Unit 3, Lesson 02: Enthalpy Changes in Chemical Reactions

Chemical Potential Energy refers to the energy that is "stored" within an atom or molecule because of electrostatic attraction and repulsion between protons and electrons within and between atoms and molecules. There is also nuclear potential energy between the particles in the nucleus, which we will discuss later.

There are three forms of chemical potential energy in a substance:

1. Electrostatic attraction between electrons and nuclei within atoms:

- the further an electron is from the nucleus, the higher the electron's potential energy (remember Bohr and quantum levels?)

2. Inter-molecular forces of attraction between molecules:

- the more polar a molecule is, the stronger the inter-molecular attractions
- the state of a substance at SATP depends on the strength of inter-molecular attraction
- particles in a solid are very close together so they have low potential energy; the particles in a liquid are less tightly packed and orderly so they have higher potential energy; and the particles in the gas state are very far apart so they have very high potential energy

3. Intra-molecular forces of attraction (chemical bonds within molecules):

- the atoms within a molecule are attracted to one another by electrostatic attraction between the nuclei of one atom and the electrons of the another atom
- when two nuclei are simultaneously attracted to the same electrons, a chemical bond is created

Bond length: the distance between the nuclei of bonding atoms

- measured by X-ray crystallography, units are picometers (pm, 1.0×10^{-12}m)
- the closer the atoms are together, the shorter the bond length and the lower the potential energy
- recall, double bonds are shorter than single bonds, so double bonds have lower potential energy

Some bond lengths for different bonds (McGraw-Hill on page 599):

Bond	**Bond Length (pm)**
C-C	154
C=C	134
C≡C	121
C-O	143
C=O	123
C-H	109
N=N	122
N≡ N	110
O=O	121

Each bond represents a different amount of chemical potential energy, and this depends, in part, on how close together the bonded atoms are. Depending on the number and types of bonds in a molecule, each molecule has different amounts of chemical potential energy.

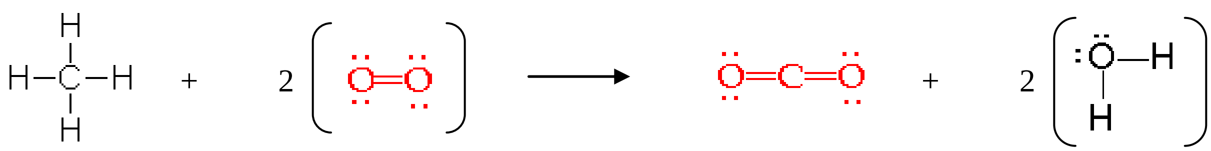
The total energy content (kinetic and potential) of a substance is called its "**enthalpy**" (symbol **H**).

- we can not measure the absolute enthalpy of a substance, we can only measure changes in enthalpy (ΔH) between the reactants and products of a reaction

During chemical reactions, as bonds are broken and new bonds are formed, the arrangement of the atoms changes:

- if the overall arrangement of the atoms in the products is more stable (for example, if bonds are shorter), then some of the chemical potential energy will be released. Reactions that give off energy are called "exothermic reactions"
- if the overall arrangement of the atoms in the products is less stable (for example, if bonds are longer), then the chemical potential energy will increase. These reactions will not occur unless energy is absorbed. Reactions that absorb energy are called "endothermic reactions"

eg.



4 (C – H) bonds = 4 x (109 pm) = 436 pm	4 (O = O) bonds = 2 x (121pm) = 242 pm	2 (C = O) bonds = 2 x (123 pm) = 246 pm	4 (O – H) bonds = 4 x (96pm) = 384 pm

Total distance between atoms = 678 pm

Total distance between atoms = 630 pm

In the example above, the atoms in the products are closer together, overall, than the atoms in the reactants. Also, because water is polar and can hydrogen bond, water molecules in the products are closer together than the non-polar reactant molecules. The chemical potential energy of the products is lower than the reactants. Energy will be released by this reaction as heat. This is the source of the heat that is produced when hydrocarbons burn. Cool, huh?

Summary:

Enthalpy (H) is the total energy content of a substance, which can not be measured.

The **change in enthalpy** (ΔH) is the difference in the enthalpy of the reactants and products of a particular reaction

- if the total enthalpy of the products is less than the total enthalpy of the reactants, then the reaction is exothermic and energy is released
- if the total enthalpy of the products is greater than the total enthalpy of the reactants, then the reaction is endothermic and energy will be absorbed

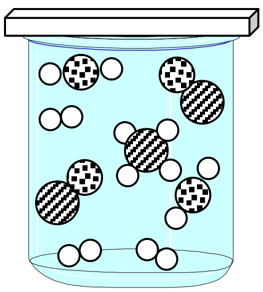
All of the reactants and products for a chemical reaction is called the “system”.

A **system** refers to all of the chemical components that are involved in a chemical reaction- the reactants, products and whatever solvents they are in (air, water etc).

Everything outside of the system we are studying is called the **surroundings**. In theory, the surroundings include the rest of the universe.

Chemists usually study “closed systems” which allow energy, but not matter, to be transferred between a system and its surroundings.

Example:



The **system** includes the reactant and product molecules in the beaker and the water in which the reaction takes place.

The **surroundings** include everything outside of the system: the beaker, its cover, the air outside, the surface it is sitting on and the rest of the Universe.

This is a **closed system** because the molecules (matter or mass) can not leave the system, but energy can be transferred from the system to the surroundings by heating or cooling the outside of the beaker.

This would be an **open system** if there was no cover on the beaker, because then molecules (matter or mass) could escape into the surroundings.

If a reaction takes place inside a well-insulated container such as a calorimeter, then it is an **isolated system** because neither energy nor mass can enter or leave the calorimeter. In this situation, the calorimeter and its contents can be considered to be the surroundings because they are insulated and isolated from the rest of the universe. Within the calorimeter, energy can be transferred between a chemical reaction and the contents of the calorimeter (the surroundings), but no energy should be lost outside of the calorimeter.

Using a calorimeter to isolate the system and surroundings from the rest of the universe allows us to measure the energy that is transferred between a chemical reaction and the contents of the calorimeter. The change in energy (enthalpy) of the reaction will be transferred to, or from, the contents of the calorimeter as heat (Q). By measuring the temperature change of the contents of the calorimeter (in high school it is usually water), then the amount of energy transferred as heat can be calculated using the equation : $Q = mc\Delta T$ (see detailed notes on calorimetry in the next lesson). The amount of heat gained or lost by the contents of the calorimeter will equal the amount of enthalpy lost or gained by the chemical reaction, so Q and ΔH are equal but opposite in sign. That is,

- if the contents of the calorimeter increase in temperature (Q is positive), then the reaction must have released this energy by going to a more stable, lower enthalpy state, making ΔH negative
- if the contents of the calorimeter decrease in temperature (Q is negative), then the reaction must have absorbed this energy as it went to a less stable, higher enthalpy state, making ΔH positive

FINAL NOTE: Defining the system and surroundings can be very confusing. Chemists set up their experiments and define the system to suit the reaction they are studying. In this course, we will usually be studying physical and chemical reactions that take place in aqueous (water) solutions within a calorimeter. For simplicity, in this course, we will consider the ***system*** to be the physical or chemical reaction that we are studying and the ***surroundings*** to be whatever changes temperature; usually it will be the water in the calorimeter in which the reactions take place.

Key Points:

- Energy can not be created nor destroyed, but it can change form and be transferred between objects
- Energy is either kinetic (due to an object's motion) or potential (due to an object's position and attraction to other objects)

The total kinetic energy (amount of motion) of the particles in a substance is called "**thermal energy**"

- thermal energy depends on how many particles there are (the mass or number of moles) and temperature (average kinetic energy) of the particles
- the transfer of thermal energy between particles is called "**heat**" (symbol is Q, units are J or kJ).
- thermal energy always travels from objects with higher temperature to objects with lower temperature

The total potential and kinetic energy of a substance is called "**enthalpy**" (H)

- one of the major determinants of enthalpy is the number and nature of the bonds in a substance
- 'longer,' less stable bonds have higher potential energy while 'shorter,' more stable bonds have lower potential energy
- when bonds break and form during a chemical reaction, the enthalpy of the system changes; this can be measured as the enthalpy change of the reaction or ΔH_{rxn} (units are kJ/mol)
- energy changes during a chemical reaction are due to the difference in enthalpy (ΔH) between the reactants and products in a system

$$\underbrace{\Delta H_{rxn}}_{\text{the change in enthalpy for the reaction (the change in total energy) of the molecules in the system}} = \underbrace{\Sigma H \text{ of the products}}_{\text{the sum of the enthalpy (total energy) of the molecules of the products}} - \underbrace{\Sigma H \text{ of the reactants}}_{\text{the sum of the enthalpy (total energy) of the molecules of the reactants}}$$

ΔH_{rxn} is often written simply ΔH, unless there is a reason to specify what energy change is being discussed. ΔH is also often referred to as the "heat of reaction". If ΔH is written as ΔH^o, the ^{o} (nought) means that ΔH was measured under standard conditions, such as SATP.

There are two possibilities:

1. ΣH of the products is less than ΣH of the reactants:

- ΔH will be negative
- the products have less total energy than the reactants
- the reaction is exothermic because energy will be given off

2. ΣH of the products is greater than ΣH of the reactants:

- ΔH will be positive
- the products will have more total energy than the reactants
- the reaction is endothermic because energy will be absorbed

Let's look at each situation in more detail:

Case 1: **the total enthalpy of the products is less than the total enthalpy of the reactants**

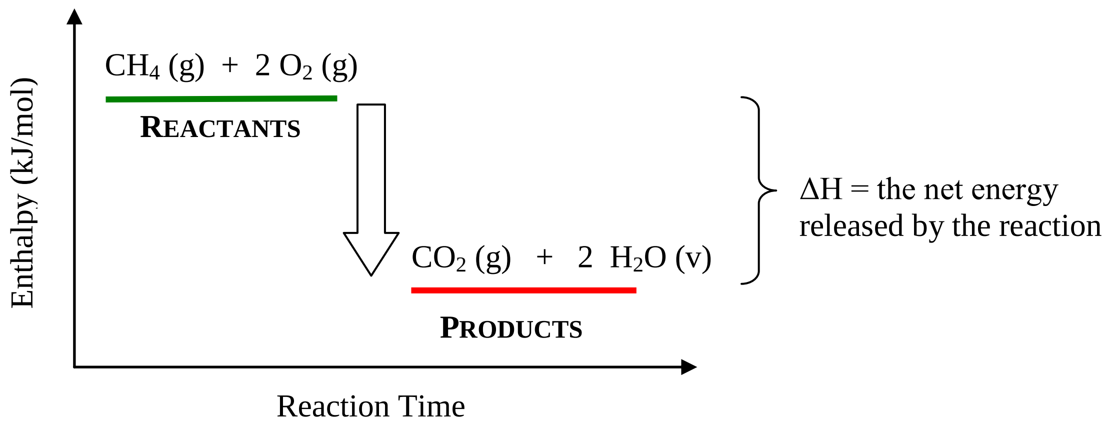
- the total energy of the products is lower than the total energy of the reactants
- chemical potential energy is converted **TO** kinetic thermal energy, so the molecules in the system move faster and the temperature of the system increases
- the system is now warmer than the surroundings, so heat will flow out from the system to the surroundings
- the reaction is **exothermic**: it gives off heat
- from the equation: $\Delta H = \sum H$ of the products $-$ $\sum H$ of the reactants

  $\sum H$ of the products is less than $\sum H$ of the reactants, so ΔH is negative

For example: CH_4 (g) + 2 O_2 (g) → CO_2 (g) + 2 H_2O (v) + heat

We can represent the energy change that accompanies this chemical reaction three different ways:

1. As a potential energy (enthalpy) diagram:



2. As a **thermochemical equation** that shows the amount of potential energy released as a ***product*** of the reaction (because heat is given off) per mole of reactant

   eg. CH_4 (g) + 2 O_2 (g) ⟶ CO_2 (g) + 2 H_2O (v) + 982 kJ

3. As a balanced chemical equation that is followed by a **separate energy term**

   eg. CH_4 (g) + 2 O_2 (g) ⟶ CO_2 (g) + 2 H_2O (v) $\Delta H = -$ 982 kJ

(Because energy is released by an exothermic reaction, it is shown on the product side of the thermochemical equation. If written as a separate energy term, the negative value of ΔH indicates an exothermic reaction.)

Case 2: **the total enthalpy of the products is greater than the total enthalpy of the reactants**

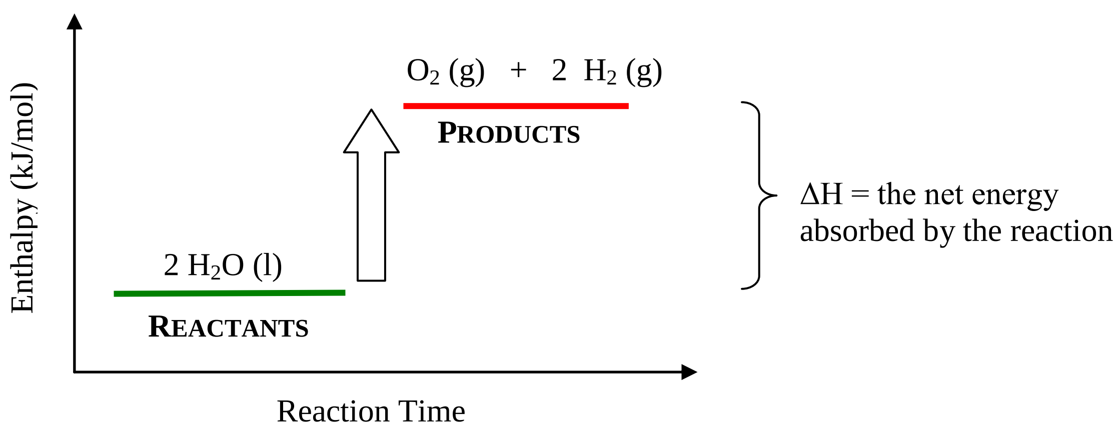
- the total energy of the products is higher than the total energy of the reactants
- chemical potential energy is converted **FROM** kinetic thermal energy, so the molecules in the system move slower and the temperature of the system decreases
- the system is now cooler than the surroundings, so heat will flow into the system from the surroundings
- the reaction is **endothermic**: it absorbs heat
- from the equation: $\Delta H = \sum H$ of the products $-$ $\sum H$ of the reactants

$\sum H$ of the products is greater than $\sum H$ of the reactants, so ΔH is positive

For example: $2\ H_2O\ (l)\ +\ \text{heat (energy*)}\ \rightarrow\ O_2\ (g)\ +\ 2\ H_2\ (g)$

We can represent the energy change that accompanies this chemical reaction three different ways:

1. As a potential energy (enthalpy) diagram:



2. As a **thermochemical equation** that shows the amount of potential energy absorbed as a ***reactant*** of the reaction (because heat is absorbed)

eg. $2\ H_2O\ (l)\ +\ 571\ kJ\ \longrightarrow\ O_2\ (g)\ +\ 2\ H_2\ (g)$

3. As a balanced chemical equation that is followed by a **separate energy term**

eg. $2\ H_2O\ (l)\ \longrightarrow\ O_2\ (g)\ +\ 2\ H_2\ (g)$ $\qquad \Delta H = +\ 571\ kJ$

(Because energy is absorbed by an endothermic reaction, it is shown on the reactant side of the thermochemical equation. If written as a separate energy term, the positive value of ΔH indicates an endothermic reaction.)

* the needed energy could also be supplied by an electric current

Activity: Energy Changes During Chemical Reactions

Consider the following situations and then answer the questions below. Consider the physical or chemical reaction to be the ***system*** and the water in which the reaction takes place to be the ***surroundings***.

A About 20 mL of water is placed in a small beaker. Ten (10) pellets of solid sodium hydroxide are added and swirled to dissolve. The temperature of the water in the beaker increases.

$$\mathbf{NaOH\ (s) \rightarrow NaOH\ (aq)}$$

B About 20 mL of water is placed in a small beaker. A scoopful of solid ammonium chloride is added and swirled to dissolve. The temperature of the water in the beaker decreases.

$$\mathbf{NH_4Cl\ (s) \rightarrow NH_4Cl\ (aq)}$$

C About 20 mL of 3.0 M hydrochloric acid are placed in a small beaker. A scoopful of solid calcium oxide is added and swirled to dissolve. The temperature of the mixture increases.

$$\mathbf{CaO\ (s) + 2\ HCl\ (aq) \rightarrow CaCl_2\ (aq) + H_2O\ (l)}$$

D A scoopful of solid ammonium thiocyanate is put in a test tube. Two scoopfuls of solid barium hydroxide are added. The test tube is sealed with a rubber stopper and shaken vigorously. The solids mix and an icy cold liquid forms.

$$\mathbf{2\ NH_4SCN\ (s) + Ba(OH)_2\ (s) \rightarrow 2\ NH_3\ (g) + 2\ H_2O\ (l) + Ba(SCN)_2\ (s)}$$

For each of the reactions, answer the following questions:

1. Is the reaction endothermic or exothermic? How did you know?
2. Is the enthalpy (total) energy of the ***system*** increasing or decreasing?
3. Is thermal energy (heat) flowing into or out of the ***system***?
4. Describe what is happening to the kinetic energy of the ***surroundings***.
5. Re-write the above equations and add the term "heat" to the correct side of the equation to show that heat is either produced or absorbed by the reaction.
6. Is ΔH positive or negative for each reaction? Explain.
7. Draw an enthalpy level diagram for each reaction.

Homework:
1. Read pages 222 – 225 in McGraw-Hill
2. Answer questions 1-4 on page 226
3. Complete the answers to the lab