Thermodynamics

What is energy? If you're like most students, you probably have an idea of what energy is but might find it hard to actually define it.

Energy is defined as the ability to do work or produce heat. You likely know that energy can come in many forms - light energy, nuclear energy, and electrical energy to give just a few examples. In chemistry, heat energy is often what we are interested in, and the second part of the definition for energy will have more meaning for us. We will often discuss energy in terms of heat.

So, what exactly is **heat**, or thermal energy? This is something else that we "know it when we see it" but find it difficult to define.

In previous science classes you've most likely learned that the individual atoms and molecules that make up all substances are in constant motion. This energy of motion is called **kinetic energy**. The energy associated with this motion is heat, or thermal energy.

How does the temperature of two objects change when brought into contact?

Link 2

Select two metals and adjust the starting temperatures of one or both. What happens to the temperature of the two samples as they are brought together? How do the temperatures of the two objects compare at the end?

Source: Source: Ted Greenbowe, Chemical Education Research Group Iowa State University (http://www.chem.iastate.edu/)

What happens to molecular motion as temperature is increased? Link 1 Follow this link to see how temperature and molecular motion are related. The molecular motion within sample of metal is shown. The initial temperature is set at 50°C. Use the slider control to increase the temperature -

Heat can also be defined as the *flow* of energy. This energy transfer is always from the hotter substance to the colder object. For example, If you hold an ice cube in your hand, your hand feels colder. Your hand feels colder because it is giving heat (or losing heat) to the ice cube; the ice cube does not transfer "coldness" to your hand. This is an important point, so keep it in mind.

In addition to kinetic energy there is another basic form of energy - **potential energy**. Potential energy is **energy of position**; we often refer to it as **stored energy**.

Kinetic Energy

Energy of motion.

A rock rolling down a hill has kinetic energy.

Atoms and molecules have kinetic energy as they are always in motion (click **here** for more information).

Potential Energy

Stored energy.

A rock sitting on top of the hill has stored energy.

Many of the different forms of energy that you may think of, such as **light energy**, **electrical energy**, and **thermal energy** are specific types of kinetic energy.

What about potential energy - can you think of an example? We will be concerned about one type of potential energy in this unit - **chemical bond energy**. Chemical bond energy arises from the attractive forces between molecules, and between atoms. This form of energy plays an important role in chemical reactions.

Nuclear energy is another form of potential energy, and is the energy stored within an atom as the forces holding the parts of an atom together. Chemical reactions do not involve nuclear changes or energy, and we won't be examining it further in this unit.

1.2 The Law of Conservation of Energy

One of the key principles of chemistry is the Law of Conservation of Energy:

Law of Conservation of Energy

During physical and chemical processes, energy may change from one form to another but it may not be created or destroyed.

Also known as the First Law of Thermodynamics

To give a few examples of how energy is converted from one form to another:

- When octane (C₃H₈, the main component of gasoline) is burned in your car engine, chemical bond energy (potential energy) is converted into mechanical energy (pistons moving in the car engine; kinetic energy) and heat.
- When we eat, our bodies convert the chemical energy of the food into movement of our muscles; again heat is also a product of this conversion.
- When we turn on a light switch, electrical energy is converted into light energy and, you guessed it, heat energy.

1.3 Heat Energy & Temperature

It is important to understand the difference between heat and temperature.

Heat, as we saw in Section 1-1, is the amount of kinetic energy in a sample of matter. It flows in the direction from the warmer object to the colder object.

The SI unit of energy, including heat energy, is the **joule** (\mathbf{J}) , and is formally defined as the amount of energy produced when a force of one newton acts over a distance of one meter. How much energy is one joule?

- One joule is the amount of energy used by a 100 W light bulb in 0.01 s.
- One joule is approximately equal to the amount of energy you expend when you bring a cheeseburger to your mouth.
- An ordinary paper match, burned completely, releases a little over 1,000 J.

1.3a The Calorie - Another Unit of Energy

One calorie is defined as the amount of heat required to raise the temperature of one gram of water by one degree Celsius (1°C).

A dietary calorie, written with a big C (Calorie, not calorie) is actually a kilocalorie, or 1000 calories.

To convert between joules and calories, use the following conversion factors:

1 J = 0.2390 cal

1 cal = 4.184 J

Temperature is measured in degrees **celsius** (°C) or in **kelvin** (K). Kelvin is the SI temperature scale. You may already know that at the temperature known as **absolute zero** (0 K), particle motion is as slow as it can possibly be. That's as cold as you can theoretically get!

To convert between celsius and kelvin:

°C = K - 273

 $K = {}^{\circ}C + 273$

, - K 2/3

Convert 25°C into Kelvin.

K = 25°C + 273 = **298 K**

(the degree symbol is not used with K)

Convert 500 K into degrees celsius

°C = 500 K - 273 = 227°C

For example:

Movie Link

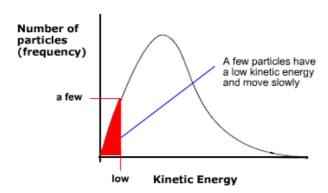
This link describes the molecular events that occur during changes of state.

1.4 Kinetic Energy Curves

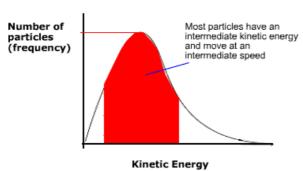
Consider a beaker of water sitting on a counter. The individual water molecules in the beaker are in constant motion. But - and this is the important point - the water molecules are not all moving at the same speed because they do not all have the same amount of kinetic energy. Some water molecules are sluggish and move slowly (they have a low kinetic energy). Some are very energetic (they have a high kinetic energy) and moving very fast. Most, however, are moving at some intermediate speed (or intermediate kinetic energy).

How could we best graph this variation in kinetic energy of particles? What would a graph of this look like?

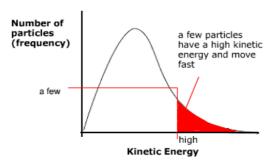
Kinetic Energy Curve



Kinetic Energy Curve



Kinetic Energy Curve



You may recognize the general shape as a basic bell curve (also called a normal curve.) As it applies to the kinetic energy distribution of a sample of matter, it is called a Boltzmann distribution, but we'll refer to it as a Kinetic Energy Curve. Learn this graph well - we'll see it again.

Something to think about . . .

Which has more heat energy - an iceberg or a cup of boiling water?

1.5 Endothermic & Exothermic Reactions

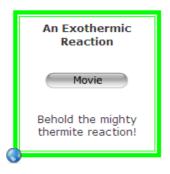
All chemical reactions (and physical changes and nuclear changes as well) involve energy changes.

Exothermic reactions are reactions in which there is a net **release** of energy. When energy is released, an energy term will appear on the **product side** of the equation.

The thermite reaction is a highly exothermic reaction between ferric oxide and aluminum, producing aluminum oxide and molten iron:

$$\text{Fe}_2\text{O}_3 \text{ (s)} + 2\text{Al}_{(\text{S})} \rightarrow \text{Al}_2\text{O}_{3(\text{S})} + 2\text{Fe}_{(\text{I})} + 847.6 \text{ kJ}$$

If you had this reaction occurring in your hand (don't try this at home!!!) your hand would feel warmer because the reaction is releasing heat.



Endothermic reactions are reactions that require a net **input** of energy. This is indicated by writing the energy term on the **reactant side** of the equation.

Consider the reaction when sulfur trioxide decomposes into sulfur trioxide and oxygen. This reaction requires a net input of 198 kJ of energy in order to occur:

$$2~\mathrm{SO_3(g)} + 198~\mathrm{kJ} \rightarrow 2~\mathrm{SO_2(g)} + \mathrm{O_2(g)}$$

If you held this reaction in your hand, your hand would feel colder because the energy required for the reaction to occur would be taken from the surroundings, in this case your hand.

Want another movie?

- Formation of aluminum bromide, an exothermic reaction.
 - ex) 1) sweat evaporating from skin?
 - 2) water freezing in freezer?
 - 3) wood burning in a fire?

1.6 Heat & Its Measurement: Calorimetry

All chemical reactions involve energy changes, often in the form of heat. How can you measure the amount of heat exchanged during a reaction?

An instrument called a **calorimeter** is used. A **very** simple calorimeter that may be used is shown here. We will use a calorimeter like this one in order to measure the amount of heat exchanged during several simple processes.

In our lab we will dissolve some salts in water. If the reaction is an **exothermic reaction**, energy is given off, or **released**, causing the temperature of the water in the calorimeter to rise.

If, however, the reaction is **endothermic**, energy will be **required** for the reaction to occur. This energy will be removed from the water, causing the water temperature to drop.

Specific Heats of various substances at 298 K (25°C)	
Substance	Specific Heat J/(g∙°C)
water (liquid)	4.184
water (solid)	2.03
water (steam)	2.01
ethanol (I)	2.44
aluminum (s)	0.897
granite (s)	0.803
iron (s)	0.449
lead (s)	0.129
silver (s)	0.235

The Calculations

Once we know the mass of water used, the temperature change, and the specific heat of water, the amount of heat transferred by the chemical reaction can now be calculated using the following formula:

where

Q = amount of heat transferred, in kJ m = mass of the sample in grams ΔT= change in temperature, in °C

Note - by convention, we indicate an *increase* in temperature as a *positive* change and we indicate a *decrease* in temperature as a *negative* change. So, if the temperature started at 50°C and ended at 40°C, then ΔT will have a value of -10°C.

Example 1

2,000.0 g of water in calorimeter has its temperature raised 3.0°C by an exothermic chemical reaction. How much heat was transferred?

Example 2

A 1000.0-g mass of water whose temp was 50° C lost 33,600 J of heat over a 5-min period. What was the temperature of the water at the end of the 5-min period?

1.7 Chemical Bond Energy

As we have seen, whenever a chemical reaction occurs, there is always a change in energy. Where does this energy come from?

In any chemical substance, energy is stored in the chemical bonds that hold atoms together to form molecules (intramolecular bonds), and in the bonds that hold individual molecules together in the solid and liquid state (intermolecular bonds). During a chemical change, these bonds are rearranged - some bonds are broken, other bonds are formed.

Energy is required to break chemical bonds

Energy is released when new bonds form

Almost all chemical reactions involve changes in which some bonds are both broken and formed. Thus, some energy will be needed to break bonds, but energy will also be released as new bonds form. When we write a chemical equation that includes the energy change, the equation shows the **net difference** in energy change.

During exothermic reactions there is a net **release** of energy. More energy is given off than is put into the reaction.

For example, consider what happens at a molecular level when hydrogen and fluorine gas combine to produce hydrogen fluoride:

Energy is required to break the bonds of the reacting molecules

Energy is released when bonds form on the product side

H-H + F-F \rightarrow

2 H-F

As atoms rearrange, both H—H and F—F bonds must be broken while H—F bonds must form. In this particular reaction, more energy is released when HF bonds form than is needed to break the other bonds. For this particular reaction, the net difference is a release of 546 kJ of energy so the energy term (546 kJ) appears on the product side of the equation:

$$H_2(g) + F_2(g) \rightarrow 2 HF(g) + 546 kJ$$

Endothermic reactions require a net **input** of energy. More energy is needed to break bonds than is given off when new bonds form.

For example consider the when sulfur trioxide decomposes into sulfur trioxide and oxygen. Energy is needed to break apart the SO_3 molecule, but is released when the bonds within SO_2 and O_2 are formed. In this case, more energy is needed to break bonds than is released. The energy term (198 kJ) is written on the reactant side of the equation.

$$2 SO_3(g) + 198 kJ \rightarrow 2 SO_2(g) + O_2(g)$$

To help you understand the concept of **net energy change** consider this analogy:

Say you have a lemonade stand.

On Day 1, you had to spend \$8.00 to buy your supplies - lemonade, sugar, cups. At the end of the day you had \$10.00. What is your profit, or **net difference** for the day? You had a profit of \$2.00. This would be like an **exothermic reaction** - there is more money at the end of the day than was initially put in.

On Day 2, the supplies cost \$15.00, but you only sold \$10.00 worth of lemonade. Not such a good day - a net loss of \$5.00. This is like an **endothermic reaction** - more was put in then was gained at the end.



2.1 Heat Content - Enthalpy

Let's put a name to the branch of chemistry we have been studying-Thermodynamics.

Thermodynamics is the study of energy changes during chemical reactions, and the influence of temperature on those changes.

Here's another important term — Enthalpy

Enthalpy is the **heat content** of a system, or the **amount** of energy within a substance, both kinetic and potential.

ENTHALPY

"heat content" of a system

Symbol for enthalpy: H

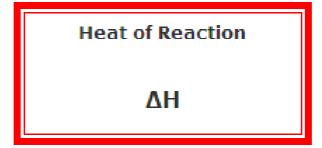
Unit for enthalpy: the joule, J

For chemical reactions it is more practical to record enthalpy in kJ.

Every substance possesses both stored energy, due to the nature of the chemical (and nuclear) bonds holding the substance together, and kinetic energy which arises from to the constant motion of the particles. This total amount of energy is **enthalpy**.

However, it is not possible to actually measure the heat content of a substance that is just "sitting there" - chemists can only measure how much enthalpy **changes** during a reaction. We use the symbol delta (Δ) to refer to represent change. Therefore, we will generally always refer to the **change in enthalpy, or \Delta H**.

We also refer to the change in enthalpy as the **Heat of Reaction**. The energy term you see as part of a chemical reaction is this "heat of reaction", or enthalpy change.



Exothermic Reactions

During exothermic reactions, more energy is released during bond formation than is required to break bonds. A typically exothermic reaction would be written like this:

$$Cu(s) + Cl_2(g) \rightarrow CuCl_2(g) + 220.1 \text{ kJ}$$

In this reaction, there is a net release of 220.1 kJ of energy, and the energy term (220.1 kJ) appears on the product side of the equation.

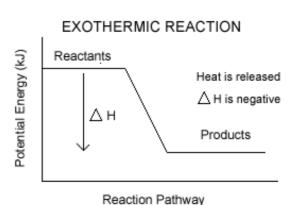
Exothermic reactions release energy because the heat content of the reactants is greater than that of the products. We will think of this difference in terms of potential energy - in exothermic reactions, the reactants have more potential energy than the products. The "excess" energy is released to the surroundings during the reaction.

We can show this graphically as well. These graphs will be very important to you, so be sure you understand them well.

The graph illustrates that the amount of potential energy stored in the products is less than that stored in the reactants; potential energy decreased during the reaction.

Think of this graph as a boulder rolling downhill - as it does, potential energy (the energy stored while the boulder is on top of the hill) is converted to kinetic energy (the rolling rock) which can do work (roll over and crush a house at the bottom of the hill).

A potential energy graph of an exothermic reaction:



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We typically indicate that something has decreased by using a negative sign. For example, if the temperature drops 10°C, we would indicate that as a change of -10°C. An increase of 5°C would be recorded as a change of +5°C.

We do the same with enthalpy changes. When the amount of entropy in a system decreases a negative sign to indicate the drop. Thus, we could rewrite the equation shown above as:

$$Cu(s) + Cl_2(g) \rightarrow CuCl_2(g)$$

$$\Delta H^{\circ} = -220.1 \text{ kJ}$$

With our new terminology, we say that the heat of this reaction was -220.1 kJ. During the formation of 1 mole of $CuCl_2(g)$ from 1 mole of Cu(s) and 1 mole of $Cl_2(g)$, 220.1 kJ of energy was released (given off to the surroundings).

Endothermic Reactions

During endothermic reactions, energy is absorbed from the surroundings. A typical endothermic reaction is written with the energy term on the reactant side of the equation:

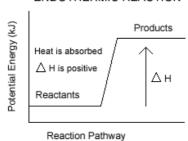
$$H_2O(g) + C(s) + 132 \text{ kJ} \rightarrow CO_2(g) + 2H_{2(g)}$$

A net input of energy is required to make this reaction occur. The potential energy of the reactants is *lower* than the potential energy of the products; energy must be supplied to the reaction in order for it to occur.

Think of this as the boulder being pushed up the hill. It takes energy to roll a boulder up a hill.

A potential energy graph of an endothermic reaction

ENDOTHERMIC REACTION



As with the exothermic reaction, we can remove the energy term from the equation and record the enthalpy change with a positive value, indicating that enthalpy increased during the reaction:

$$H_2O(g) + C(s) \rightarrow CO_2(g) + 2H_{2(g)}$$

$$\Delta H^{\circ} = +132 \text{ kJ}$$



2.2 Heat of Formation

Turn now to a special type of chemical reaction, one in which we **form one mole of a compound from its elements**. We are interested in how much energy is either absorbed or released during this synthesis reaction.

For example, the formation reaction for liquid water is described by the following equation:

$$H_{2\,(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow H_{2}O_{(I)} + 285.8 \text{ kJ}$$

Key items to note regarding this definition:

- one mole of the compound is formed
- from its elements

Standard Heat of Formation

ΔH°_f

the amount of energy gained or lost when 1 mole of the substance is formed from its elements under standard conditions (25°C, 1 atm = 101.3 kPa) Important
Data Table

Heats of Formation

Pick a format:

Word | RTF | PDF

You will find the standard heats of formation listed for a variety of compounds in the **Table of Thermochemical Data**. Print a copy of this table and keep it handy.

The heat of formation for pure elements, such as $H_2(g)$, $O_2(g)$, Al(s), etc. is 0 kJ·mole⁻¹. You'll find it useful to remember this.

Reference Chart Table of Common Ions Word | RTF | PDF

Writing heat of formation reactions is an important skill. Keep the following points in mind:

- Balance the equation so that one mole of the compound is produced.
- Remember the diatomic molecules and write them correctly (H₂, N₂, O₂, F₂, Cl₂, Br₂, I₂).
 ■ The reactants must be **elements**, **not polyatomic ions**.

Examples of polyatomic ions are hydroxide, OH, carbonate, CO32-, and ammonium, NH4+.

Return for a moment to our earlier reaction:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) + 285.$$

If 285.8 kJ of energy are released during the formation of one mole of $H_2O(I)$ (as is shown in the balanced equation), how much energy do you imagine would be released if two moles of water were produced?

Our new equation looks like this:

$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(I) + 571.6 \text{ kJ}$$

Since the equation does not form **one** mole of the compound, it is not a strict heat of formation reaction. **Be careful!** Watch this.

Write heats of formation reactions for each of the following compounds. Be sure to include the energy term with the
equation, either as part of the equation or separately as Δ H. You will need to refer to a Table of Thermochemical
Data.



The standard heat of formation, ΔH°_f, for sulfur dioxide (SO₂) is -297 kJ/mol. How many kJ of energy are given off when 25.0 g of SO_{2 (e)} is produced from its elements?





2.3 The Direction of Chemical Change

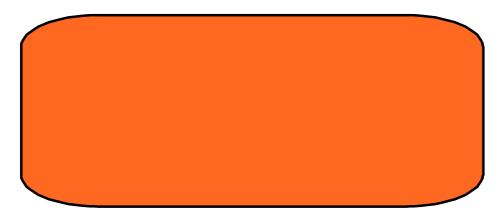
What determines whether a reaction will actually occur spontaneously or not? In chemistry, a "spontaneous" reaction is a reaction that will occur on its own - it may be fast or it may be slow.

Here are some examples of spontaneous chemical reactions:

$$Na(s) + \frac{1}{2}CI_{2}(g) \rightarrow NaCI(s) + 411.2 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) + 242 \text{ kJ}$$

$$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l) + 1461.9 \text{ kJ}$$

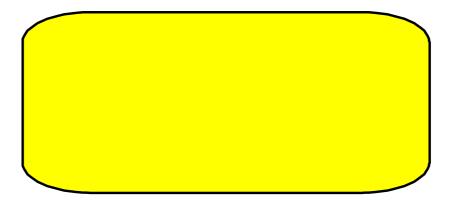


Exothermic reactions tend to be spontaneous

But of course some endothermic reactions that are also spontaneous:

$$Br_2(I) + Cl_2(g) + 29.3 \text{ kJ} \rightarrow 2 \text{ BrCl}(g)$$

$$H_2(s) + \frac{1}{2}O_2 + 6.01 \text{ kJ} \rightarrow H_2O(l)$$





2.4 Hess's Law

Many chemical reactions occur in a series of steps rather than a single step.

For example, the following reaction describes the burning (combustion) of carbon:

(1)
$$C(s) + O_2(g) \rightarrow CO_2(g)$$
 $\Delta H = -393.5 \text{ kJ}$

If not enough oxygen is present, CO rather than ${\rm CO_2}$ is produced:

(2) C (s) + ½
$$O_2(g) \rightarrow CO(g)$$
 $\Delta H = -110.0 \text{ kJ}$

If more oxygen is now added, CO will undergo further combustion with oxygen:

(3) CO (g) +
$$\frac{1}{2}$$
 O₂(g) \rightarrow CO₂ (g) Δ H = -283.0 kJ

Watch what happens if we add together the second and third reaction:

(2) C (s) +
$$\frac{1}{2}$$
 O₂(g) \rightarrow CO (g)

Be sure you see how these equations can be added together

Add things that are on the same side of the equation:

and cross things out on opposite side of the equation (the ${\rm CO}$)

Sometimes you will be left with a "remainder" - things won't cancel completely



Now compare the total energy released in the second and third reactions with the amount of energy released in the original reaction:

$$\Delta H_{Reaction 2}$$
 + $\Delta H_{Reaction 3}$ = $\Delta H_{Reaction 1}$
-110.5 kJ + (-283.0 kJ) = -393.5 kJ
-393.5 kJ = -393.5 kJ

The end result is that it doesn't matter if the reaction proceeds all at once or in series of steps; the net energy change is the same. This illustrates Hess's Law of Constant Heat Summation:

Hess's Law

The enthalpy change for any reaction depends only on the energy states of the final products and initial reactants and is independent of the pathway or the number of steps between the reactant and product. **Example:** Given the intermediate steps in the production of tetraphosphorus decaoxide, P_4O_{10} , calculate ΔH_f for P_4O_{10}

Recall the the heat of formation reaction involves the production of **one mole** of the compound **from it's elements**. Thus, we want to calculate ΔH for:

Given the following reactions:

(2)
$$P_4O_6 + 2 O_2 \rightarrow P_4O_{10} \Delta H = -1344 \text{ kJ}$$

Some Important Things to Know:

 If you reverse an equation, be sure to move the energy term to the other side of the equation as well. If you write the enthalpy term separately from the equation as ΔH, be sure to reverse the sign of ΔH

(1)
$$4 P + 3 O_2 \rightarrow P_4 O_6$$
 $\Delta H = -1840 kJ$

Reversed becomes:

$$P_4O_6 \rightarrow 4 P + 3 O_2 \quad \Delta H = +1640 \text{ kJ}$$

OR

$$P_4O_6 + 1640 \text{ kJ} \rightarrow 4 \text{ P} + 3 O_2$$

 If you change the balancing coefficients within an equation, be sure to adjust the value of the energy term.

For example, if 1640 kJ of energy are released when 1 mole of P₄O₆ is formed from its elements:

then producing 2 moles of P4O6 will release 3280 kJ of energy (2 \times 1640 kJ):

Tips for for Using Hess's Law:

- lacktriangle Consider the intermediate steps involved in a reaction and ΔH values for each.
- $\,\blacksquare\,$ Reverse intermediate reactions and change the sign of ΔH if necessary.
- Multiply intermediate reactions as necessary to balance the overall equation and multiply ΔH values of the steps as required
- Determine the final ΔH from the algebraic sum of ΔH values for the intermediate reactions.





Another Example:

You are given the following two reactions (Reactions 1 and 2):

(1) $C_2H_2(g) + 5/2 O_2(g) \rightarrow 2 CO_2(g) + H_2O(I)$

 $\Delta H = -1299 \text{ kJ}$

(2) $C_6H_6(I) + 15/2 O_2(g) \rightarrow 6 CO_2(g) + 3 H_2O(I)$

 $\Delta H = -3287 \text{ kJ}$

Find ΔH for the following reaction (Reaction 3) and tell whether it is exothermic or endothermic:

(3) $3 C_2H_2(g) \rightarrow C_6H_6(g)$

More Practice





1. Calculate the standard enthalpy change, ΔH° , for the formation of 1 mol of strontium carbonate (the material that gives the red color in fireworks) from its elements.

$$Sr(s) + C(graphite) + \frac{3}{2}O_2(g) \rightarrow SrCO_3(s)$$

The informatio n available is

(1)
$$Sr(s) + \frac{1}{2}O_2(g) \rightarrow SrO(s)$$
 $\Delta H^{\circ} = -592 \text{ kJ}$

(2)
$$SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$$
 $\Delta H^{\circ} = -234 \text{ kJ}$

(3) C(graphite) +
$$O_2(g) \rightarrow CO_2(g)$$
 $\Delta H^{\circ} = -394 \text{ kJ}$

2. The combination of coke and steam produces a mixture called coal gas, which can be used as a fuel or as a starting material for other reactions. If we assume coke can be represented by graphite, the equation for the production of coal gas is

$$2 C(s) + 2 H_2O(g) \rightarrow CH_4(g) + CO_2(g)$$

Determine the standard enthalpy change for this reaction from the following standard enthalpies of reaction:

(1)
$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$
 $\Delta H^{\circ} = 131.3 \text{ kJ}$

(2)
$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$
 $\Delta H^{\circ} = -41.2 \text{ kJ}$

(3)
$$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$$
 $\Delta H^{\circ} = 206.1 \text{ kJ}$

The next one is challenging!

3. One reaction involved in the conversion of iron ore to the metal is

$$\text{FeO}\left(\text{s}\right) \ + \ \text{CO}\left(\text{g}\right) \ \rightarrow \ \text{Fe}\left(\text{s}\right) \ + \ \text{CO}_{2}\left(\text{g}\right)$$

Calculate the standard enthalpy change for this reaction from these reactions of iron oxides with CO:

(1)
$$3 \text{ Fe}_2\text{O}_3(s) + \text{CO}(g) \rightarrow 2 \text{ Fe}_3\text{O}_4(s) + \text{CO}_2(g) \quad \Delta \text{H}^\circ = -47.0 \text{ kJ}$$

(2)
$$\text{Fe}_2\text{O}_3(s) + 3 \,\text{CO}(g) \rightarrow 2 \,\text{Fe}(s) + 3 \,\text{CO}_2(g)$$
 $\Delta \text{H}^\circ = -25.0 \,\text{kJ}$

(3)
$$Fe_3O_4(s) + CO(g) \rightarrow 3 FeO(s) + CO_2(g)$$
 $\Delta H^{\circ} = 19.0 \text{ kJ}$

2.5 Hess's Law - The Equation

There is another way to calculate enthalpy changes that occur during chemical reactions that is based on the principal of Hess's Law.

 ΔH for a reaction may be calculated using the published $\Delta H_{f} \, values$ and the equation:

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

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Example:

Using a Table of Thermochemical Data, calculate ΔH for the combustion of benzene, C_0H_0 , as shown by the following reaction:

$$C_6H_6(I) + 15/2 O_2(g) \rightarrow 6 CO_2(g) + 3 H_2O(I)$$

I suggest that you begin by writing all the ΔH_f values directly below all participants in the equation.

C ₆ H ₆ (I)	ΔH = +49.0
CO ₂ (g)	ΔH = -393.5
H ₂ O (I)	ΔH = -285.8

$$C_6H_6\ (I)$$
 + $15/2\ O_2\ (g)$ \rightarrow $6\ CO_2\ (g)$ + $3\ H_2O\ (I)$
 49.0 + $15/2\times (0)$ $6\times (-393.5)$ + $3\times (-285.8)$
 49.0 -3218.4
Reactants Products

Using the formula $\Delta H = \Sigma \Delta H_{products} - \Sigma \Delta H_{reactants}$

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

 $\Delta H = -3218.4 - (+49.0)$
 $\Delta H = -3267.4 \text{ kJ}$ answer

example:

Table of data for a Hess' law calculation:

Substance	ΔH° _f kJ mol ⁻¹
CH ₄ (g)	-75
O ₂ (g)	0
CO ₂ (g)	-394
H ₂ O (I)	-286

Using this data, ΔH^{\bullet}_{c} for the reaction below can be found:

$$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(I)$$

Example : Calculate the Δ H of the following reaction using heats of formations

$$C_3H_8(l) + O_2(g) \Rightarrow CO_2(g) + H_2O(g)$$

$$C_3H_8$$
 (I) = - 103 .8 kJ/mol
 O_2 (g) = 0 kJ/mol
 CO_2 (g) = -393.5 kJ/mol
 H_2O (g) = - 242.0 kJ/mol

Calculate the heat of the following reaction using the listed heats of formation.

$$Fe(s) + CO_2(g) \Rightarrow Fe_2O_3(s) + CO(g)$$
(unbalanced)

Heats of Formations:

Fe = 0 kJ/mol

$$CO_2$$
 (g) = -393.5 kJ/mol
 Fe_2O_3 (s) = -824.2 kJ/mol
 CO (g) = -110.5 kJ/mol

Summation of Heats formula:

$$\Delta H_{\text{overall}} = \sum_{\text{sum}} \Delta H_{\text{of products}} - \sum_{\text{sum}} \Delta H_{\text{of reactants}}$$

Table of Heats of formation

$$2 \text{ CO}_2(g) + \text{N}_2(g) \Rightarrow 2 \text{ NO}(g) + 2 \text{CO}(g)$$
 $\Delta H = ?$

Answer: + 746.4 kJ

$$4 \text{ CH}_3 \text{OH (I)} + 4 \text{ O}_2(g) \implies 2 \text{ CO(g)} + \text{CO}_2(g) + 8 \text{H}_2 \text{O (g)} + \text{C (s)} \qquad \Delta \text{ H} = ?$$

Answer: - 1592.1 k

$$C_2H_4(g)$$
 + Cl_2 \Rightarrow $C_2H_3Cl(g)$ + $HCl(g)$ $\Delta H = ?$

Answer :- 107.5 kJ

$$4 \text{ NH}_3 \text{ (g)} + 5 \text{ O}_2 \text{ (g)} \implies 4 \text{NO (g)} + 6 \text{ H}_2 \text{O (g)} \qquad \Delta \text{ H} = ?$$

Answer: - 907.6 kJ

NO (g) +
$$2HNO_3$$
 (l) \rightarrow H_2O (l) + $3NO_2$ (g) $\Delta H = ?$

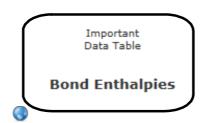
Answer: +71.8 kJ



2.6 Bond Enthalpies

There is another way to calculate the heat of reaction, using bond enthalpies.

Bond enthalpy refers to the amount of energy stored in the chemical bonds between any two atoms in a molecule. Bond enthalpies have been experimentally determined and can be found in a Table of Bond Enthalpies.



Amount of energy required to break the bonds of the reactant molecules Amount of energy released when the bonds of the products form

 $\Delta H = \Sigma$ (bonds broken) – Σ (bonds formed)

 $\Delta H = \Sigma$ (reactant bonds) - Σ (product bonds)

Example 1.

Using bond enthalpies, provided in the table below, calculate the heat of reaction, ΔH , for: $\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g)$

Given the following bond enthalpies:

H - H	436 kJ
Cl – Cl	243 kJ
H – Cl	433 kJ

Draw structural formulas for all molecules.

Chemical formula	Structural Formula				
H ₂	H — H				
Cl ₂	Cl — Cl				
HCl	H — Cl				

	RE	AKING	PRODUCTS: BOND FORMATION							
Bond	No. bonds per molecule		Bond Enthalpy		Total Energy	No. bonds per molecule	I	Bond Enthalpy		Total Energy
H - H	1	×	436	=	436					
Cl - Cl	1	×	243	=	243					
H-Cl						1	×	433	=	433

We still need to use the balancing coefficients from the balanced equation:

$$\Delta H = \Sigma$$
 (bonds broken) – Σ (bonds formed)
 $\Delta H = [1/2(436) + 1/2(243)] - [(433)]$
 $\Delta H = 339.5 - 433 = -93.5 \text{ kJ}$ answer

Example 2:

Using the bond enthalpies provided, calculate the heat of reaction, $\Delta H,$ for:

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Given the following table of bond enthalpies:

Chemical formula

C - H413 kJ C = C614 kJ C -C 348 kJ 436 kJ H - H

Structural Formula C₂H₄ C₂H₆ H₂

REACTANTS: BOND BREAKING

Number bonds per molecule Total Energy PRODUCTS: BOND FORMATION

Number bonds per molecule bond enthalpy

2.7 The Stability of Compounds

Follow along carefully with these examples:

If ΔH_f° is large and negative, energy is released when the compound is formed.

(highly exothermic)

For example, ΔH_f° for MgO(s) is -601.7 kJ. Thus:

$$Mg(s) + \frac{1}{2}O_2 \rightarrow MgO(s) + 601.7 \text{ kJ}$$

Conversely, energy is required to decompose the compound.

$$MgO(s) + 601.7 \text{ kJ} \rightarrow Mg(s) + \frac{1}{2}O_2$$

Since a large amount of energy must be supplied for MgO to break down into its elements (601.7 kJ),

we conclude that MgO is a stable compound.

MgO were sitting on your desk, it would remain as MgO and *not* break down into solid magnesium and oxygen gas.

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2. If ΔH_f^0 is small and negative

little energy is required to decompose the compound

Let's look at HBr(g) as an example. ΔH_f° for this compound is -36.4 kJ.

$$\frac{1}{2} H_2(g) + \frac{1}{2} Br_2(g) \rightarrow HBr(g) + 36.4 \text{ kJ}$$

Again, stability of a compound refers to the reverse of the formation reaction,

$$HBr(g) + 36.4 \text{ kJ} \rightarrow \frac{1}{2} H_2(g) + \frac{1}{2} Br_2(g)$$

Since only a small amount of energy (36.4 kJ) is required for this reaction to occur, it is possible that this compound will break down spontaneously

3.

Finally, if ΔH_f^0 is positive (endothermic), the compound is likely to be unstable.

 ΔH_f^o for CS₂ is +117.4 kJ. The heat of formation reaction:

$$C(s) + 2 S(s) + 117.4 \text{ kJ} \rightarrow CS_2(q)$$

Reversing this to see the decomposition reaction:

$$CS_2(g) \rightarrow C(s) + 2 S(s) + 117.4 \text{ kJ}$$

we see that energy is released when this compound breaks down

Since we now know that exothermic reactions tend to occur spontaneously is we conclude that CS2 is an unstable compound.

