Energy and Rates of Reactions

Kenny Chen

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CONTENTS

INTRODUCTION TO ENTHALPY

The part of the universe one chooses to study is called a **system**. The three types of systems are [1]

1. **Open system:** one system that can exchange both matter and energy with its surroundings

2. **Closed system:** one that can exchange energy with its surroundings, but not matter

3. **Isolated system:** one that exchanges neither energy nor matter with its surroundings

Enthalpy

Energy transfers can either occur as heat (q) [2] or as work (w). Energy transfer affects the total energy contained within a system; that is, its internal energy (E).

The components of internal energy that interests us, as Chemists, are:

- **Thermal energy:** energy associated with random molecular motion [3]

- **Chemical energy:** energy associated with chemical bonds and intermolecular forces [4]

Enthalpy is denoted by H and represents the sum of the internal energy and the pressure-volume product of the system
$$H = E + PV$$
In a lab context, the pressure is generally constant, thus the change in enthalpy is

$$\Delta H = \Delta E + P\Delta V$$

Note: Since $P\Delta V$ is usually negligible, especially when dealing with solids or liquids, we can simply say $\Delta H \approx \Delta E$.

Thus, H is the heat content of a system and ΔH is the enthalpy change of a reaction. To determine the type of reaction, we need to consider the sign of ΔH

- For an **endothermic reaction**, $\Delta H > 0$

- For an **exothermic reaction**, $\Delta H < 0$

The internal energy of a system is known as a **function state**. This means that the internal energy, and thus enthalpy, depends on temperature, pressure, kind of substance, and amount of substance present.

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[1]**Thermochemistry:** the study of energy changes that accompany physical or chemical changes of matter.
[2]**Heat:** the amount of energy transferred between substances.
[3]**Thermal energy:** energy available from a substance as a result of the motion of its molecules.
[4]**Chemical system:** a set of reactants and products under study, usually represented by a chemical equation

Molar Enthalpy

The molar enthalpy, denoted by ΔH_x, is the enthalpy change associated with a chemical, physical, or nuclear change mole of a particular substance.

$$\Delta H_x = \frac{\Delta H}{n}$$

In other words, molar enthalpy is just a rate of enthalpy, with respect to moles.

Measuring Energy Change (Enthalpy Change)

Enthalpy change is the difference in enthalpies between the reactants and products during a change. For most chemical reactions, it is very difficult to measure the energy change of a substance through an entire reaction. Most significantly, because the chemicals change into new substances; therefore, what is present at the beginning is different than what is produced.

Therefore, chemists most often measure energy changes **indirectly** using devices called calorimeters [5] and calculating the energy change of the surroundings to infer the energy change of the chemical system.

$$\Delta H_{\text{system}} = -q_{\text{surroundings}}$$

This relationship exists because the energy lost by the system will be gained by the surroundings, and vice versa. This is via the conservation of energy.

The three different types of enthalpy changes are

1. **Physical change:** a change in the form of a substance, in which no chemical bonds are broken

2. **Chemical change:** a change in the chemical bonds between atoms, resulting in the arrangement of atoms into new substances

3. **Nuclear change:** a change in the protons or neutrons in an atom, resulting in the formation of new atoms

Calculating Energy Change

The heat energy can be calculated by using the equation

$$q = mc\Delta T$$

Recall that m is the mass, c is the specific heat capacity, and ΔT is the change in temperature, in degrees celsius.

Sample: A common refrigerant, Freon-12, molar mass 120.91 g/mol, is alternately vaporized in test tubes inside a refrigerator, absorbing heat, and condensed in tubes outside the refrigerator, releasing heat. This results in energy being transferred from the inside to the outside of the refrigerator. The molar enthalpy of vaporized for the

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[5]**Calorimetry:** the technological process of measuring energy changes in a chemical system.

Table 0.1: Molar enthalpies for changes in states of selected substances

Chemical formula	Formula	Molar enthalpy of fusion (kJ/mol)	Molar enthalpy of evaporation (kJ/mol)
sodium	Na	2.6	101
chlorine	Cl_2	6.4	20.4
sodium chloride	$NaCl$	28	171
water	H_2O	6.03	40.8
ammonia	NH_3	-	1.37
freon-12	CCl_2F_2	-	34.99
methanol	CH_3OH	-	39.23
ethylene glycol	$C_2H_4(OH)_2$	-	58.8

refrigerant is 34.99 kJ/mol. If 500.0 g of the refrigerant is vaporized, what is the expected enthalpy change ΔH?

Answer: Solve for the number of moles of Freon-12

$$n = \frac{500.0\,\text{g}}{120.91\,\text{g mol}^{-1}}$$
$$= 4.13497\,\text{mol}$$

Multiply the number of moles by the molar enthalpy

$$\Delta H = (4.13497\,\text{mol})(34.99\,\text{kJ mol}^{-1})$$
$$= 144.6826\,\text{kJ}$$

Sample: What amount of ethylene glycol would vaporize while absorbing 200.0 kJ of heat?

Answer: The enthalpy of vaporization of ethylene glycol is 58.8 kJ mol^{-1}. Using the formula for enthalpy heat, we can solve for n

$$\Delta H_{\text{vap}} = \frac{\Delta H}{n}$$
$$n = \frac{\Delta H}{\Delta H_{\text{vap}}}$$
$$= \frac{200.0\,\text{kJ}}{58.8\,\text{kJ mol}^{-1}}$$
$$= 3.40\,\text{mol}$$

Therefore, the amount of ethylene glycol evaporated is 3.40 mol.

Sample: Calculate the enthalpy change for the vaporization of 100.0 g of water at 100.0 °C.

Answer: From the formula $\Delta H_x = \frac{\Delta H}{n}$, $\Delta H = n\Delta H_x$, all we need to solve for is n then multiply it by ΔH_x

$$n = \frac{100.0\,\text{g}}{16.00\,\text{g mol}^{-1} + 2(1.01\,\text{g mol}^{-1})}$$
$$= 5.54938957\,\text{mol}$$
$$\Delta H = (5.54938957\,\text{mol})(40.8\,\text{kJ mol}^{-1})$$
$$= 226.415\,\text{kJ}$$

Sample: Ethylene glycol is used in automobile coolant systems because its aqueous solutions lower the freezing point of the coolant liquid to prevent freezing of the system during Canadian winters. What is the enthalpy change needed to completely vaporize 500.0 g of ethylene glycol?

Answer: Using the formula for molar enthalpy and solving for enthalpy change $\Delta H = n\Delta H_{\text{vap}}$

$$n = \frac{500.0\,\text{g}}{2(12.01\,\text{g}\,\text{mol}^{-1}) + 6(1.01\,\text{g}\,\text{mol}^{-1}) + 2(16.00\,\text{g}\,\text{mol}^{-1})}$$

$$= 8.05412\,\text{mol}$$

$$\Delta H = n\Delta H_{\text{vap}}$$

$$= (8.05412\,\text{mol})(58.8\,\text{kJ}\,\text{mol}^{-1})$$

$$= 473.58\,\text{kJ}$$

Calorimetry of Physical Changes

Studying energy change requires an isolated system. Two nested disposable polystyrene cups are a fairly effective calorimeter. There are three simplifying assumptions often used in calorimetery:

1. No heat is transferred between the calorimeter and the outside environment

2. Any heat absorbed or released by the calorimeter materials, such as the container, is negligible

3. A dillute aqeuous solution is assumed to have a density and specific heat capacity equal to that of pure water (1.00 g/mL and 4.18 J/(g°C))

Note: what this section boils down to is using specific heat capacity and enthalpy change to calculate the molar enthalpy, and vice versa.

Calorimetry of Chemical Changes

Chemical reactions are also studied using calorimeters. This setup usually involves aqeuous reactant solutions that are considered to be equivalent to water (recall the three rules). Thus, the procedure is the same as the ones in the caorimetry of physical changes. When aqeuous solutions of acids and bases react, they neutralize, while producing enthalpy.

REPRESENTING ENTHALPY CHANGES

The equations used to represent enthapy changes are called **thermochemical equations**. For instance, the decomposition of water

$$H_2O_{(\ell)} \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)} \quad \Delta H_{\text{decomp}} = +285.8\,\text{kJ}\,\text{mol}^{-1}\,H_2O$$

The law of conservation of energy implies that the reverse is also true, only with a opposite enthapy energy change

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)} \quad \Delta H_{\text{comb}} = -285.8\,\text{kJ mol}^{-1}\,H_2$$

Since the former is endothermic, the enthalpy change is positive, while the latter is exothermic, so the enthalpy change is negative. There are four main ways to represent energy changes
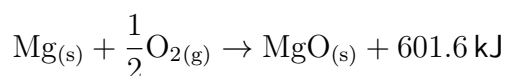
1. Thermochemical equations with energy terms

2. Thermochemical equations with ΔH values

3. Molar enthalpies of reactions

4. Potential energy diagrams

Method 1: Thermochemical Equations with Energy Terms

In this method, we add the energy as a reactant/product into the BCE. For instance, in the electrolysis of water

$$H_2O_{(\ell)} + 285.5\,\text{kJ} \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)}$$
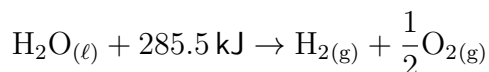
In this case, the energy is a reactant, which means the reaction is endothermic. In the case where the reaction is exothermic, for instance in the synthesis of magnesium oxide

$$Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)} + 601.6\,\text{kJ}$$

In this case, the energy is a product, which means the reaction is exothermic.

Sample: Write a thermochemical equation to represent the exothermic reaction that occurs when two moles of butane burn in excess oxygen gas. The molar enthalpy of combustion butane is -2871 kJ mol^{-1}

Answer: The BCE is

$$2\,C_4H_{10(g)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(g)}$$
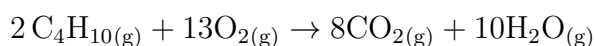
Using mole ratios

$$\Delta H_{\text{comb}} = 2\,\text{mol} \times -2871\,\text{kJ mol}^{-1}]$$
$$= -5742\,\text{kJ}$$

Therefore, since this is an exothermic reaction, the thermochemical equation is

$$2\,C_4H_{10(g)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(g)} + 5742\,\text{kJ}$$

Sample: Write a thermochemical equation to represent the dissolving of one mole of silver nitrate in water. The molar enthalpy of solution is +22.6 kJ mol^{-1}

Answer: This is an endothermic reaction

$$AgNO_{3(s)} + 22.6\,\text{kJ mol}^{-1} \rightarrow Ag^+_{(aq)} + NO_3^-{}_{(aq)}$$
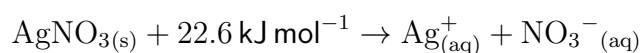
Method 2: Thermochemical Equations with ΔH Values

This method involves writing a BCE and then the ΔH_x value beside it.

Sample: Sulfur dioxide and oxygen react to form sulfur trioxide. The molar enthalpy for the combustion of sulfur dioxide, ΔH_{comb}, in this reaction is $-98.9\,\text{kJ}\,\text{mol}^{-1}$. What is the enthalpy change for this reaction?

Answer: The BCE is

$$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$$
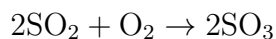
Therefore, with mole ratios

$$\Delta H = 2\,\text{mol} \times -98.9\,\text{kJ}\,\text{mol}^{-1}$$
$$= -197.8\,\text{kJ}$$

Therefore, the thermochemical equation is

$$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3 \quad \Delta H = 197.8\,\text{kJ}$$
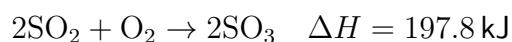
Sample: Write a thermochemical reaction, including a ΔH value, to represent the exothermic reaction between xenon gas and fluorine gas to produce solid xenon tetrafluoride, given that the reaction produces 251 kJ per mole of Xe reacted.

Answer:

$$\text{Xe}_{(g)} + 2\text{F}_{2(g)} \rightarrow \text{XeF}_{4(s)} \quad \Delta H = -251\,\text{kJ}$$
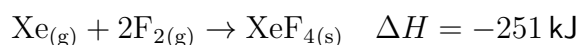
Method 3: Molar Enthalpies of Reaction

The **standard molar enthalpy of reaction** is molar enthalpy that is determined when the initial and final conditiions of the chemical systems are at SATP. The symbol ΔH_x° distinguishes standard molar enthalpies from molar enthalpies, ΔH_x. The table below shows some molar enthalpies of a reaction For an exothermic reaction, the standard molar enthalpy

Table 1 Some Molar Enthalpies of Reaction

Type of molar enthalpy	Example of change
solution (ΔH_{sol})	$\text{NaBr}_{(s)} \rightarrow \text{Na}^+_{(aq)} + \text{Br}^-_{(aq)}$
combustion (ΔH_{comb})	$\text{CH}_{4(g)} + 2\,\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)}$
vaporization (ΔH_{vap})	$\text{CH}_3\text{OH}_{(l)} \rightarrow \text{CH}_3\text{OH}_{(g)}$
freezing (ΔH_{fr})	$\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(s)}$
neutralization (ΔH_{neut})*	$2\,\text{NaOH}_{(aq)} + \text{H}_2\text{SO}_{4(aq)} \rightarrow 2\,\text{Na}_2\text{SO}_{4(aq)} + 2\,\text{H}_2\text{O}_{(l)}$
neutralization (ΔH_{neut})*	$\text{NaOH}_{(aq)} + 1/2\,\text{H}_2\text{SO}_{4(aq)} \rightarrow 1/2\,\text{Na}_2\text{SO}_{4(aq)} + \text{H}_2\text{O}_{(l)}$
formation (ΔH_f)**	$\text{C}_{(s)} + 2\,\text{H}_{2(g)} + 1/2\,\text{O}_{2(g)} \rightarrow \text{CH}_3\text{OH}_{(l)}$

* Enthalpy of neutralization can be expressed per mole of either base or acid consumed.

** Molar enthalpy of formation will be discussed in more detail in Section 5.5.

is measured by taking into account all the energy required to change the reaction system from SATP; in order to intitiate the reaction, and all the energy released following the reaction, as the products are cooled to SATP. For instance, the synthesis to form methanol

$$CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(\ell)} \quad \Delta H_r^\circ = -128.6 \, \text{kJ mol}^{-1}$$
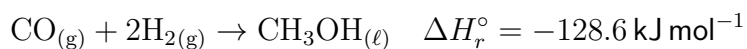
Method 4: Potential Energy Diagrams

This is a visual method of communicating energy transferred by using a **potential energy diagram**. In this theoretical description, the energy transferred during a change is represented as changes in the chemical potential energy of the particles as bonds are broken or formed.
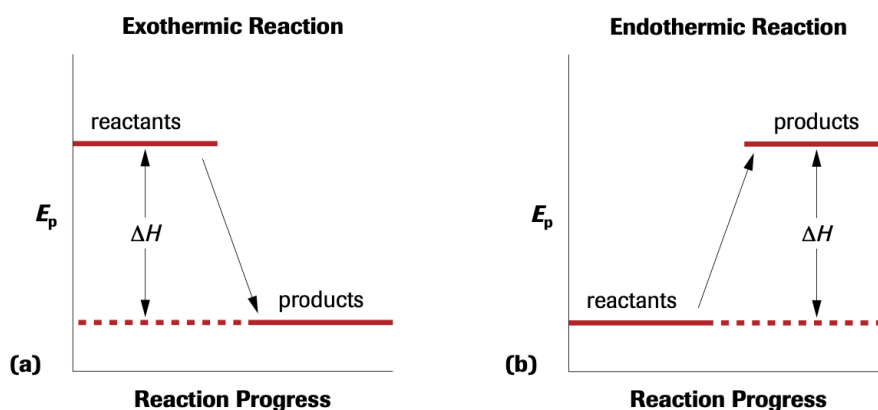

Figure 1: During an exothermic reaction, the products have less potential energy than the reactants. During an endothermic reaction, the products have more potential energy than the reactants.
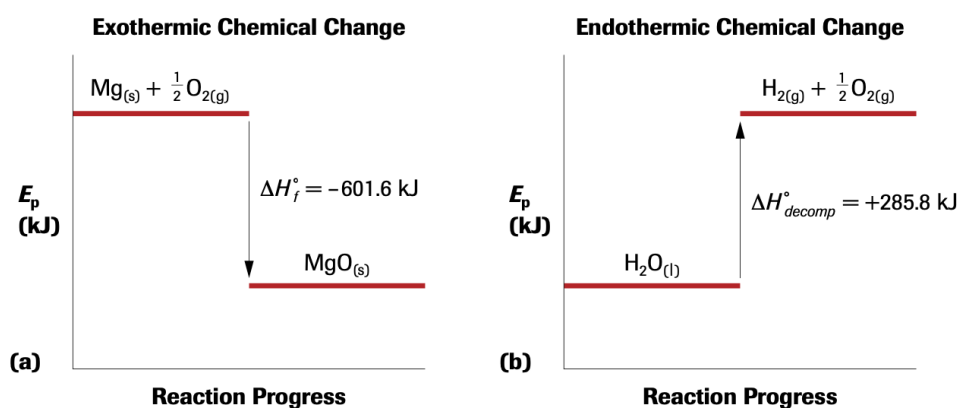

Figure 2: In (a), it is a exothermic reaction in which one mole of magnesium oxide is formed. In (b), it is an endothermic reaction in which water decomposes to hydrogen and oxygen.

HESS'S LAW AND SUMMATION METHOD

Hess's Law states that the value of ΔH for any reaction that can be written in steps equals the sum of the values of ΔH for each of the individual steps.

$$\Delta H_{\text{target}} = \Sigma \Delta H_{\text{known}}$$
$$= \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$$

We can use Hess's Law to estimate the enthalpy change of a large reaction, that may be dangerous for instance, into smaller reactions and estimate the enthalpy change of the large reaction.

The summation method is a method that utilizes Hess's Law to calculate the enthalpy change of a reaction as the sum of the enthalpy change's of smaller reactions

$$\Delta H_{\text{r}}^{\circ} = \Sigma \Delta H_{\text{f}}^{\circ} \text{ products} - \Sigma \Delta H_{\text{f}}^{\circ} \text{ reactants}$$

Note: this method must use enthalpies of formation, ΔH_f.

STANDARD ENTHALPY OF FORMATION

Denoted by ΔH_f°, this is the energy associated with the formation of one mole of a substance from its elements in their standard states. For instance, the standard formation of carbon dioxide

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H_f^{\circ} = -393.5 \,\text{kJ/mol}$$
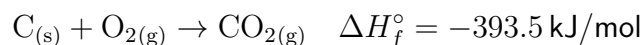
Note: though the name does not include the word "molar", it is always a quantity of energy measured in *energy per mole*. That is, kJ/mol.

> **Important.** Since ΔH_f° deals with the energy associated with the formation of a substance from its elements in standard states, the standard enthalpy of formation for ELEMENTS to be 0. For instance, $Fe_{(s)}$, $O_{2(g)}$, $H_{2(g)}$, $Br_{2(\ell)}$, etc. all have $\Delta H_f^{\circ} = 0$.
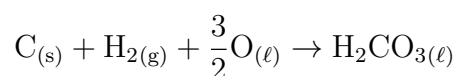
Sample: Write the formation equation for liquid ethanol.
Answer: Liquid ethanol has chemical formula $C_2H_3OH_{(\ell)}$

$$2\,C_{(s)} + 3\,H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow C_2H_3OH_{(\ell)}$$
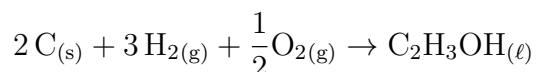
Sample: Write the formation equation for liquid carbon acid.
Answer: Liquid carbon acid has chemical formula $H_2CO_{3(\ell)}$

$$C_{(s)} + H_{2(g)} + \frac{3}{2}O_{(\ell)} \rightarrow H_2CO_{3(\ell)}$$

Hess's Law is also applied to the standard enthalpy of formation

$$\Delta H_f^{\circ} = \Sigma \Delta H_f^{\circ} \text{ products} - \Sigma \Delta H_f^{\circ} \text{ reactants}$$
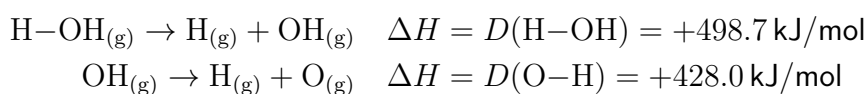
BOND ENERGY METHOD

Bond energy and bond length are related; the greater the bond energy, the shorter the bond.

- Energy is **released** when atoms join together to form covalent bonds

- Energy is **absorbed** to break apart covalently bonded atoms

- **Bond-dissociation energy** (D) is the quantity of energy required to break one mole of covalent bonds in a gaseous species (kJ/mol)

Sample: Calculate the bond dissociation energy in water
Answer: We can consider one mole of water as bonds between $H_{(g)}$ and $OH_{(g)}$; H-OH. Then, the $OH_{(g)}$ will be have a bond considered as O-H.

$$H-OH_{(g)} \rightarrow H_{(g)} + OH_{(g)} \quad \Delta H = D(H-OH) = +498.7\,\text{kJ/mol}$$
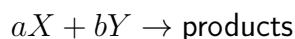$$OH_{(g)} \rightarrow H_{(g)} + O_{(g)} \quad \Delta H = D(O-H) = +428.0\,\text{kJ/mol}$$

Important. The bond dissociation energy provided in a table is not the actual value, but rather the average. An **average bond energy** is the average of the bond-dissociation energies for a number of different species containing one particular bond. Therefore, using them to estimate enthalpy change is not as accurate as with Hess's Law and the Summation Method.

The overall enthalpy change of a reaction can be done by using either of the equations below

$$\Delta H_{\text{rxn}} = \Delta H(\text{bond breakage}) + \Delta H(\text{bond formation})$$
$$\Delta H_{\text{rxn}} = \Delta BE(\text{reactants}) - \Delta BE(\text{products})$$

RATE EQUATIONS AND ORDER OF REACTIONS

Experimental evidence suggests that the rate of a reaction is exponentially proportional to the product of the initial concentrations of the reactants. That is, in a balanced chemical equation
$$aX + bY \rightarrow \text{products}$$
The rate law states that

$$r \propto [X]^m[Y]^n$$
$$= k[X]^m[Y]^n$$

Where m and n describe the relationship between initial concentration and rate, determined emrpically. k is the rate constant, which is determined in several different units, depending on the **overall order of the reactants**. The **order of reaction** is the exponent value that describes the initial concentration dependence of a particular reactant.

Figure 3

When a series of kinetics experiments is performed on a given system, the rates of reaction (1/time) are measured for different initial concentrations of a reactant. When the evidence is graphed, you may see one or more of these results.

(a) In this plot, $r \propto [A]^0$. The reaction is zeroth order with respect to [A].

(b) In this plot, $r \propto [A]^1$. The reaction is first order with respect to [A].

(c) In this plot, $r \propto [A]^n$, where n is greater than 1.

(d) In this plot, $r \propto [A]^2$. The reaction is second order with respect to [A].
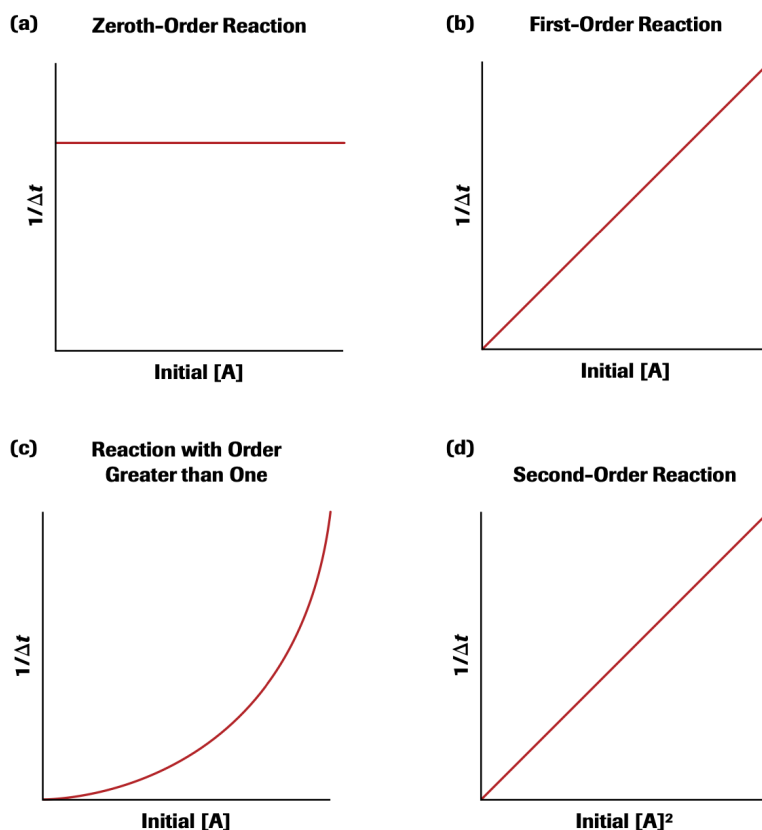

Figure 3: Note that (d) is most likely wrong. It should be curved.

Sample: Consider the data in the table below and calculate the overall order of the reaction. And the rate constant.

Table 0.2

Trial	[A] (mol/L)	[B] (mol/L)	Rate (mol/(Ls))
1	1.0	2.0	0.523
2	5.0	2.0	2.610
3	1.0	3.0	1.177

Answer: Analyzing the trials for [A]

$$(\frac{5.0}{1.0})^y = \frac{2.610}{0.523}$$
$$5^y = 4.99043977$$
$$y = 1$$

Therefore, [A] is a order 1 reactant. Analyzing the trials for [B]

$$(\frac{3.0}{2.0})^y = \frac{1.177}{0.523}$$
$$(1.5)^y = 2.25047801$$
$$y = 2$$

Therefore, [B] is a order 2 reactant. Plugging in these values for k

$$k = \frac{r}{[A][B]^2}$$
$$= \frac{2.610 \, \text{mol L}^{-1} \text{s}^{-1}}{(5.0 \, \text{mol L}^{-1})(2.0 \, \text{mol L}^{-1})^2}$$
$$= 0.1305 \, \text{mol}^{-1} \text{L}^2 \text{s}^{-1}$$

Important. A particular common type of first degree reaction is a **decomposition reaction**. Specifically, **radioactive decay** is a first order reaction.

COLLISION THEORY

Collision theory helps explain the reaction rates of different reactions. According to collision theory, chemical reactions can only occur if energy is provided to break those bonds, the source of that energy being the kinetic energy of molecules.

Concepts of Collision Theory

- A chemical reaction must involve *collisions of particles* which each other and the walls of the container

- An **effective collision** is one that has sufficient energy and correct orientation of the colliding particles so that bonds can be broken and new bonds form (Figure 4)

- **Ineffective collisions** involve particles that rebound from the collision, essentially unchanged in nature

- The rate of a given reaction depends on the *frequency of collisions* and the *fraction* of those collisions that are effective
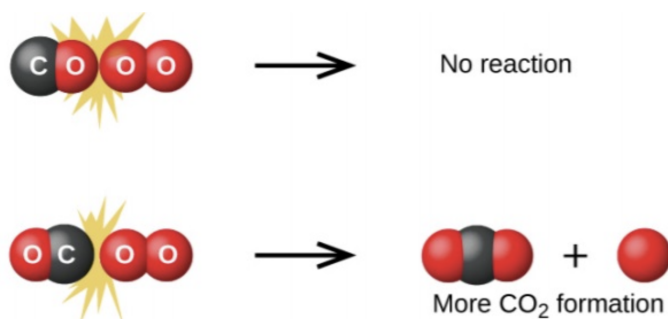

Figure 4: Orieentation of colliding molecules

The formula for the rate in terms of the frequency collisions and fraction of effective collisions is

$$\text{rate} = (\text{frequency of collisions}) \times (\text{fraction of effective collisions})$$

For instance, consider the rate when the frequency of collisions is 1000 collisions per second and the fraction of effective collisions is 1 in 100, the reaction rate is

$$\text{rate} = (\text{frequency of collisions}) \times (\text{fraction of effective collisions})$$
$$= \frac{1000\,\text{collisions}}{1\,\text{s}} \times \frac{1\,\text{reaction}}{100\,\text{collisions}}$$
$$= 10\,\frac{\text{reactions}}{\text{s}}$$

Activation Energy

Activation energy, denoted by E_{act}, is the minimum increase in potential energy of a system required for molecules to react. See Figure 5. Once the activation energy is reached for a reaction, the kinetic energy is either converted into potential energy in an endothermic reaction or potential energy is converted into kinetic energy in an exothermic reaction. Keep in mind that temperature is a measure of the **average kinetic energy** in a system.

For instance, for the sulfur tip of a match, it is particularly easy to create an ignition reaction. However, on the wood end, it requires much more energy to create a reaction. This implies that the sulfur has a lower activation energy compared to wood.

Important. In an exothermic reaction, kinetic energy (measured by temperature) is released into the surroundings, which would increase the kinetic energy of neighbouring molecules and thus cause more exothermic reactions. Consequently, a positive feedback loop is achived. An example of this is can be seen in a wildfire, where the kinetic energy released causes the fire to grow. Increasing temperature has a particular dramatic effect on the reaction rate because it increases both collision frequency and the fraction of effective collisions (due to increase in kinetic energy).

Important. Any reaction, exothermic or endothermic, requires an initial investment of energy; namely, **activation energy**.

- If the molecules have enough kinetic energy, they can approach closely enough for their bond structures to rearrange to form an **activated complex**[6]

- When the reacting system reaches the activated complex, it may reverse the reaction to become the original reactants or form new products

Important. When the products of a reaction have higher potential energy than the reactants, they will have lower kinetic energy (temperature). In their subsequent collisions with other molecules in the system, they will tend to decrease the speed of the molecules, resulting in a drop in temperature of the system. This is why endothermic reactions reduce the temperature of their surroundings.

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[6]**Activated complex:** an unstable molecule with particular geometry. It is unstable because it possesses the maximum potential energy possible. The activated complex is also called the **transition state**.
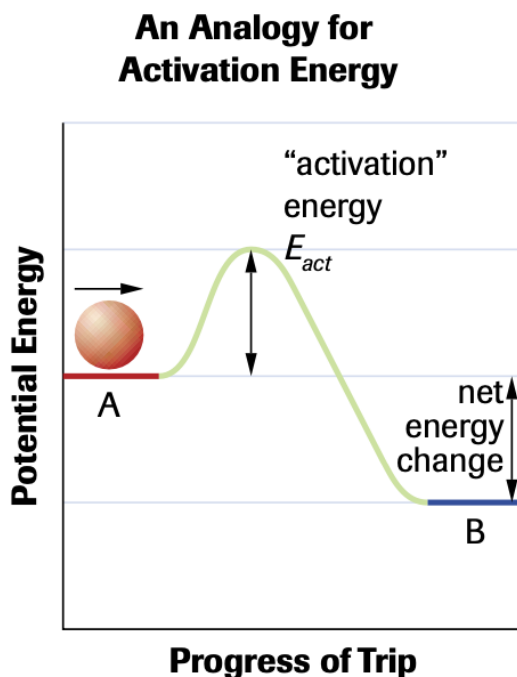
An Analogy for Activation Energy

Figure 5: The activation is required to start the reaction. This figure demonstrates an exothermic reaction, since the products have less potential energy than the reactants.

rate = collision frequency × fraction effective

collision frequency	fraction effective
concentration	nature of reactant
surface area	catalyst
temperature	temperature

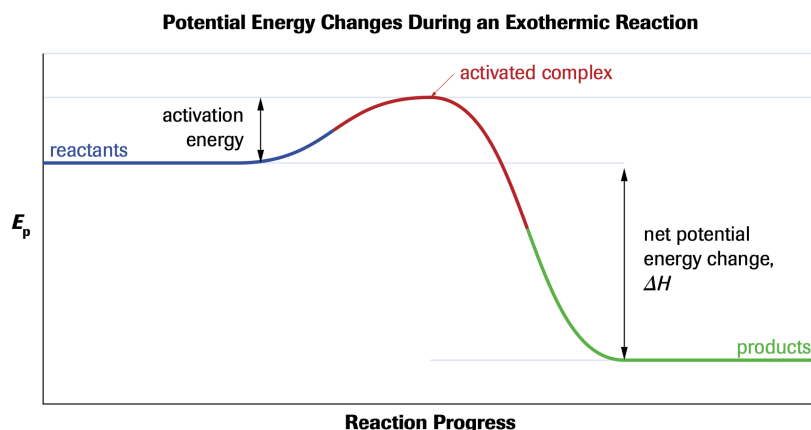**Potential Energy Changes During an Endothermic Reaction**

Figure 5

Over the progress of an effective collision between molecules in the gas phase, the potential energy increases to a maximum at the point of closest approach, then decreases to a final value higher than the initial energy (as the reaction is endothermic). The potential energy gain of the molecules comes from conversion of kinetic energy. The overall reaction would lower the temperature of the system and surroundings.
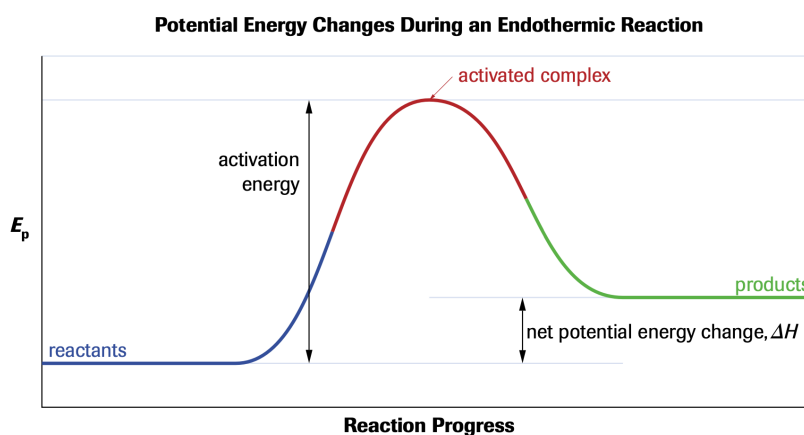
Reaction Mechanisms

- Scientists believe that most chemical reactions occur in a series of **elementary steps**. This overall sequence is called a **reaction mechanism**

- **Elementary step**: a step in a reaction mechanism that only involves one-, two-, or three-particle collisions
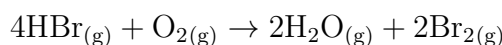
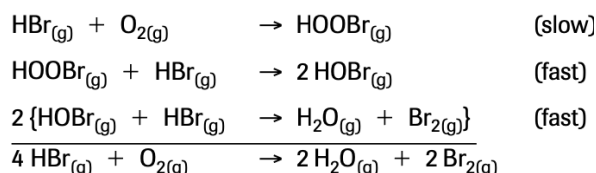**Potential Energy Changes During an Exothermic Reaction**

- **Reaction mechanism:** a series of elementary steps that make up an overall reaction

One good analogy is the Ford automobile production line. Each elementary step can be represented as a worker, specializing in one part of the manufacturing of an automobile. Furthermore, the production rate would be most affected by the slowest worker in the production line. Increasing the concentration at fast steps will have negligible impact on the overall rate, whereas increasing the concentration at the slowest step will have significant impact.

For instance, consider the reaction mechanism of the oxidation of hydrogen bromide

$$4\text{HBr}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)} + 2\text{Br}_{2(g)}$$

Which can be represented as a series of reactions

$$
\begin{array}{llll}
\text{HBr}_{(g)} + \text{O}_{2(g)} & \rightarrow \text{HOOBr}_{(g)} & \text{(slow)} \\
\text{HOOBr}_{(g)} + \text{HBr}_{(g)} & \rightarrow 2\,\text{HOBr}_{(g)} & \text{(fast)} \\
2\,\{\text{HOBr}_{(g)} + \text{HBr}_{(g)} & \rightarrow \text{H}_2\text{O}_{(g)} + \text{Br}_{2(g)}\} & \text{(fast)} \\
\hline
4\,\text{HBr}_{(g)} + \text{O}_{2(g)} & \rightarrow 2\,\text{H}_2\text{O}_{(g)} + 2\,\text{Br}_{2(g)} \\
\end{array}
$$

The products, such as HOBr and HOOBr, which are formed but are reacted immediately again to form new products are called **reaction intermediates**.

Important. The slowest step in any reaction is called the **rate-determining step**. **Reaction intermediates** are short-lived products formed in reaction mechanisms.

In general, if the empirically determined rate equation is

$$r \propto [X]^n [Y]^m$$

The rate-determining step in the reaction mechanism must be

$$nX + mY \rightarrow \text{products or reaction intermediates}$$
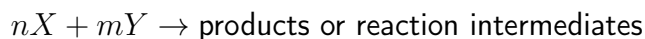
Reaction mechanisms are only "best guesses" at the behaviour of molecules, but there are three rules that must be followed
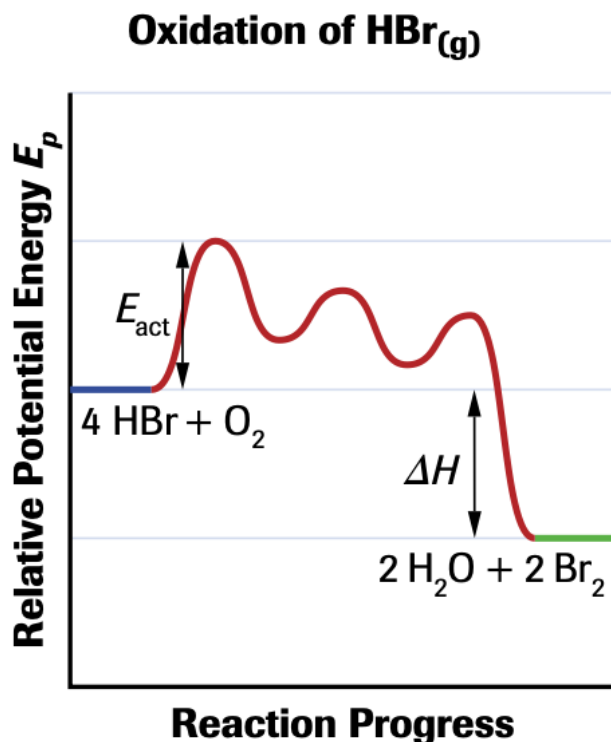
Oxidation of HBr$_{(g)}$

Figure 6: Keep in mind that the first peak is the reaction intermediate because it requires the most substantial increase in energy, and likewise the slowest. Energy released as kinetic energy past this point is sufficient to carry out the reaction mechanism.

1. Each step must be elementary; involving no more than three reactants

2. The slowest rate-determining step must be consistent with the rate equation

3. The elementary steps must add up to form the overall equation

**Theoretical Effect of Chemical Nature of Reactants**

There is a distribution that represents the number of molecules with respect to the kinetic energy. This distribution is called the **Maxwell-Boltzmann Distribution**. In a chemical reaction, an effective collision requires kinetic energy that is converted to potential energy. The minimum energy is called the **threshold energy**[7]

Sample: Use collision theory to explain why the permanganate ion (MnO_4^-) reacts much more quickly with iron(II) ions (Fe^{2+}) than with oxalate ions $(C_2O_4^{2-})$

Answer: This is because oxalate ions are more complex than permanganate ions, requiring more precise collision geometry and a higher activation energy. Thus, the fraction of successful collisions is smaller.

The chemical nature of reactants affects the threshold energy in 2 possible ways:

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[7]**Threshold energy:** the minimum kinetic energy required to convert kinetic energy to activation energy during the formation of the activated complex.

Maxwell-Boltzmann Distribution
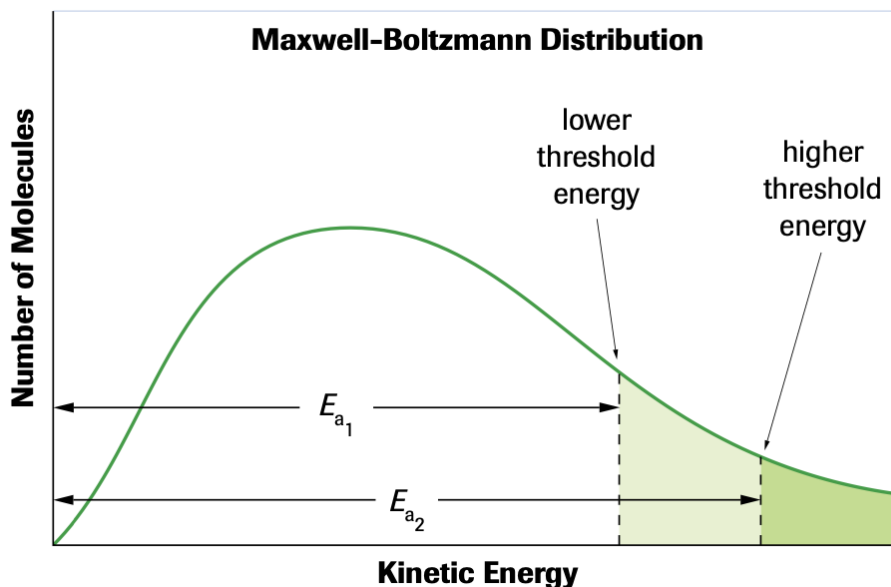
1. Some molecules have bonds that are relatively weak and small activation energy barriers, so the threshold energy is relatively low and a large fraction of them are able to collide effectively

2. Some molecules have complex geomtry with multiple bonds to be broken, thus requires correct orientation when colliding

Theoretical Effect Concentration and Surface Area

- **Concentration:** generally, as the concentration of a reactant increases, so does the reaction rate

- **Surface area:** this only applies to heterogeneous reactions. As surface area of the reactants increases, the reaction rate also increases

Sample: Use collision theory to explain why in a flame, a steel wool burns while a steel nail just glows.
Answer: This is because the steel wool has more surface area than the steel nail. Thus, the collision frequency is higher.

Sample: Use collision theory to explain why liquid nitroglycerin is a dangerous explosion but people with heart conditions take nitroglycerin tablets.
Answer: This is bceause nitroglycerin tablets have a much lower concentration than liquid nitroglycerin.

Theoretical Effect of Temperature

An increase in temperature has a dramatic effect on the reaction rate, because it increases both kinetic energy and collision frequency. This equates to a shift in the Maxwell-Boltzmann distribution curve, where there will be significantly more particles under the curve that are beyond the minimum threshold energy.

Theoretical Effect of Catalysis

Theoretically, a catalyst accelerates a reaction by providing an alternative lower energy pathway from reactants to products. That is, the catalyst allows the reaction to occur through a different reaction mechanism, with different elementary steps that require less energy. If the new mechanism has a lower activation energy, a greater fraction of molecules possesses the minimum required threshold/activation energy (as described by the Maxwell-Boltzmann distribution curve), and thus the reaction rate increases.