Salt}} = -Q_{\text{Water}}$$

$$Q_{\text{Salt}} = -3.84928 - kJ$$

Calorimetry Example III

- $Q_{\text{salt}} = -3.849\text{-kJ}$ is the heat released due to 56.0-g of H_3BO_3 . We need to convert this to a per mole ratio for ΔH° .

$$n_{\text{salt}} = 56\text{-g H}_3\text{BO}_3 \times \frac{1\text{-mol}}{61.8\text{-g}} = .9061\text{-mol}$$

$$\Delta H^\circ = \frac{Q_{\text{salt}}}{n_{\text{salt}}}$$

$$\Delta H^\circ = \frac{-3.84928\text{-kJ}}{.9061\text{-mol}} = -4.24$$

$$\Delta H^\circ = \boxed{-4.2\text{-kJ/mol}}$$