Chapter 6 Thermochemistry

Thermochemistry can be quite involved. Following this outline will help you focus on specific topics that are appropriate for our course.

First you should know the unit of energy, the joule, J.

The SI unit of energy is the joule, J. It base units involve force and distance since energy can apply a force over a distance. Getting any more into this would be the start of a good physics class. For our purposes in chemistry energy is the ability to do work and is usually expressed in heat, either stored as chemical energy or released as thermal energy.

6.1 The Nature of Energy and the Types of Energy

Energy

Kinetic energy, the energy produced by a moving object
Thermal Energy is associated with the random motion of atoms and molecules

It is import to distinguish between thermal energy and temperature.
This is hard to express in terms of a definition but the example given expresses the difference very nicely.

A cup of coffee at 70°C has a higher temperature than a tub of warm water at 40°C.
A tub of water at 40°C has more thermal energy than a cup of coffee at 70°C.

Temperature is an intensive property that is independent of the amount of matter that has that temperature. A liter of hot coffee would have the same temperature as a milliliter of hot coffee.

Energy is an extensive property. A liter of hot coffee would have more energy than a milliliter of hot coffee.

Chemical energy is stored within the structural units of chemical substances. It is a form of potential energy

***H*, Enthalpy is the symbol for this stored chemical energy within a substance.**

Stored chemical energy is measured as joules per mole of substance or more commonly kilojoules/mole.

While changes in chemical energy, ΔH_{rx} , can be deduced, the total, absolute amount of energy in a substance, H ,cannot be determined.

Law of Conservation of Energy: **The total quantity of energy in the universe is constant.**

6.2 Energy Changes in Chemical Reactions

Thermochemistry is the study of heat change in chemical reactions.

It compares the stored Chemical Energy, ***H***, of the Products to the Reactants

Hydrogen and oxygen can combine to make water. When this happens kinetic energy is released. Burning hydrogen and oxygen releases a lot of energy.

$2H_2 + O_2 \rightarrow 2H_2O$ + kinetic energy EXOTHERMIC **Δ*H*$_{rx}$ *is negative***

Chemists always look at changes in energy as the change in the stored energy of the chemicals.

The compound of hydrogen and oxygen, water, must have less stored chemical energy, enthalpy, since some of the stored chemical energy was released in the form of kinetic energy, heat and light. The change in enthalpy for this reaction, C is a drop in stored energy, it is a negative value. The water produced has less stored chemical energy than the hydrogen and oxygen gas.

Exothermic Reactions

All reactions that release kinetic energy must be exothermic reactions with a Δ*H*$_{rx}$ that is negative. Stored chemical energy decreases since some of it is changed into kinetic energy.

Endothermic Reactions

All reactions that absorb kinetic energy (changing kinetic energy into stored chemical energy) must be endothermic reactions with a Δ*H*$_{rx}$ that is positive. Stored chemical energy increases.

If you convert water into hydrogen and oxygen, you must put kinetic energy into the reaction that will be stored as chemical energy H in the hydrogen and oxygen**. This reaction has a a Δ*H*$_{rx}$ that is positive,**

kinetic energy + $2H_gO \rightarrow 2H_2 + O_2$ ENDOTHERMIC **Δ*H*$_{rx}$ *is positive***

6.3 Introduction to Thermodynamics

Remember the Law of Conservation of Energy:

The total quantity of energy in the universe is constant.

So if one substance "loses energy" that energy does not disappear, it just goes somewhere else.

The energy lost from one substance must be gained by something else.

6.4 Enthalpy of Chemical reactions.

H **enthalpy** = Heat Content -a measure of internal (stored) energy.

H**, the total or absolute amount of Enthalpy of a substance cannot be determined**.
No one knows what hidden, uncharted stored energy may be lurking in a compound (chemical, nuclear, quark).

Only the, ΔH_{rx} the CHANGE in enthalpy of a reaction can be determined.

Enthalpy of Reactions

Enthalpy measurements are changes of stored energy.

The change will always be stored energy of products minus stored energy of reactants.

$$\Delta H_{rx} = H_{products} - H_{reactants}$$

The ΔH_{rx} can be determined experimentally but the absolute $H_{products}$ and $H_{reactants}$ are never known.

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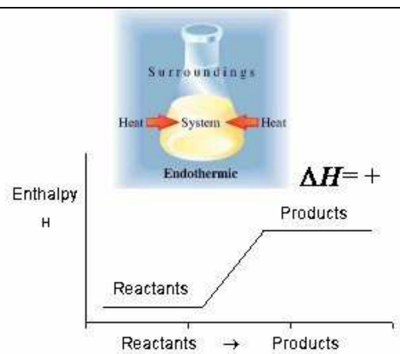
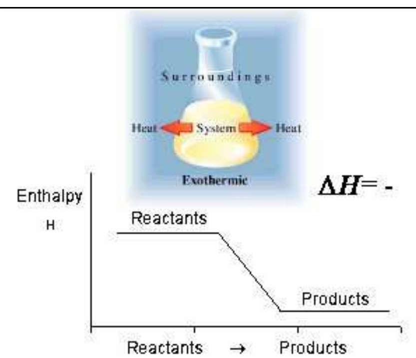
<tr><td>
</td><td>
</td></tr>
<tr><td>Energy in an endothermic reaction is stored in the substances as potential chemical energy.

Reactants + Heat → Products</td><td>Energy in an exothermic reaction raises the temperature of the surroundings

Reactants → Products + Heat</td></tr>
<tr><td colspan="2">While the difference of the Enthalpy of products and reactants can be measured, the absolute value of the H cannot be shown.</td></tr>
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Thermochemical Equations

In order to melt ice, you must add energy to break the bonds locking the water molecules in place.

$$6.01\text{ kJ} + H_2O(s) \rightarrow H_2O(l)$$

6.01 kJ are needed to melt 18.02 g of ice, 1.00 mole. Here is how the endothermic thermochemical equation should be written:

$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = +6.01\text{ kJ/mol}$$

Fusion (melting) absorbs energy as the crystal lattice is broken.
Fusion is always endothermic.

The opposite reaction, freezing ice requires that water's stored energy be released:

$$H_2O(l) \rightarrow H_2O(s) + 6.01\text{ kJ}$$

6.01 kJ must be released to freeze 18.02 g of water. Asa n exothermic thermochemical equation:

$$H_2O(l) \rightarrow H_2O(s) \qquad \Delta H = -6.01\text{ kJ/mol}$$

Freezing releases stored energy as the molecules hydrogen bonds snap together to form crystals.
Freezing is always exothermic.

6.5 Calorimetry

Calorimetry is a method of experimentally determining the heat changes.

Specific Heat

Specific Heat, *s*, is the amount of heat energy needed to change the temperature of 1 g of the substance 1°C

The units for specific heat capacity are: **J/g°C ← units are important!**

Specific heat of water = 4.18 J/g°C

Specific heat of gold = 0.129 **J/g°C**

Most Calorimetry experiments are performed in water.
You are expected to have memorized the specific heat of water:

4.18 J/g°C specific heat of water

Constant Pressure Calorimetry

q = the experimental energy change.
m = mass of substance being heated.
s = specific heat capacity

$q = m \times s \times \Delta T$

Every Calorimetry experiment will involve a temperature change.

$\Delta t = t_{final} - t_{initial}$ order and therefore the sign of the change are critical!

Every Calorimetry experiment will involve a substance changing temperature. Materials change temperature differently when absorbing heat energy.

Change temperature very little, a high heat capacity or specific heat

1.0 g of water will change temperature 2.4°C on absorbing 10. J.

Change temperature a lot, a low heat capacity or specific heat

1.0 g of gold will change temperature 78°C on absorbing 10. J.

If you wear gold jewelry you probably noticed that it changes temperature very easily.

IMPORTANT!
The change in heat of the chemicals in the reaction q_{rxn} will always be the opposite sign of the $q_{experiment}$. The reason for this is the stored energy lost by the reaction will equal the kinetic energy gained by the calorimeter.

$$q_{rxn} = - q_{experiment}$$

6.6Standard Enthalpy of Formation and Reaction

$\Delta H_f°$ Standard Enthalpy of Formation

The heat change when 1 mole of a compound is formed from its elements (at 1 atm & 25°)

I have put together two enthalpy of formation tables. One shows the complete reaction for all the formations. This is the beginner's chart. The second is just shows the product. Even though Enthalpy of formation table tables just show the product, it is very important to realize that the value is for a reaction .

The $\Delta H_f°$ is the enthalpy change for making the substance from its elements.

ALL ΔH values are for reactions! You have to have something happen to have a Δ!

$\Delta H_f°$ $H_2O(l)$ -286 kJ/mol really means $\Delta H_f°$ $H_2(g) + ½ O_2(g) \rightarrow H_2O(l)$ -286 kJ/mol

Two methods for finding the Δ*H of a reaction:*

The Direct Method

With a Standard Enthalpy of Formation Table you can directly find the ΔH_{rx} by summing the products and subtracting the sum of the reactants for this reaction.

$$\Delta H_{rx} = \sum \Delta H_{f\ \text{products}} - \sum \Delta H_{f\ \text{reactants}}$$

Working problems with a Standard Enthalpy of Formation Table is an simple exercise in math. Just be careful with the signs, coefficients and above all remember it is **products minus reactants!**

The Indirect Method

A series of equations for which the experimental change in enthalpy have been determined are given. You then must manipulate these equations to add up to a reaction that is difficult or impossible to determine experimentally. It is just like adding systems of equations in math.
Example 6.5 explains this process with all its possible complications perfectly.

Enthalpy Changes are often categorized

Heat of Solution (enthalpy change on dissolving a solute).
Heat of Vaporization (boling)
Heat of Fusion (melting)
Heat of Combustion (burning a substance in oxygen)