Thermochemistry is the area of chemistry that focuses on the amount of heat absorbed or released during chemical and physical changes.

All chemical reactions involve energy transformations, changing from one form (chemical potential energy found in the bonds of the reactants or the kinetic energy of moving molecules) to another form such as heat, light and sound. In some reactions, these energy changes can be observed by either an increase or a decrease in the overall energy of the system.

Heat Energy

Heat or thermal energy is kinetic energy which is related to the random movement of atoms and molecules. Temperature is a quantitative measure of “hot” or “cold.” When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and the object is “hot.” When the atoms and molecules are moving slowly, they have lower KE; the object is “cold”. Increasing the amount of thermal energy of a substance will cause its temperature to increase and the substance will expand. Likewise, decreasing the amount of thermal energy in a substance will cause its temperature to decrease and the substance will contract.
What causes the energy changes in chemical reactions?

When substances participate in a chemical reaction they either release or absorb heat. During a reaction, the bonds in the reactants are broken and new bonds are formed, creating the product(s). Energy is required to break bonds, which is then released when new bonds are formed. The amount of energy needed or released for a reaction depends on the balance of energy between that which is required to break the bonds and that which is released when the new bonds are formed.

Example: Forming Water

Hydrogen reacts with oxygen to form water, as is seen by the following equation:

\[ 2H_2 + O_2 \rightarrow 2H_2O \]

In this reaction, the bond between the two hydrogen atoms in the \( H_2 \) molecule breaks, as will the bond between the oxygen atoms in the \( O_2 \) molecule. New bonds will form between two of the hydrogen atoms and a single oxygen atom in the water molecule (the product).

When bonds break, energy is absorbed from the surroundings, making this an endothermic process. Energy is released when new bonds form, this is an exothermic process.

Making and Breaking Bonds

There are several factors which affect the ability of a bond to be broken.

Bond Order:

This is the number of electron pairs shared between two bonded atoms.

- Bond order one – where two electrons are shared in a single bond between two atoms.
- Bond order two – two electron pairs (i.e. four electrons in total) in a double bond.
- Bond order three – three electrons pairs (6 electrons in total) between two atoms in a triple bond.
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Bond Length:
This is the **distance** between the nuclei of the atoms in a bond at the minimum point of energy. Bond lengths depend on the **size** of the atoms involved and the bond **order**. Where there is a bond order of two or three, the levels of attraction between the nuclei are much **stronger** and the atoms are **closer together** (i.e. there is a smaller bond length). Therefore, as the bond order **increases**, the bond length **decreases**. The table below shows the bond length for some common carbon bonds.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (picometers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C―O</td>
<td>143</td>
</tr>
<tr>
<td>C = O</td>
<td>122</td>
</tr>
<tr>
<td>C―C</td>
<td>154</td>
</tr>
<tr>
<td>C = C</td>
<td>134</td>
</tr>
<tr>
<td>C ≡ O</td>
<td>120</td>
</tr>
</tbody>
</table>

Bond Energy:
The energy required to break a bond is called the **bond energy** or bond dissociation energy. Bond energies are measured in the units of kilojoules per mole (kJ.mol\(^{-1}\)).

Practice Questions:
1. **What is thermochemistry?**
   *How the study of how heat absorbed or released affects chemical and physical changes.*

2. **Name the types of observable energy released in a chemical reaction.**
   *Heat, light, sound, electricity*

3. **Define temperature**
   *The amount of kinetic energy possessed by the molecules in a substance.*

4. **Why is energy required for a chemical reaction?**
   *To break the bonds in the reactants*
5. List the three factors which affect the strength of a chemical bond.
   - Bond order
   - Bond length
   - Bond energy

Calculating Bond Energies
Since energy is always needed to break a bond (i.e. the process is endothermic), bond energy is always represented as a positive number. The same amount of energy needed to break a bond is then released when that particular bond forms. The table below shows some of the common bonds seen in this course and their respective bond energies. The examples that follow show how this information can be used to calculate the change in energy (called bond enthalpy) during the course of a reaction.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—H</td>
<td>414</td>
</tr>
<tr>
<td>C—O</td>
<td>358</td>
</tr>
<tr>
<td>C=O</td>
<td>804</td>
</tr>
<tr>
<td>H—O</td>
<td>463</td>
</tr>
<tr>
<td>N—H</td>
<td>391</td>
</tr>
<tr>
<td>H—H</td>
<td>436</td>
</tr>
<tr>
<td>C—C</td>
<td>346</td>
</tr>
<tr>
<td>C=C</td>
<td>614</td>
</tr>
</tbody>
</table>

Example Question
The combustion of methane forms carbon dioxide and water, as shown in the equation below:

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]

Calculate the enthalpy change for this reaction.
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Drawing the diagrams as Lewis diagrams enables the bonds to be viewed:

\[
\begin{align*}
\text{CH}_4 & \quad \text{O}_2 \\
\text{O} & \quad \text{C} = \text{O} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

**Step 1: Identify and total the bonds which are broken for each reactant:**

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Number of bonds</th>
<th>Enthalpy of bonds broken</th>
<th>Total enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{4}</td>
<td>4 mol x C—H</td>
<td>4 x 414 kJ mol\textsuperscript{-1}</td>
<td>1656 kJ</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>2 mol x O=O</td>
<td>2 x 498 kJ mol\textsuperscript{-1}</td>
<td>996 kJ</td>
</tr>
</tbody>
</table>

**Step 2: Total the energy for the bonds broken:**

1656 + 996 = 2652 KJ

**Step 3: Identify and total the bonds which are made for each product:**

<table>
<thead>
<tr>
<th>Product</th>
<th>Number of bonds</th>
<th>Enthalpy of bonds formed</th>
<th>Total enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>2 mol x C=O</td>
<td>2 x 804kJ mol\textsuperscript{-1}</td>
<td>1608 kJ</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>4 mol x O—H</td>
<td>4 x 463 kJ mol\textsuperscript{-1}</td>
<td>1852 kJ</td>
</tr>
</tbody>
</table>

**Step 4: Total the energy for the bonds made:**

1608 + 1852 = 3460 kJ

**Step 5: Use the equation change in energy = energy required to break bonds – energy required to form bonds**

\[
\Delta H = 2652 - 3460 = -808 \text{ kJ mol}^{-1}
\]

**Practice Question:**

Use the bond enthalpies in the table below to calculate the enthalpy change for formation of HCl.

The equation for this reaction is:

\[
\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)
\]
Bond Energy and the Types of Reactions
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<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Enthalpy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—H</td>
<td>436</td>
</tr>
<tr>
<td>Cl—Cl</td>
<td>242</td>
</tr>
<tr>
<td>H—Cl</td>
<td>431</td>
</tr>
</tbody>
</table>

Answer: - 184 kJ mol\(^{-1}\)

Explanation:
Bonds broken:
H—H = 436 kJ mol\(^{-1}\)    Cl—Cl = 242 kJ mol\(^{-1}\)
Enthalpy of bonds broken: 436 = 242 = 678 kJ
Bonds formed:
2 x H—Cl = 431
Enthalpy of bonds formed = 2 x 431 = 862 kJ
Difference: 678 – 862 = - 184 kJ mol\(^{-1}\)

Endothermic Reactions
The features of an endothermic reaction include:

- They remove heat energy from their surroundings in order to break the bonds in the reactants.
- The energy required to break these bonds is greater than the total energy released when the products are formed.
- As the reaction progresses, the products have more energy than the reactants.
- The enthalpy change will be positive
- This type of reaction can be represented by the following formula:

Reactants + Energy \(\rightarrow\) Product

Examples of Endothermic reactions
- The thermal decomposition of limestone
The breakdown of limestone into quicklime (calcium oxide) and carbon dioxide is a very important process used in a variety of industries. Quicklime is used to make steel from iron and also to neutralize soils that are too acidic. The limestone must be heated in a kiln at a temperature of over 900°C before the thermal decomposition reaction, which breaks the bonds in the calcium carbonate will take place. The equation for the reaction is shown below:

\[
\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)
\]

- Ammonium nitrate dissolving in water
  When solid ammonium nitrate (NH₄NO₃) dissolves in a beaker of water, the water becomes colder since the ammonium nitrate absorbs energy from the water. The equation for this reaction is shown below:

\[
\text{NH}_4\text{NO}_3(s) + H_2O \rightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq)
\]

The dissolved ammonium nitrate (NH₄⁺ [aq] and NO₃⁻ [aq] ions) contain more energy than the solid ammonium nitrate.

Other Examples of Endothermic Reactions:
- Photosynthesis
- Liquids evaporating
- Solids melting

Exothermic Reactions

The features of an exothermic reaction include:

- They release energy into their surroundings in the form of heat and light.
- The products have less energy than the reactants since energy is lost from the system
- The enthalpy change will be negative
- We can represent an exothermic reaction using the following general formula:
Examples of Exothermic reactions

- **Combustion Reactions**
  When a fuel such as methane gas in burns oxygen it produces large amounts of heat and light. The burning of fuel is an example of a combustion reaction and is heavily relied on to produce the energy used in the production of electricity. Recall that the general equation for complete combustion is:

  Fuel + Oxygen → Heat + Water + Carbon Dioxide

  The following equation describes the combustion of a hydrocarbon such as methane (CH₄)

  \[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{Heat} + \text{H}_2\text{O} + \text{CO}_2 \]

- **Dissolving Sodium Hydroxide**
  When solid sodium hydroxide pellets, NaOH (s) are dissolved in a beaker of water, the water becomes warmer. This is an exothermic reaction since the heat energy that has been produced has been transferred to the surrounding water. The chemical equation for this reaction is:

  \[ \text{NaOH}_{(s)} \xrightarrow{\text{H}_2\text{O}} \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)} \]

  The dissolved sodium hydroxide (Na⁺_{(aq)} and OH⁻_{(aq)} ions) contains less energy than the solid sodium hydroxide.

Other Examples of Exothermic Reactions:

- Burning magnesium to form magnesium oxide
- Acid-Base (neutralization) reactions
- Explosions such as the Hindenburg disaster

**Practice Questions:**
Decide if the following reactions are endothermic or exothermic. Give a reason for your answer.

1. Magnesium metal is added to hydrochloric acid. The test tube becomes warm and the metal fizzes rapidly, releasing hydrogen gas. Water is vaporized to steam.
   
   Answer: Exothermic
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Justification: There is an increase in the temperature of the surroundings, indicating that heat energy is being released rather than being absorbed.

2. Ice melts
   Answer: Endothermic
   Justification: Ice absorbs heat from its surroundings in order to increase the amount of kinetic energy in its water particles.

3. Two chlorine atoms combine to form a chlorine molecule.
   Answer: Exothermic
   Justification: Bond formation is exothermic as energy is released.

4. Alcohol evaporates when placed on the skin
   Answer: Endothermic
   Justification: The liquid alcohol absorbs the heat from the surroundings to increase the kinetic energy of the particles.

5. Plants use photosynthesis to generate the carbohydrate glucose.
   Answer: Endothermic
   Justification: Plants use solar (light) energy to convert the water and carbon dioxide into the carbohydrate, glucose.

Dissolving and Energy
The process of dissolving a solid such as those described in the examples above contains both endothermic and exothermic processes. When a solid dissolves two processes occur:

1. The solid particles separate. This process must overcome the attractive forces which hold the solid particles together and therefore requires energy to be put into the system. This process is endothermic.

2. The solvent particles are attracted to and surround the separated solid particles. This process is exothermic as it releases energy.
Whether the overall dissolving process is endothermic or exothermic depends on the amount of energy required by the first step in the process compared to the energy released in the second step.

- If less energy is needed for the first process, than is released in the second process, then the process will be exothermic. This will be observed by the test tube or beaker becoming hotter.
- If more energy is needed for the first step, than is released in the second step then the process is endothermic and the test tube or beaker will cool down.

Practice Question:
Explain the 2 types of processes which occur in dissolving. Discuss which process is endothermic and which is exothermic.

The first process involves breaking the solid. This requires energy to overcome the attraction between the solid particles. The second process involves the solvent being attracted to the solid particles. The first process requires energy to be put into the system from the surroundings to break the bonds of the solid, therefore this process is endothermic. The second process releases heat into the environment due to the attraction of the solvent molecules for the solid (solute). This process is therefore exothermic.