

Thermochemistry

Energy

What is energy? The simplest definition of energy is the capacity to do work. There are two types of energy kinetic energy, or the energy a moving body possesses, and potential energy, the energy a body has due to its position.

There are many different kinds of energy. Some of these are mechanical, electrical, chemical, nuclear, and radiant (light). All of these kinds of energy and the two types of energy listed above are measured in the same units.

The units for energy can be determined by looking at the formula for kinetic energy.

$$E_k = \frac{1}{2}mv^2$$

Here m is the mass of the object in kilograms and v is the velocity of the object in m s^{-1} . This gives a unit of energy as being $\text{kg m}^2 \text{s}^{-2}$. This unit is the SI unit of energy. It has been renamed the **Joule** (J) in honor of James Prescott Joule who did some of the earlier work on energy transfer and heat.

Another unit of energy that has been used and is still in use in some places, like nutrition, is the calorie. A **calorie** (cal) is defined as the amount of energy needed to increase the temperature of 1.00 g of water from 14.5 °C to 15.5 °C. 1 calorie is the same as 4.184 J.

Heat

What is heat? It is NOT the same thing as temperature. Temperature is a measure of how much heat can flow but it is not a measure of the heat itself. Heat is a form of energy. As a result heat is measured in Joules. It is energy that flows due to a temperature difference. Heat is given the symbol **q**.

Heat that is transferred during a chemical reaction is called the **heat of reaction**. These heats can flow into or out of the reaction. In order to describe this so that everyone has the same definitions, we describe the reaction as the **system**. Everything else is the **surroundings**. When we talk about the heat transferred, we always describe it from the system's point of view.

When heat flows from the system into the surroundings, the system loses heat and therefore has a negative value ($q < 0$). The temperature of the surroundings will increase in this situation. This reaction would be described as being **exothermic**. If the heat flows from the surroundings into the system, it has a positive value ($q > 0$). The temperature of the surroundings will decrease in this situation. This reaction would be described as being **endothermic**.

Enthalpy

Enthalpy (symbol is H) is a measure of the heat of reaction. It is related to the q discussed above. If the heat, q, is measured at constant pressure, q_p , it is called the enthalpy. Enthalpy is a **state function**, which means that it is dependent only on the present state of the system, not how it got there. What we measure when we measure a heat of reaction is really not enthalpy, but change in enthalpy, **ΔH**

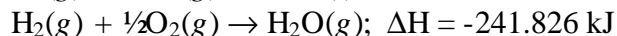
$$\Delta H = q_p$$

The change in enthalpy can be determined in a variety of ways that will be described shortly.

First let's discuss a more complete form of chemical reaction called the **thermochemical equation**. A thermochemical equation is a chemical equation that is given a molar interpretation and the enthalpy change for the reaction **as it is written** is given immediately after it. For example,



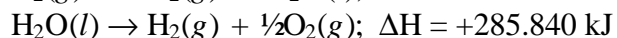
The thermochemical equation must include phase labels because the enthalpy change will change if the phases present are different.



It will also change if the molar amounts are different

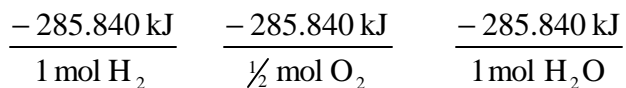


It will change if the reaction changes direction.



Heats of reaction and Stoichiometry

The enthalpy of a reaction from the thermochemical equation is a conversion factor that can be used to calculate the amount of heat generated or absorbed by a reaction for an amount different than the stoichiometric amounts from the balanced chemical equation. The conversion factors are based on the chemical equation as it is written. From above we see that for water we get the following conversion factors:



For example, if we have a reaction, like the production of water above, and we do not have 1 mole of hydrogen or $\frac{1}{2}$ mole of oxygen, then the amount of heat generated will depend on the amount that we actually have. The amount of heat generated or absorbed will be equal to the molar enthalpy of the reaction (ΔH) multiplied by the number of moles of the limiting reactant. So 2.45 moles of hydrogen reacting with excess oxygen will produce:

$$2.45 \text{ mol H}_2 \times \frac{-285.840 \text{ kJ}}{1 \text{ mol H}_2} = -7.00 \times 10^2 \text{ kJ}$$

Measuring heats of reaction

Heats of reaction can be measured in a device called a **calorimeter**. This device is usually insulated to avoid heat loss or gain from outside the calorimeter during the reaction, which could introduce errors into the measurement. In a coffee cup calorimeter, the type used in lab, the pressure remains constant. Therefore, the heat measured is an indication of the change in enthalpy of the reaction. In order to use this device, we must look at the relationship between the heat and the variables that are measured.

Earlier, we stated that heat is a measure of the amount of energy that can flow due to a temperature difference. Therefore, the heat is proportional to the temperature difference. It is, as we have seen with the thermochemical equations, proportional to the amount of substance present, which is measured as the mass. In order to get these proportionalities to be equalities we must insert a constant of proportionality. This constant is called the **specific heat, s**, of the substance and has units of $\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$. The heat measured can be calculated then as

$$q_p = m s \Delta T$$

Sometimes the mass of the calorimeter and its contents and the overall specific heat are combined into a single number called the **heat capacity, C**. Then the heat can be calculated as

$$q_p = C \Delta T$$

The heat measured here is for the calorimeter and its contents. Whenever we measure a temperature it is **always** for the surroundings (i.e., the calorimeter). To get the heat for the reaction, we need to realize that, because it is insulated, the heat for the reaction is of the same magnitude as the heat for the calorimeter but of the opposite sign.

$$q_{\text{rxn}} = -q_{\text{cal}}$$

In order to get the molar enthalpy change, ΔH , for the reaction we have to divide the heat for the reaction by the number of moles (keeping limiting reactants in mind).

$$\Delta H = \frac{q_{rxn}}{n_{\text{limitingreactant}}}$$

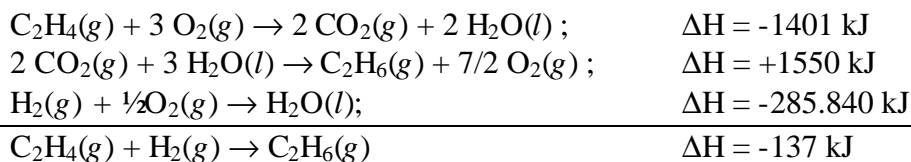
In this way we can calculate the molar enthalpy change for reactions that do not occur high temperatures. At higher temperatures we need to use another method that is dealt with in chapter 18.

Hess' Law

Hess' Law is a restatement of the fact that enthalpies are state functions. What Hess' Law says is

If a series of reactions add up to give another reaction, then the enthalpies of those reactions add up to give the enthalpy of the overall reaction.

We can show this in the following way:



Utilizing Hess' Law can enable us to find an enthalpy of reaction for a reaction that occurs at a higher temperature by finding reactions that occur at lower temperatures that add to give the correct overall equation.

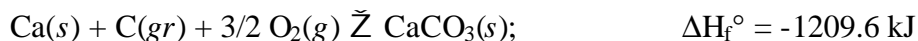
Standard Enthalpies of Formation

Another way to determine the enthalpy of reaction is to utilize **standard enthalpies of formation, ΔH_f°** . These are tabulated values (see appendix C of your text). An enthalpy of formation is the heat of reaction when one mole of substance is formed from its elements in their standard states. The standard states are 1 atm pressure and 25.00°C. The phase of the element or compound is what the phase would be under these conditions. Most metals are solid under these conditions, except for Mercury, which is a liquid. The elements that are gases are Hydrogen, Nitrogen, Oxygen, Fluorine, Chlorine and the Noble gases. The standard enthalpy of formation for all elements in their standard states and reference forms is 0.00 kJ. The reference forms are the forms for elements with more than one **allotrope**. An allotrope is one form of an element that has two or more distinct forms. Examples of allotropes are Oxygen (O_2 , reference form) and Ozone (O_3), also Carbon has Diamond, Graphite (reference form), and buckminsterfullerenes (C_{60}).

To calculate the enthalpy of a reaction we apply Hess' Law. For the reaction



we can write this in terms of Hess' Law with formation reactions:



If we reverse the first reaction and add them up we get the correct overall equation. This means that we change the sign on the first heat of formation and add them up also.

$$\Delta H = +1209.6 \text{ kJ} + (-635.1 \text{ kJ}) + (-393.5 \text{ kJ}) = +181.0 \text{ kJ}$$

We can simplify this process by realizing that all reactants' formation reactions will have to be reversed and the products' formation reaction will remain the same. This gives us a general formula

$$\Delta H = \sum n \Delta H_f^\circ (\text{products}) - \sum m \Delta H_f^\circ (\text{reactants})$$