SECTION 11: ENERGY AND CHEMICAL REACTIONS

In Chem 101A, we will be most interested in the energy that is given off or absorbed in chemical reactions. Three vital facts must be understood from the start:

1) The First Law of Thermodynamics always applies. Chemical energy may be given off or absorbed in the form of heat, in the form of work, or in a combination of the two, but in all cases, \( \Delta E = q + w \).

2) Although \( \Delta E \) is virtually independent of the reaction conditions, \( q \) and \( w \) depend strongly on the method you choose to carry out the reaction. A chemical reaction will produce (or consume) roughly the same amount of energy regardless of the temperature, pressure, volume, etc. of the reacting chemicals, but that energy can be divided up between heat and work in many different ways, depending on the precise conditions under which the reaction occurs.

3) The amount of energy released or absorbed is proportional to the amounts of chemicals that react. This should seem reasonable, based on your experience: for example, you will get twice as much energy from burning 2 gallons of gasoline as you will from burning 1 gallon.

Let us examine the combustion of hydrogen as a typical illustration:

\[
\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)
\]

\( \Delta E \) for this reaction has been measured very precisely: if you burn one mole (2.01588 grams) of gaseous hydrogen, and you allow the product (a mole of water) to return to the original temperature of the reactants, 282.11 kJ of energy will be given off (in the form of heat, work, or a combination of the two). This means that the surroundings will have 282.11 kJ more energy after the reaction than they did before the reaction.

Where is this energy coming from? Since energy cannot be created or destroyed, the energy must be coming from the system. The actual source of the energy is the potential energy of the hydrogen/oxygen mixture. We have no way to measure the potential energy of a mole of \( \text{H}_2 \) and a half mole of \( \text{O}_2 \), or the potential energy of a mole of water, but conservation of energy guarantees that the \( \text{H}_2/\text{O}_2 \) mixture had 282.11 kJ more energy than the \( \text{H}_2\text{O} \). We can represent this graphically:
The potential energy that is lost during the reaction does not simply vanish, though. It is converted to kinetic energy, just as the potential energy of a ball that is dropped from the top of a building becomes kinetic energy as the ball falls. This kinetic energy is in the form of thermal energy: the atoms and molecules in the reaction mixture move faster and faster as the reaction proceeds.

We observe this increasing thermal (kinetic) energy as a rise in the temperature of the reaction mixture. However, it is a fundamental law of nature that whenever a hot object and a cool object are in contact, heat will flow from the hot object to the cool object (until they reach the same temperature): this is one statement of the Second Law of Thermodynamics. We have produced water at a high temperature, much higher than the temperature of the surroundings. Heat immediately starts to flow from the system (the reaction mixture) to the surroundings, and it continues to flow until the reaction products have returned to room temperature. For the reaction of hydrogen and oxygen, which is virtually instantaneous, we see the following graph:
Two distinct steps are observed: a rapid conversion of potential energy to kinetic energy, followed by a loss of the kinetic energy in the form of heat. This heat will increase the kinetic energy of the surroundings, so we can complete our analysis by including this as well. Here is a plot that includes the kinetic energy of the surroundings:

![Energy vs Time Graph](image1)

For a slow reaction, the second step (transfer of KE to the surroundings) will overlap with the first (conversion of PE to KE), so we will see something like this:

![Energy vs Time Graph](image2)

Regardless of the speed of the reaction, though, the end result is the same: the chemical potential energy of the reactants (really the difference in PE between the reactants and the products) is released to the surroundings in the form of heat and/or work.
What if the products are not brought back to their original temperature? If the final temperature is higher than the initial temperature, some of the kinetic energy that was produced in step 1 would remain inside the products. This would produce a different value for $\Delta E$ for the reaction. To avoid this difficulty, we define $\Delta E$ for a reaction in terms of the potential energy change. When 1 mole of hydrogen burns, the potential energy of the mixture of hydrogen atoms and oxygen atoms decreases by 282.11 kJ, regardless of whether all 282.11 kJ leave the chemicals, or some of this energy is retained as kinetic energy. With this definition, we can make the following statement:

“For the combustion of 1 mole of $H_2$, $\Delta E = -282.11 \text{ kJ}$”

Note the sign of $\Delta E$: it reflects the fact that the potential energy of the chemical mixture is decreasing during the reaction. The following picture may help you see what’s going on:

In some reactions, the potential energy of the chemical mixture increases during the reaction. This is a much less common situation, but it occurs often enough that it needs to be considered. For example, consider the reaction of 1 mole of solid $\text{NaHCO}_3$ with 1 mole of aqueous $\text{HCl}$.

$$\text{NaHCO}_3(s) + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{CO}_2(g) + \text{H}_2\text{O(l)}$$
In this reaction, 26 kJ of energy is absorbed from the surroundings. This occurs because the potential energy of the products (sodium chloride, carbon dioxide, and water) is higher than that of the reactants (sodium bicarbonate and hydrochloric acid). We can draw an energy diagram for the potential energy:

![Energy Diagram](image)

Since energy cannot be created from nothing, the additional potential energy must come from somewhere. Initially, it comes from the kinetic (thermal) energy of the reaction mixture: kinetic energy is converted to potential energy.

![Energy Graph](image)

The decreasing kinetic energy of the reaction mixture is reflected in its temperature: the entire mixture becomes colder. Once this happens, though, heat will flow from the surroundings into the reaction mixture until thermal equilibrium is re-established:
The end result is that the surroundings become colder.

As before, we use the change in the potential energy of the chemical mixture to define ΔE for the reaction, so we would say:

“For the reaction of 1 mole of NaHCO₃ with aqueous HCl, ΔE = 26 kJ”

The sign is positive, since the potential energy of the mixture increased during the reaction.

Let us summarize these results in a table:

<table>
<thead>
<tr>
<th>Sign of ΔE</th>
<th>What happens to the potential energy of the chemicals?</th>
<th>What happens to the kinetic energy of the chemicals?</th>
<th>What happens to the kinetic energy of the surroundings?</th>
<th>What happens to the temperature?</th>
<th>Which way does heat flow?</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>Increases</td>
<td>Decreases during the reaction, then increases to restore thermal equilibrium</td>
<td>Decreases</td>
<td>The reaction mixture and/or the surroundings become <strong>colder</strong></td>
<td>From the surroundings to the reaction mixture</td>
</tr>
<tr>
<td>−</td>
<td>Decreases</td>
<td>Increases during the reaction, then decreases to restore thermal equilibrium</td>
<td>Increases</td>
<td>The reaction mixture and/or the surroundings become <strong>hotter</strong></td>
<td>From the reaction mixture to the surroundings</td>
</tr>
</tbody>
</table>