7.6: Energy Changes and Chemical Reactions

All chemical reactions are accompanied by energy changes. Under most circumstances, particularly when the pressure and volume are kept constant, these changes can be ascribed to changes in enthalpy ΔH. For example, combustion reactions (redox reactions involving oxygen) are a major source of energy for most organisms. In warm-blooded organisms, the energy released through such reactions is used to maintain a set body temperature. Within organisms, combustion reactions occur in highly-controlled stages (which is why you do not burst into flames), through the process known as respiration (different from breathing, although breathing is necessary to bring molecular oxygen to your cells).

Not all biological forms of respiration use molecular oxygen.[23] There are other molecules that serve to accept electrons; this process is known as anaerobic (air-free) respiration. All known organisms use the molecule adenosine triphosphate (ATP) as a convenient place to store energy. ATP is synthesized from adenosine diphosphate (ADP) and inorganic phosphate. As two separate species, ADP and inorganic phosphate are more stable than ATP and the energy captured from the environment use to drive the synthesis of ATP can be released again via the formation of ADP and inorganic phosphate:

$$ADP + Pi + \text{ energy } \rightleftarrows ATP + H_2O \tag{7.6.1}$$

If we looked closely at the molecular level mechanism of ATP synthesis, we would see that it is another example of an electrophile–nucleophile interaction. But regardless of the type of reactions, we can ask the same question: Where (ultimately) does the energy released in an exothermic reaction come from? When an exothermic reaction occurs and energy is transferred from the system to the surroundings, the result is a temperature increase in the surroundings and a negative enthalpy change $-\Delta H$.) What is the source of that energy? Of course, you already know the answer—it has to be the energy released when a bond is formed!

The defining trait of a chemical reaction is a change in the chemical identity of the reactants: new types of molecules are produced. In order for this to occur, at least some of the bonds in the starting material must be broken and new bonds must be formed in the products, otherwise no reaction occurs. So to analyze energy changes in chemical reactions, we look at which bonds are broken and which are formed, and then compare their energies. As we will discuss later, the process is not quite so simple, given that the pathway for the reaction may include higher energy intermediates. As we will see it is the pathway of a reaction that determines its rate (how fast it occurs), whereas the difference between products and reactions determines the extent to which the reaction will occur. The following analysis will lead to some reasonable approximations for estimating energy changes during a reaction.

As we have already seen, bond formation releases energy and bond breaking requires energy. Tables of bond dissociation energies are found in most chemistry books and can be easily retrieved from the Internet.[24] One caveat: these measurements are typically taken in the gas phase and refer to a process where the bond is broken homolytically (each atom in the original bond ends up with one electron and the species formed are known as radicals).[25] The bond dissociation energy for hydrogen is the energy required to drive the process:

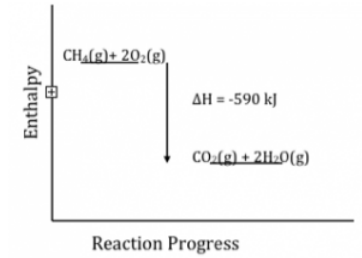
$$H-H(g) \rightleftarrows 2H\cdot \tag{7.6.2}$$

where the dot represents an unpaired electron. The enthalpy change for this process is $\Delta H = +436 \text{ kJ/mol}$. Note that tables of bond energies record the energy required to break the bond. As we noted earlier, enthalpy is a state function – its value does not depend on the path taken for the change to occur, so we also know what the enthalpy change is for the reverse process. That is, when a hydrogen molecule forms from two hydrogen atoms the process is exothermic:

$$2H\cdot \rightleftarrows H-H(g) \quad \Delta H = -436 \text{ kJ/mol} \tag{7.6.3}$$

We have tables of bond energy values for most common bond types, so one way to figure out energy changes (or at least the enthalpy changes) for a particular reaction is to analyze the reaction in terms of which bonds are broken and which bonds are formed. The broken bonds contribute a positive term to the total reaction energy change whereas bond formation contributes a negative term. For example, let us take a closer look at the combustion of methane:[26]

$$CH_4(g) + 2O_2(g) \rightleftarrows CO_2(g) + 2H_2O(g) \tag{7.6.4}$$



In the course of this reaction, four $C—H$ bonds $[4 \times C—H(436\ kJ/mol)]$ and two $O=O$ bonds $(498\ kJ/mol)$ are broken. The new bonds formed are $2 \times C=O(803\ kJ/mol)$ and $4 \times O—H(460\ kJ/mol)$. If you do the math, you will find that the sum of the bond energies broken is $2740\ kJ$, whereas the sum of the bond energies formed is $-3330\ kJ$. In other words, the bonds in the products are $706\ kJ$ more stable than the bonds in the reactants. This is easier to see if we plot the progress of enthalpy versus reaction; it becomes more obvious that the products are lower in energy (more stable).

There are several important aspects to note about this analysis:

1. This is only an estimation of the enthalpy change, because (as noted above) bond energies are averages and are measured in the gas phase. In the real world, most reactions do not occur in the gas phase. In solutions, there are all kinds of other interactions (intermolecular forces) that can affect the enthalpy change, but for an initial approximation this method often gives surprisingly good results.
2. Remember, every reaction must be considered as a part of the system. Both the reactants and products have to be included in any analysis, as well as the direction of energy transfer between the reaction system and the surroundings.
3. An exothermic reaction occurs when the bonds formed are stronger than the bonds that are broken. If we look closely at this calculation, we can see that combustion reactions are so exothermic because they produce carbon dioxide. The bond energy of the carbon—oxygen double bond is very high (although not two times the $C—O$ single bond—can you think why?) The production of CO_2 is very favorable from an energy standpoint: it sits in a deep energy well because it has such strong bonds. This point has important ramifications for the world we live in. Carbon dioxide is quite stable; although it can be made to react, such reactions require the input of energy. Large numbers of us expel CO_2 into the atmosphere from burning fossil fuels and breathing, at a higher rate than is currently being removed through various types of sequestration processes, including chemical reactions and photosynthesis. You have certainly heard of the greenhouse effect, caused by the build-up of CO_2. CO_2 is difficult to get rid of because strong bonds give it stability. (Given the notoriety of CO_2 in terms of climate change, we will come back to this topic later.)

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Questions to Answer

- Many biology texts refer to energy being released when high-energy bonds in ATP are broken. In light of what you know, is this a reasonable statement? What do these texts really mean?
- Why do you think the enthalpy change for most Brønsted–Lowry acid–base reactions is independent of the nature of the acid or base? (Hint: What is the reaction that is actually occurring?)
- Using tables of bond dissociation energies, calculate the energy change for the reaction of $CH_2 = CH_2 + HCl \rightleftarrows CH_3CH_2Cl$. What steps do you have to take to complete this calculation? Make a list.
- If you look up the enthalpy change for this reaction (ΔH°) you will find it is not exactly what you calculated. Why do you think that is? (Hint: This reaction typically takes place in a solvent. What role might the solvent play in the reaction?)
