

Chapter 5 – Thermochemistry

As you might guess from the title, we're going to discuss aspects of chemistry that involve heat changes. As it turns out, work is directly related to heat and we'll discuss that as well, but in a more limited sense. You already know from personal experience that heat affects chemical reactions. For example, we refrigerate food to slow the rate of spoiling. What you may not realize is that when reactions occur, heat is almost always released. Combustion is the prototypical example of this.

Why is this important? Consider the following question: Why does any reaction occur as written? That is: Why doesn't it run in reverse? or Why are those specific products made and not others? We begin to examine these questions in this chapter. The study of energy and the interconversion of types of energy is called thermodynamics. Thermochemistry is the part of thermodynamics that applies to chemical reactions.

5.1 Energy Basics

The first thing we need is a definition of energy. It is the capacity to transfer heat or do work. Work is the energy used when a force moves an object through a distance.

$$w = (\text{force})(\text{distance})$$

Back in Chapter 1, we introduced potential and kinetic energies. We need to expand on those definitions now. Potential energy is the energy of the position of one object relative to other objects when a force is operating on all of the objects. This is stored energy available for use. For example, a glass sitting on a table has more potential energy than an identical one sitting on the

floor because of the force of gravity. The additional potential energy the glass on the table possesses equals the energy used to lift it from the floor.

Kinetic energy is the energy of motion (or energy in use).

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

where m = mass and v = velocity. As you can see, if you want to increase the energy of a moving object, it is better to speed it up than to make it heavier. This is why baseball players generally choose light bats over heavier ones. They can accelerate the lighter bat more rapidly which more than makes up for the loss in mass. It is also why a car accident at 60 mph is much more serious than one at 15 mph (16 times more energy is transferred).

Thermal energy is the form of kinetic energy associated with the random motion of atoms and molecules. Temperature is a qualitative measure of thermal energy and is part of the formula for quantifying it. Thus, an object's thermal energy increases with increasing temperature. Heat (q) is the transfer of thermal energy between bodies at different temperatures. The study of heat greatly interests chemists because most chemical reactions involve the production or consumption of heat. Thermal energy depends on the temperature of an object, with the same object possessing more thermal energy at higher temperatures. It also depends on the amount of material present. At any temperature, a larger amount of a material contains more thermal energy than a smaller amount. For example, 1 quart of boiling water possesses twice the thermal energy of 1 pint of boiling water.

There are two important energy units you will encounter in chemistry. Almost all textbooks at any level use the joule (J) which has units $\text{kg} \cdot \text{m}^2/\text{s}^2$. The other important unit, frequently found in older research journals and books, is the calorie ($1 \text{ cal} = 4.184 \text{ J}$). It is related to the

dietary calorie (C) which equals 1000 cal.

As you can see, the joule has component units, which means it is calculated. It is derived from the equation:

$$\text{Force} = \text{mass} \times \text{acceleration}$$

Force is any kind of push or pull exerted on an object.

5.2 Calorimetry

We now turn our attention to how we measure the energy/heat content of objects. Implicit in the need to measure is the idea that objects (including molecules) retain and produce heat in differing amounts. For example, consider dropping pulling a ball bearing and a plastic ball of the same size out of boiling water. Which would feel hotter? You picked the metal ball, right? Why? Because you know the metal would hold more heat and be more likely to burn you even though there were at the same temperature. The same is true if the balls were the same weight. You'd still expect the plastic ball to retain less heat than the metal ball. There are 3 quantities that are used to describe the ability of materials to retain heat.

When studying chemical reactions or physical processes, we need to divide the world into two parts. The system is that part of the universe being studied. The surroundings are everything else. A closed system does not exchange matter with its surroundings, while an open system does. Depending on the type of study, it may or may not exchange energy with the surroundings. An isolated system does not exchange anything with its surroundings. In reality, it's not possible to stop all energy flow between a system and its surroundings, but isolated systems can be closely

approximated.

We now introduce three related terms that people sometimes mix up because the terms are similar. Specific heat, c_s , is the heat required to raise the temperature of one gram of a substance one °C.

$$c_s = \frac{\text{heat added (J)}}{[\text{mass (g)}][\Delta T (\text{K, or } ^\circ\text{C})]} = \frac{q}{m\Delta T}$$

You'll notice that the book uses a slightly different term (specific heat capacity). I used the shortened term you see because it is both common and less confusing. Similarly, molar heat capacity, c_P , is the heat required to raise a mole of the substance by 1 °C. It can be calculated by multiplying the specific heat by the molecular weight of the substance. Finally, the heat capacity of an entire object, C_P , is the energy required to raise the temperature of that object by 1 °C. This last quantity is interesting because the object may be a single substance, a mixture, or a device.

Example: How much heat must be added to warm 125 mL of water from 25 °C to 100 °C?

$$\begin{aligned} \text{heat transferred} = q &= C(\text{mass})(\Delta T) \\ &= (4.184 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}})(125 \text{ mL})\left(\frac{1.00 \text{ g}}{\text{mL}}\right) (100 ^\circ\text{C} - 25 ^\circ\text{C})\left(\frac{1 \text{ K}}{^\circ\text{C}}\right) \\ &= 39,000 \text{ J} = 39 \text{ kJ} \end{aligned}$$

Use care with the symbols: c_s , c_P , and C_P . Particularly the last two will be difficult to distinguish when written down. I would recommend writing something like molar c_P or object C_P so there isn't any confusion.

It turns out that it's fairly easy to measure how much energy is required to heat a substance to a higher temperature. Calorimetry is the experimental method of measuring the energy changes

associated with chemical or physical changes. The device used for such measurements is the calorimeter. Experimentally, reagents react in an insulated container while the temperature inside the vessel is monitored. Assuming no heat loss to the surroundings, the heat of reaction is then calculated.

Constant Pressure Calorimetry – The simplest of the constant pressure calorimetry experiments involves mixing two reagents in a Styrofoam[®] coffee cup and measuring the initial and minimum/maximum temperatures. If the specific heat of the solution is known, the heat transferred is simple to calculate:

$$q_{\text{soln}} = (\text{specific heat of solution})(\text{mass of solution})\Delta T$$

The heat of reaction will be the negative of the heat of solution since one is giving up energy and the other is absorbing it.

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

Skip constant volume calorimetry (discussion around bomb calorimetry).

5.3 Enthalpy

All substances possess/contain energy, which is found in a variety of forms. Most obviously, there is thermal energy (usually manifested as molecular movement), but there are always vibrational and rotational energies present. There are other less common energies that are sometimes present in materials, for example light energy (e.g. glowsticks and fireflies). The total amount of energy from all of these sources is called its internal energy, U , which is also the sum of the kinetic and potential energies for a substance.

Measuring the absolute energies of molecules is impossible and calculating them is possible only for the simplest species. Fortunately, the relative energies of molecules provide us with what we really need: the difference in energy between the reactants and products. This turns out to be relatively easy to determine. Mathematically, the change in energy is given by:

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

Thus, the system loses energy when $\Delta U < 0$ and gains energy when $\Delta U > 0$.

Which of these conditions allows processes to occur? In other words, when a process happens, does the system usually gain (absorb) or lose (release) energy? The answer to this question probably isn't obvious, so we will use an example to see what happens in a real system. Consider a dinner glass on a countertop and a second, identical glass sitting on the floor. Which is more stable? You probably picked the one on the floor. Why? Now imagine the glass on the countertop falling to the floor. Did it gain or lose energy? What happened when it hit the floor and why?

Thus, a more stable situation results from a loss of energy. If so, the reverse process must require the input of energy. (You have to lift the glass from the floor to the counter and that requires you to put energy into the glass (the act of lifting). The same is true of chemical reactions. A basic rule of chemistry is that systems tend to attain the lowest energy state possible.

The energy change in any system can be expressed as:

$$\Delta U = q + w$$

*where q is the thermal energy (heat) added to the system and w is the work (all other kinds of energy) done on the system. Chemists tend to be more interested in heat because it is a component of all reactions. Except for reactions that produce or consume gases, work is generally **not***

important. The change in energy is measured for the system, thus if a system draws heat from the surroundings (i.e. the system cools), ΔU is positive. If the container warms, ΔU is negative because heat is being transferred to the surroundings. Be careful because it's easy to get this backwards. A natural question to ask here is "why only heat and work, when U takes a wide range of forms?" The short answer is that other forms of internal energy are converted into heat and work or vice-versa when transfers occur.

This formula, $\Delta U = q + w$, is a mathematical statement of the **first law of thermodynamics** (sometimes called the Law of Conservation of Energy). More commonly, it is stated as "**Energy can neither be created nor destroyed.**" This is never violated.

Most chemical reactions are conducted in open systems, so any gas is either absorbed or released to the atmosphere and this causes no change in pressure. From the definition of work in Section 5.1, the work done by or on a gas is given by

$$w = -P\Delta V$$

It is a negative term because expansion of a gas ($\Delta V > 0$) does work on the surroundings and so transfers energy out of the system. Substituting back into our internal energy equation, we get

$$\Delta U = q - P\Delta V$$

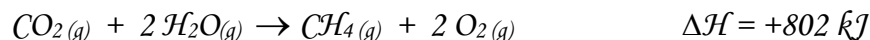
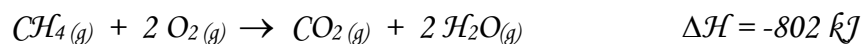
$$q_P = \Delta U + P\Delta V$$

where q_P is the heat at constant pressure. We give this quantity a special name, enthalpy, and designate it as ΔH . Enthalpy is the heat gained or lost at constant pressure. We use this because it is much easier to measure than either internal energy or work. It is frequently called the heat of reaction. (Skip the discussion on state functions.)

In addition, enthalpy is more important than the change in internal energy for most processes and, from here forward, we will use it exclusively. Exothermic reactions release energy ($\Delta H < 0$) to the surroundings. When reactions absorb energy from the surroundings ($\Delta H > 0$), the process is said to be endothermic. Hence, melting ice is an endothermic process, while burning (combustion) is an exothermic process. An exothermic reaction may be warm to the touch and an endothermic cool to the touch (never the reverse), although sometimes the temperature change is too small to feel.

There are 3 important aspects to enthalpy that you should remember.

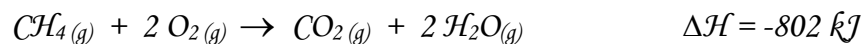
1) **When a reaction is reversed, the sign on ΔH changes.**



A physical change illustrates this point well. A 1 gram block of ice at 0 °C requires 4.184 J of heat to melt. To freeze 1 gram of water at 0 °C, then, one must remove the same amount of energy.

2) **The enthalpy of a reaction depends on the quantity of reactants present.**

One way to think about this is that you get twice as much heat from two burning charcoal briquettes than from one. Returning to the burning of methane example:



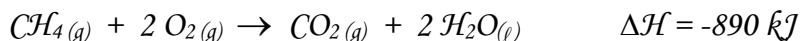
This tells us that the reaction of 1 mole of methane with 2 moles of oxygen releases 802 kJ. So, reacting 2 moles of methane with 4 moles of oxygen releases 1604 kJ. Thus, the balancing coefficients are important. This is one reason why you were told to use only whole number

coefficients when balancing equations.

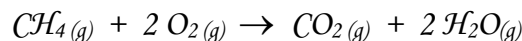
- 3) **The physical state of the reactants and products matters.** Since additional heat is required to vaporize gases and melt solids (and vice-versa), ΔH will be different if the physical state of a substance changes. Consider the condensation of water:



This extra 44 joules explains why steam burns are so much worse than hot water burns. The burning of methane would change as follows if the water were allowed to condense.



Example: Let's go back to the methane combustion example from earlier:



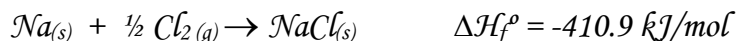
$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= \left[(1 \text{ mol}_{\text{CO}_2}) \left(\frac{-393.5 \text{ kJ}}{\text{mol}_{\text{CO}_2}} \right) + (2 \text{ mol}_{\text{H}_2\text{O}}) \left(\frac{-241.8 \text{ kJ}}{\text{mol}_{\text{H}_2\text{O}}} \right) \right] \\ &\quad - \left[(1 \text{ mol}_{\text{CH}_4}) \left(\frac{-74.85 \text{ kJ}}{\text{mol}_{\text{CH}_4}} \right) + (2 \text{ mol}_{\text{O}_2}) \left(\frac{0 \text{ kJ}}{\text{mol}_{\text{O}_2}} \right) \right] \\ &= -802.2 \text{ kJ} \quad (\text{This is the same value as found from the experiment.}) \end{aligned}$$

Standard Enthalpies of Reaction ($\Delta H_{\text{rxn}}^{\circ}$)

Enthalpy measurements usually depend on the conditions under which the experiment is conducted leading to a set of standard conditions being defined. Standard conditions are: $T = 25^{\circ}\text{C}$ (298 K) and $P = 1 \text{ atm}$. When reactions occur under these conditions a superscript $^{\circ}$ is added to the enthalpy symbol (e.g. ΔH_f°).

Heats of formation represent an important subclass of heats of reaction. The heat of

formation, ΔH_f , of a substance is the enthalpy change associated with the synthesis of one mole of a compound from its constituent elements. The formation reaction for sodium chloride is



The reason for the $\frac{1}{2}$ coefficient is that we want the energy for only 1 mole of sodium chloride. All heat of formation reactions yield one mole of the desired product and zero moles of any other material. For that reason, heats of formation represent one of the rare situations that it is acceptable to balance a chemical equation using fractional coefficients.

Hess's Law

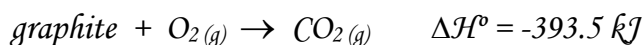
This is another fundamental law in chemistry and one that you will see again and again over the next few years. Hess's law states that the enthalpy of a reaction does not depend on the reaction pathway. This means the enthalpy of reaction is the same no matter how many steps the reaction takes and only the identity of the reactants and products and their physical states matter.

Hess' law is important for two very practical reasons:

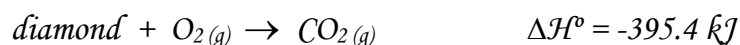
- 1) Once you know ΔH for a collection of substances, running experiments may no longer be necessary. If all of the chemicals in a reaction have measured ΔH s, no measurement of ΔH_{rxn} is necessary.
- 2) It allows determination of ΔH_{rxn} for reactions that would otherwise be too difficult or impossible to make an accurate measurement.

The following example is a classic problem. Which is more stable: graphite or diamond? Your initial response was almost assuredly diamond. Interconversion of these materials is quite difficult experimentally, so measuring ΔH_{rxn} is not possible. One way to determine it is to look at the

combustion reaction of each.



Now reverse the second reaction and add the resulting pair of equations



Since energy is released when diamond is converted to graphite, graphite must be more stable than diamond.

It is important to note that the reaction need not actually occur. For example, consider the reaction of graphite and hydrogen. One can write the following reactions, both balanced and correct:



There are thousands of compounds containing only carbon and hydrogen. The formation reactions only differ in the C/H ratio (and then, not always). Clearly one can't run any of these reactions and get 100% of one material. Nonetheless, formation reactions of these species are still quite useful, as you will see below.

The standard heat of formation of any element in its most stable form is defined as zero.

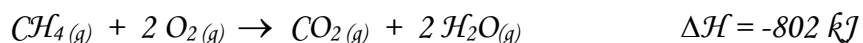
Consider oxygen and ozone. Given how much more of the former there is in the atmosphere you might correctly guess that it's more stable. How much more?

$$\Delta H_f^\circ(\text{O}_2) = 0 \text{ kJ/mol}$$

$$\Delta H_f^\circ(\text{O}_3) = 142.3 \text{ kJ/mol}$$

This is why there is so much concern about ozone at ground level for people with breathing disorders. Allotropes are different forms of the same element at the same temperature. Dioxygen and ozone are allotropes at ambient temperature because both are gases. Some standard heats of formation appear in Appendix G (p. 1211).

Closely related to enthalpies of formation are enthalpies of reaction. Enthalpies of reaction, $\Delta H_{\text{rxn}}^\circ$, are the energy changes associated with a reaction. These are regular reactions, i.e. reactants don't have to be elements, there can be several products, etc. For example, consider the burning of methane:



Thus, igniting a mixture of 1 mole of methane and 2 moles of oxygen releases 802 kJ of heat. The mathematical relationship

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

is very useful because it allows us to use formation data that has already been collected.

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