Physical Chemistry
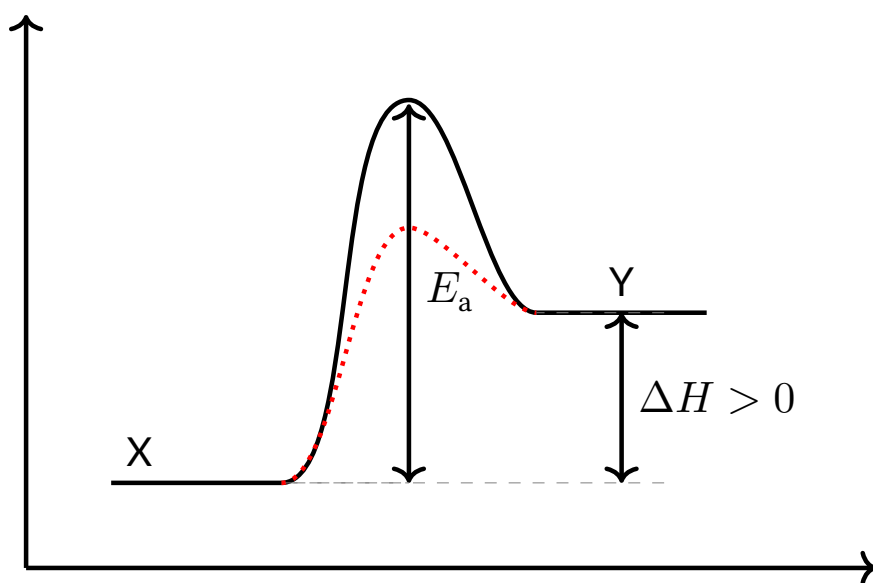

$$\Delta G = \Delta H - T \times \Delta S$$

Chapters 5 to 7, 13 and 19

Contents

Enthalpies

1   Enthalpy Change

Enthalpy refers to the total energy content of a given substance. When reacting two or more compounds together, the bonds within must first be broken, before new bonds are formed. This process involves the transfer of energy, which is measured as the *enthalpy change.*

Enthalpy change, or ΔH, measures the difference in energy content between the reactants and the products of a reaction.

For an exothermic reaction, the energy content of the products is less than that of the reactants. Since the most stable state is that with the least amount of energy, exothermic reactions are said to be *more energetically favoured* $- \Delta H < 0$. Heat is released into the surroundings, and generally, temperature increases.
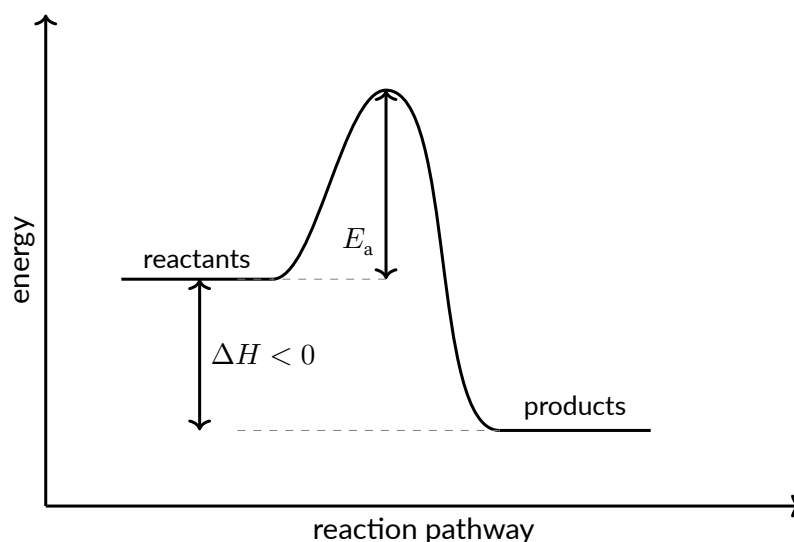
Conversely, for an endothermic reaction, the reverse is true — the energy content of the final products is greater than that of the reactants. Thus, these reactions are somewhat *less energetically favoured*, and less likely to happen. $\Delta H > 0$, and heat is absorbed from the surroundings to feed the reaction.
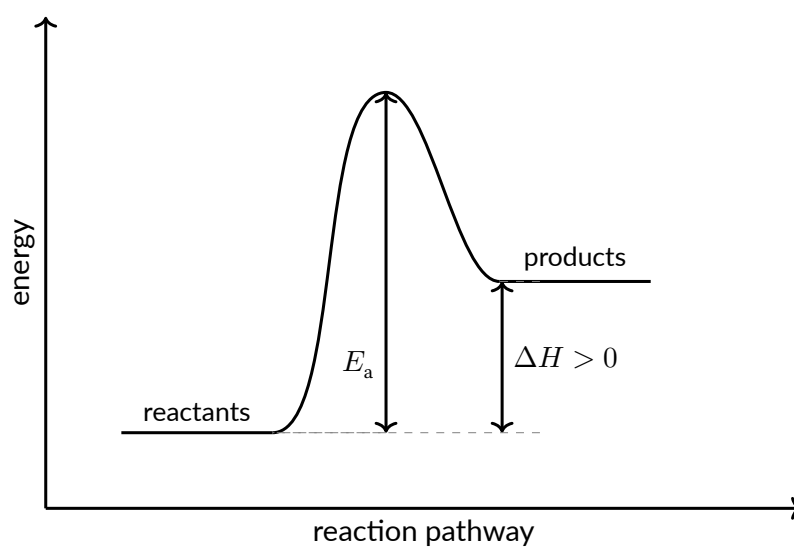
1.1 Activation Energy

Regardless of the enthalpy change of the reaction, some energy must always be input, and thus the activation energy, E_a, is always positive. This is because bonds must always be broken, which requires energy input, before new bonds can be formed.

However, the E_a for endothermic reactions is generally much higher than that for exothermic reactions, since its reactants are generally more stable.

1.2 Thermochemical Equations

A thermochemical equation is simply a normal, balanced chemical equation that has an enthalpy change of reaction associated with it. State symbols must also be included, since a change in state necessitates a change in the enthalpy of the substance.

$$H_2SO_4 \text{ (aq)} + 2\,NaOH \text{ (aq)} \longrightarrow Na_2SO_4 \text{ (aq)} + 2\,H_2O \text{ (}l\text{)}$$
$$\Delta H = -114.2 \,\text{kJ mol}^{-1}$$
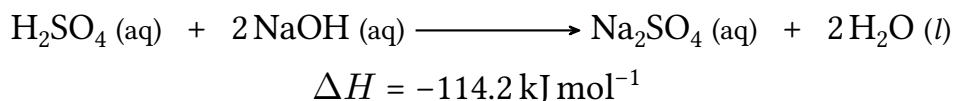
Note that the enthalpy change is per mole *of reaction*, not per mole of any one substance. Thus, if the above reaction were to be rewritten using 1 mole of NaOH instead:

$$\tfrac{1}{2}\,H_2SO_4 \text{ (aq)} + NaOH \text{ (aq)} \longrightarrow \tfrac{1}{2}\,Na_2SO_4 \text{ (aq)} + H_2O \text{ (}l\text{)}$$
$$\Delta H = -57.1 \,\text{kJ mol}^{-1}$$
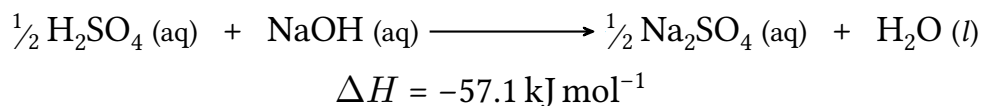
The enthalpy change of the reaction is now half the previous value.

1.3   Bond Dissociation Energy

Bond dissociation energy is the energy required to break *1 mole* worth of *covalent bonds* between two atoms in the *gaseous state*. Note that this value is always positive, since energy is required to break bonds. The larger the value, the stronger the bond.

Bonds are complex beasts; breaking seemingly identical bonds successively will require differing amounts of energy. For instance, the bond dissociation energy for the first $C-H$ bond in CH_4 is $425\,\text{kJ}\,\text{mol}^{-1}$, while that of the second $C-H$ bond (in what is now CH_3) is $470\,\text{kJ}\,\text{mol}^{-1}$.

Naturally, the bond dissociation energies can vary by significant amounts between different molecules — the BDE for a $C-H$ bond in CH_4 is smaller than that of the $C-H$ bond in $CH_2=CH_2$.

1.4   Bond Energy

Due to these problems, the *bond energy* is more frequently used. It is simply the *average* of the bond dissociation energies of the particular bond, sampled from a large variety of molecules.

Thus, it is defined as the *average energy* required to break *1 mole* worth of *covalent bonds* between two atoms in the *gaseous state*.

Furthermore, if the bond in question is between two atoms in a diatomic molecule in the gaseous state, then the bond energy and the enthalpy change of atomisation (ΔH_{atom}, below) are related: The bond energy is twice the enthalpy change of atomisation.

$$\tfrac{1}{2}\,H-H\,\text{(g)} \longrightarrow H\,\text{(g)}$$

$$\Delta H_{atom} = \tfrac{1}{2}\,\text{BE(H}-\text{H)}$$
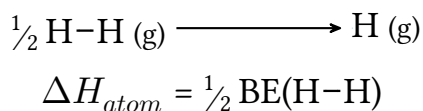
Indeed, since reactions at a fundamental level simply involve breaking and forming bonds, the enthalpy change of a given reaction can be calculated (somewhat inaccurately, due to bond energy being an average) taking the difference between the energies of the bonds formed, and that of the bonds broken.

$$\Delta H_r = \Sigma\,\text{BE(broken)} - \Sigma\,\text{BE(formed)}$$

Accounting for any required changes in state can be done by adding the enthalpy change of either fusion or vaporisation on either side.

1.5   The Law of Hess

Hess's Law of *Constant Heat Summation* states that the enthalpy change of any given reaction is determined only by the enthalpy change between the initial state and final state, regardless of the steps taken in between.
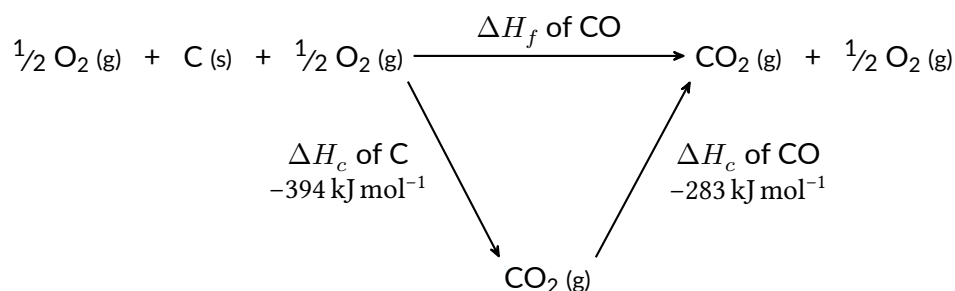
Therefore, whether the reactants reacted directly or through some convoluted pathway to get to the final state, the enthalpy change will be the same. To make use of this, typically an energy cycle diagram is drawn, inserting whatever intermediate reaction is required (with known enthalpies) to get to the final product.

$$\frac{1}{2} O_{2\ (g)}\ +\ C_{\ (s)}\ +\ \frac{1}{2} O_{2\ (g)} \xrightarrow{\ \ \Delta H_f \text{ of CO}\ \ } CO_{2\ (g)}\ +\ \frac{1}{2} O_{2\ (g)}$$

ΔH_c of C
$-394\,\text{kJ}\,\text{mol}^{-1}$

ΔH_c of CO
$-283\,\text{kJ}\,\text{mol}^{-1}$

$CO_{2\ (g)}$

Half a mole of O_2 was added on both sides of the primary reaction to balance it.

Note that the direction of the arrow can be manipulated *at will*, simply by reversing the sign of the associated enthalpy change. Indeed, extra reactants can be introduced too, as long as they are accounted for in all reactions.

1.6   Standard Enthalpy Change

For enthalpy change to have any meaning, it must be defined in terms of a set of standard conditions. In this case, the standard enthalpy change, $\Delta H^{\ominus}$, is defined as the enthalpy change at *298 K*, and a pressure of *1 atm*.

An element or substance in its standard state has the least amount of energy, and is physically stable. Elements in their standard states (C $_{(s)}$, Br$_{2}$ $_{(l)}$, N$_{2}$ $_{(g)}$, etc.) are assigned an enthalpy value of *0*.

The unit of enthalpy change is usually $\text{kJ}\,\text{mol}^{-1}$ (kilojoules per mole). This means that it is always determined per mole of some substance; the greater the number of moles of substance reacting, the greater the total enthalpy change will be, in kJ.

1.7 Determination of Enthalpy Change

Since heat is released or absorbed when a reaction takes place, the enthalpy change, which is the change in energy of the compounds involved, can be determined through the measurement of temperature. Using the formula to determine heat change, q, enthalpy change is then heat change per mole.

$$q = mc\Delta T$$

$$\Delta H = \pm \frac{q}{n}$$

q	Heat change of the reaction.
m	Mass of the solution — in a polystyrene cup experiment, this excludes solids.
c	Specific heat capacity of the solution (usually assumed to be $4.18\,\mathrm{J\,g^{-1}\,K^{-1}}$)
ΔT	Change in temperature of the solution (before and after reaction)
ΔH	Enthalpy change of reaction.

While heat change is a scalar value and is always positive, enthalpy change has a sign, which is decided by whether the reaction is exothermic or endothermic. This can be inferred from the direction of the change in temperature.

1.8 Types of Enthalpy Change

### 1.8.1 Enthalpy Change of Fusion and Vaporisation

The enthalpy change of fusion is the change in enthalpy when *1 mole* of a substance in the *solid state* is heated, at a constant temperature (the melting point), until it becomes a liquid. Similarly, the enthalpy change of vaporisation is the change in enthalpy when *1 mole* of a substance in the *liquid state* is heated at a constant temperature (the boiling point), until it becomes a gas.

These are known as *latent* heats, because the temperature of the substance remains constant at either the melting or boiling points — no heat is actually released. However, since enthalpy measures the actual, total energy content of the compound, enthalpy still increases since the internal energy increases.

As one might expect, the enthalpy changes of fusion and vaporisation are almost always positive, since they involve moving a compound to a higher energy, and thus less stable, state. There are, however, a certain number of exceptions to this. The negative of these enthalpy changes would represent the amount of energy that needs to be removed, per mole, to change the substance from liquid to solid, and gas to liquid respectively.
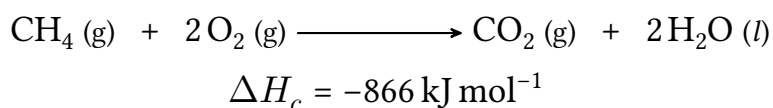
1.8.2 Enthalpy Change of Formation

The standard enthalpy change of formation a compound is the heat evolved when *1 mole* of it is formed from its constituent elements, all in their standard states, under standard conditions. This disregards the actual method of forming the compound, and instead only accounts for simply mashing elements together. For example:

$$2\,C\,(s)\ +\ 3\,H_2\,(aq)\ +\ \tfrac{1}{2}\,O_2\,(g)\ \longrightarrow\ C_2H_5OH\,(l)$$
$$\Delta H = -298\,kJ\,mol^{-1}$$
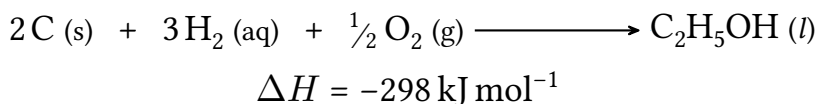
If the enthalpy change of formation of a substance, ΔH_f is > 0, then the compound is less stable than its constituent elements, meaning it is more likely to decompose — the reverse is true if $\Delta H_f < 0$. Note that ΔH_f of elements in their standard states is 0, by definition.

1.8.3 Enthalpy Change of Combustion

The enthalpy change of combustion of a compound is the heat evolved when *1 mole* of it is completely burned in excess oxygen, under standard conditions. This enthalpy change is always negative — heat is always released when things are combusted.

$$CH_4\,(g)\ +\ 2\,O_2\,(g)\ \longrightarrow\ CO_2\,(g)\ +\ 2\,H_2O\,(l)$$
$$\Delta H_c = -866\,kJ\,mol^{-1}$$

1.8.4 Enthalpy Change of Neutralisation

The enthalpy change of neutralisation is the heat evolved when *1 mole* of H_2O is formed when an acid and a base are reacted. Normally, it is the reaction between H^+ ions and OH^- ions in aqueous solution.

$$H^+\,(aq)\ +\ OH^-\,(aq)\ \longrightarrow\ H_2O\,(l)$$
$$\Delta H_{neut} = -57.1\,kJ\,mol^{-1}$$
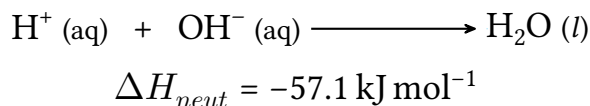
This reaction between H^+ ions and OH^- ions underlies the majority of reactions between acids and bases.

$$HCl\,(aq)\ +\ NaOH\,(aq)\ \longrightarrow\ H_2O\,(l)\ +\ NaCl\,(aq)$$
$$\Delta H_{neut} = -57.1\,kJ\,mol^{-1}$$
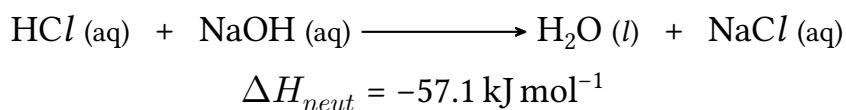
In general, the enthalpy change of neutralisation of all strong acid-base reactions will be the same, at $-57.1\,kJ\,mol^{-1}$. However, for weak acids, the H^+ and OH^- ions only dissociate partially — energy is thus

needed to break these partially dissociated bonds, which decreases the enthalpy change of neutralisation of weak acids and bases.

$$CH_3CO_2H \text{ (aq)} + NaOH \text{ (aq)} \longrightarrow H_2O \text{ (l)} + CH_3CO_2Na \text{ (aq)}$$
$$\Delta H_{neut} = -55.9 \, \text{kJ mol}^{-1}$$
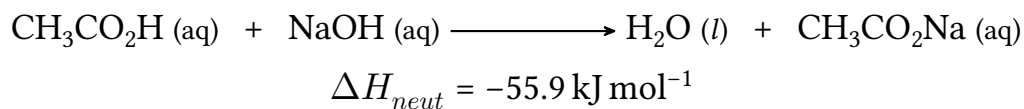
1.8.5 Enthalpy Change of Atomisation

The enthalpy change of atomisation for an element is the energy required to create *1 mole* of gaseous atoms from the element in question in the standard state.

$$\tfrac{1}{2} Cl_2 \text{ (g)} \longrightarrow Cl \text{ (g)}$$
$$\Delta H_{atom} = 122 \, \text{kJ mol}^{-1}$$

For elements that are already gaseous at their standard state, such as F_2 (g), the enthalpy change of atomisation would simply be the bond energy, in this case of the $F-F$ bond. For elements that are monatomic in the gaseous state, such as noble gases, the ΔH_{atom} is 0.

The enthalpy change of atomisation of a non-elemental compound, on the other hand, is the energy required to create gaseous atoms of its constituent elements, from the compound in its standard state. For example:

$$CH_4 \text{ (g)} \longrightarrow C \text{ (g)} + 4H \text{ (g)}$$

Of course, for compounds not initially in the gaseous state, they must first be converted, and the appropriate enthalpy change (of fusion or vaporisation) taken into account.
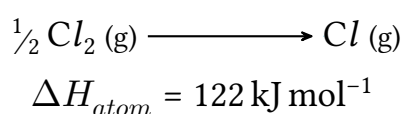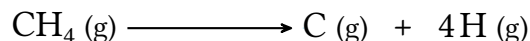
1.8.6 Enthalpy Change of Hydration

The enthalpy change of hydration is the energy released when *1 mole* of gaseous ions is dissolved in an *infinite volume* of water, under standard conditions. ΔH_{hyd} is always negative, as it involves the formation of ion-dipole interactions between the ions in question and the water molecules.

$$\Delta H_{hyd} \propto \frac{q}{r}$$

The enthalpy change of hydration is proportional to the charge density of the ions; the higher the charge density, the stronger the ion-dipole interactions and thus the larger the enthalpy change.

1.8.7 Enthalpy Change of Solution

The enthalpy change of solution is the enthalpy change when *1 mole* of a substance is dissolved in an *infinite volume* of solvent, under standard conditions. The solute and solvent can be anything, even though the solute is usually an ionic compound, and the solvent water.

If ΔH_{sol} is highly positive, then the solute is likely to be insoluble in the solvent, since the reaction would be endothermic. On the other hand, if ΔH_{sol} is negative, then the solute is likely to be soluble in the solvent.

1.8.8 Ionisation Energy

Ionisation energy is the energy required to remove *1 mole* of electrons from *1 mole* of gaseous atoms, forming *1 mole* of *gaseous cations*. The first ionisation energy involves the removal of electrons from neutral atoms, forming singly-charged gaseous cations; the second ionisation energy involves removing electrons from singly-charged gaseous cations, forming doubly-charged gaseous cations, and so on.

As should be obvious, ionisation energy increases with the number of electrons already removed. It is always positive, since energy is required to remove electrons from an atom.

1.8.9 Electron Affinity

Electron affinity is essentially the reverse of ionisation energy, measuring the enthalpy change when *1 mole* of electrons is added to *1 mole* of gaseous atoms, forming *1 mole* of *gaseous anions*. As with ionisation energy, the energy required to do this increases with the number of electrons previously added.

The first electron affinity is usually negative, due to the slight electrostatic attraction between the neutral atom (rather, its nucleus) and the incoming electron. Subsequent electron affinities are usually positive, since energy is required to move a negative electron towards a negatively charged atom.

1.9   Lattice Energy

Lattice energy is the heat released when *1 mole* of an solid ionic compound is formed from its constituent ions in the gaseous state. It is *always negative*, since it involves the formation of ionic bonds between atoms.

The magnitude of lattice energy is a measure of the strength of the ionic bond — the more exothermic it is, the stronger the ionic bond. Ionic bond strength depends on two factors; the magnitude of the charge on both ions, and the ionic radius of the atoms.

$$LE \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

q_+ and q_- represent the charge of the respective ion, and r_+ and r_- represent the ionic radius. Thus, the maximum lattice energy is achieved with the highest charge magnitude and the smallest ionic radius.

## 1.9.1   Theoretical vs. Experimental Lattice Energies

There exists no truly ionic compound — all ionic bonds will have some degree of covalent character, due to the behaviour of electrons. Naturally, some ionic bonds exhibit greater covalent character than others. This is related to the charge density of the cation and the ionic radius of the anion.

If the cation has a high charge density and the ionic radius of the anion is relatively large, then the large electron cloud will be attracted towards the cation (due to higher polarisability, shielding effect, etc.). This creates a situation where the charge is more spread out over the participating ions, resulting in a smaller ionic character and thus greater covalent character. Conversely, if the anion as a small electron cloud, it will be less polarisable, and tend to exhibit greater ionic character.

The calculation of lattice energy assumes a model where the bond is completely ionic, ie. zero covalent character. As this is clearly *not* the case, there are often discrepancies between theoretical and experimental values (from Born-Haber cycles) of lattice energy. If the discrepancy is small, then the ionic bond in question has a large ionic character. Else, it has a larger covalent character.

1.9.2 Born-Haber Cycles

Since it is impractical to determine lattice energy directly by reacting gaseous ions together, the *Law of Hess* can be applied to calculate lattice energy indirectly, using a Born-Haber cycle, which really is just a glorified energy-level diagram.
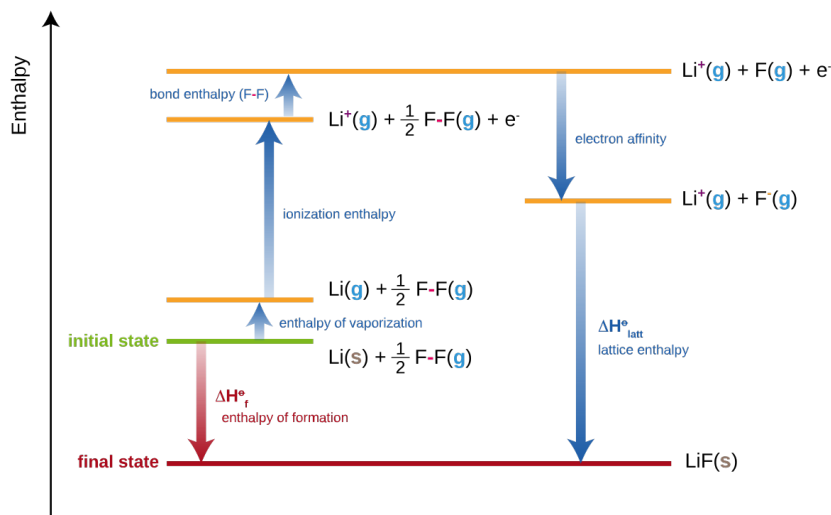

In the example above, the lattice energy of LiF, ΔH_{latt} is being calculated indirectly using various enthalpy changes. The initial state is given an enthalpy of 0. To put into words:
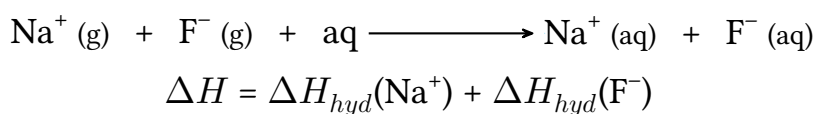
1. Atoms are at their initial, standard state; Li (s) and $\frac{1}{2}$ F$_2$ (g).
   $\Delta H = 0$.

2. Li (s) is heated into the gaseous state, forming Li (g).
   $\Delta H = \Delta H_{fus} + \Delta H_{vap}$.

3. One mole of electrons is removed from Li (g), forming Li$^+$ (g) and e$^-$.
   $\Delta H = \Delta H_{fus} + \Delta H_{vap}$ + First IE (Li).

4. The F$-$F bond is broken, forming F (g).
   $\Delta H = \Delta H_{fuS} + \Delta H_{vap}$ + First IE (Li) + BE(F$-$F).

5. One mole of electrons is added to F (g), forming F$^-$ (g).
   $\Delta H = \Delta H_{fuS} + \Delta H_{vap}$ + First IE (Li) + BE(F$-$F) + First EA (F).

6. LiF (s) is formed from its constituent gaseous ions, Li$^+$ (g) and F$^-$ (g).
   $\Delta H = \Delta H_{fuS} + \Delta H_{vap}$ + First IE (Li) + BE(F$-$F) + First EA (F) + ΔH_{latt}.

7. To determine ΔH_{latt}, ΔH_f is used $-$ the enthalpy change of formation of LiF (s) from constituent elements in their standard state.

8. Thus, applying the *Law of Hess* $-$ $\Delta H_f = \Delta H_{fus} + \Delta H_{vap}$ + First IE (Li) + BE(F$-$F) + First EA (F) + ΔH_{latt}. Rearrange to solve for ΔH_{latt}.

1.9.3 Lattice Energy, ΔH_{sol} and ΔH_{hyd}

These three energies are related; dissolving a solid, ionic compound in water can be split into two sequential processes. First, the formation of gaseous ions form the solid ionic compound:

$$\text{NaF (s)} \longrightarrow \text{Na}^+ \text{ (g)} + \text{F}^- \text{ (g)}$$
$$\Delta H = -LE$$
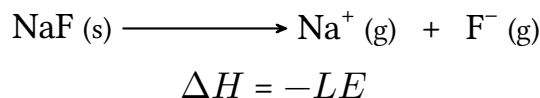
Second, the gaseous are hydrated.

$$\text{Na}^+ \text{ (g)} + \text{F}^- \text{ (g)} + \text{aq} \longrightarrow \text{Na}^+ \text{ (aq)} + \text{F}^- \text{ (aq)}$$
$$\Delta H = \Delta H_{hyd}(\text{Na}^+) + \Delta H_{hyd}(\text{F}^-)$$

Therefore, the total enthalpy change for this process is simply the sum of the enthalpy change of hydration of each ion, less the lattice energy of the final ionic compound.

$$\Delta H_{sol} = \sum \Delta H_{hyd} - LE$$

Therefore, if the magnitude of the lattice energy is greater than the magnitude of the enthalpy changes of hydration, then the overall enthalpy change will be endothermic, and vice versa.
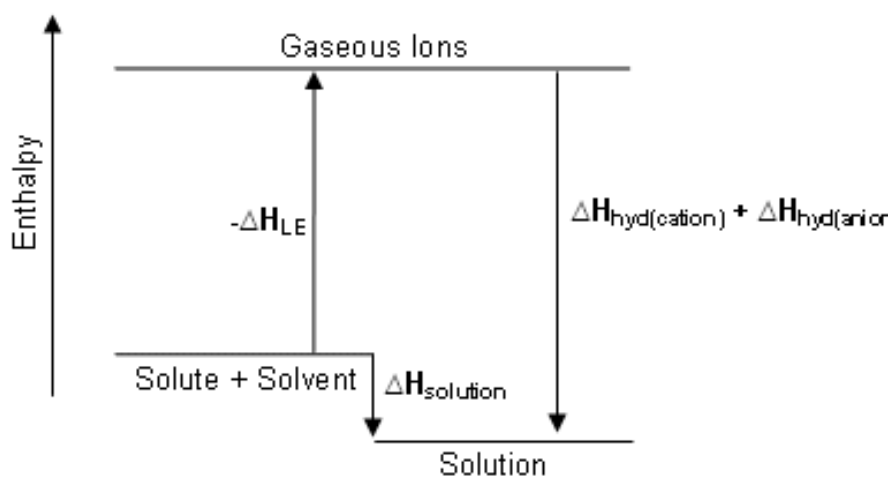
PART II

Gibbs Energy and Entropy

1 Entropy and Spontaneity

The Second Law of Thermodynamics states that for a process to be spontaneous, the total entropy of the system must increase. Entropy, represented by S, is a measure of the number of ways energy can be distributed in a given system. This is often manifested through the motion of particles.

In a solid, movement is restricted and the kinetic energy of particles can only have so many permutations. Entropy is the smallest in the solid state.

In a gas, movement is almost unrestricted, and the possible range of kinetic energies for particles within the system is huge. Thus, entropy is the greatest. The difference in entropy between a gas and a liquid is much greater than that between a solid and a liquid.

1.1 Change in Entropy (ΔS)

The entropy change of a given reaction or action is determined mainly by the effect on the number of ways to distribute energy in the system. The ways in which entropy is changed include changing the *temperature*, *number of moles of gas*, or the *state* of one or more compounds present in the system.

Throughout this terrible, tedious chapter, it is important to note that S $\neq \Delta S$. The units of ΔS are typically $J\,mol^{-1}$ (joules per mole).

1.1.1 Change in Temperature

Increasing the temperature of a system of molecules increases their average kinetic energy, and hence the range of possible energies within the system.

As such, the amount of ways to distribute energy in the system increases, resulting in greater entropy. ($\Delta S > 0$)
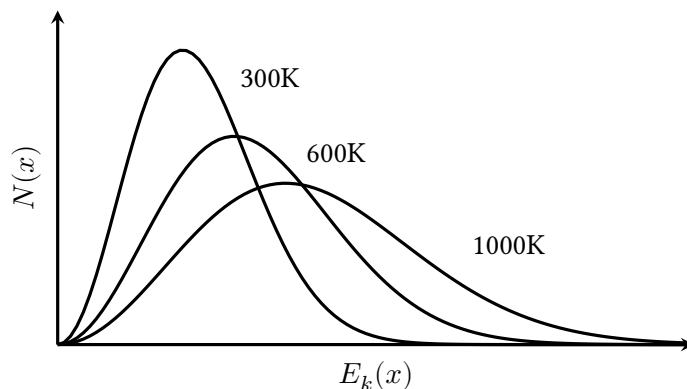

The Maxwell-Boltzmann curve above shows that as temperature increases, the possible range of kinetic energies of the system also increases, thus increasing entropy.

1.1.2 Change in Number of Gas Particles

From the diagram above, it should be obvious that, since gaseous molecules have a much greater entropy, an increase in the number of gas particles will also result in an increase in the entropy of the system ($\Delta S > 0$).

Simply put, if the reaction results in a greater number of gaseous products than reactants, then there will be a net increase in entropy. For example:

$$2\,\text{NaN}_3\text{ (s)} \longrightarrow 2\,\text{Na (s)} \;+\; 3\,\text{N}_2\text{ (g)}$$
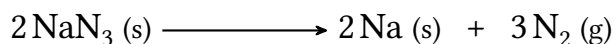
Here, the number of moles of gas *increased* from 0 to 3, hence $\Delta S > 0$. The reverse is also true, naturally — if the number of moles of gas decreases, then the entropy change will be negative.

1.1.3 Change in Phase

When a particular substance melts, boils, condenses, or freezes, the entropy of the system will change accordingly. The diagram below aptly illustrates this.
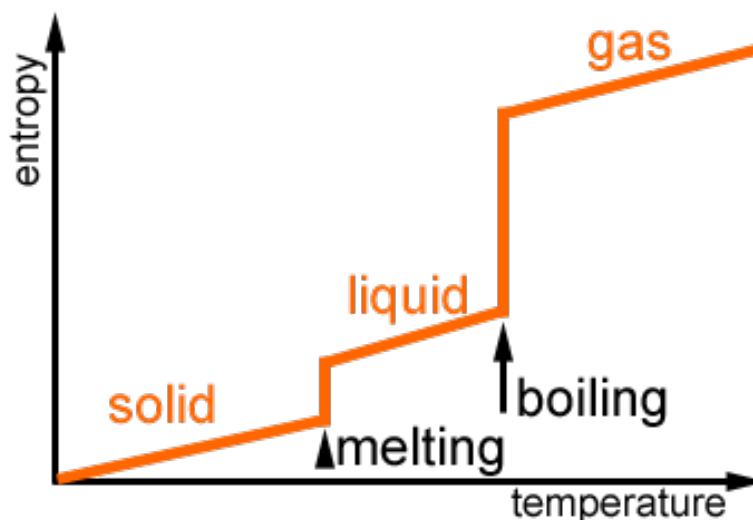
As a substance melts, its molecules are no longer constrained by the structure of the solid state; average kinetic energy increases, and $\Delta S > 0$. As the substance boils, the molecules are completely free to move; naturally, the change in entropy is much greater than for melting. $\Delta S > 0$, obviously.

1.1.4 Change in Volume

If the available volume of a gas increases (at a constant temperature, which implies a decrease in pressure), then the entropy of the system will also increase. The possible distributions of each molecule of gas increases, and hence entropy increases ($\Delta S > 0$). Naturally, the opposite is also true; if the pressure of a system increases at a constant temperature, then the entropy will decrease ($\Delta S < 0$).

Note that when two containers containing two different gases are mixed, the entropy of the system also increases — the total volume that each gas occupies is increased as well.

1.1.5 Dissolution of Ionic Solids

When solid ionic compounds are dissolved in water (or another polar solvent), the total entropy of the system will also change. However, it depends on the interposition of two separate factors; when the ionic compound is dissolved, the constituent ions are able to move around, thus increasing the entropy.

However, the water molecules that are interacting with the dissolved ions are now restricted in movement, and hence entropy decreases as well. Thus, the net change in entropy of the system depends on which of the above factors is more significant. For singly-charged ions, the net change in entropy is usually an increase ($\Delta S > 0$).

1.2   Gibbs Free Energy

Since the enthalpy change (ΔH) and the change in entropy (ΔS) are both crucial in determining whether a given reaction will be spontaneous (occurring without external energy input), they are used together to calculate the change in Gibbs free energy, ΔG. If you paid attention to the cover page, then this equation should be familiar to you:

$$\Delta G = \Delta H - T \times \Delta S$$

In short, the change in Gibbs energy of a given reaction is determined by the temperature, and the changes in both enthalpy and entropy, of the reaction. The units of ΔG are typically kJ mol^{-1} (kilojoules per mole), and that for temperature is K (kelvins).

Exergonic reactions, where ΔG < 0, are said to be energetically feasible, and take place spontaneously. Conversely, endergonic reactions where ΔG > 0 are energetically infeasible, and do not take place spontaneously. ΔG can be 0, for example during melting or boiling.

If ΔG is 0, then the system is *at equilibrium*, ie. $\Delta H = T \times \Delta S$

1.2.1   Effect of Gibbs Free Energy

Given the sign (positive or negative, duh) of both ΔH and ΔS, it is possible to determine if ΔG will increase or decrease with temperature. Thus, it is possible to predict if the reaction will be more or less spontaneous (and thus energetically feasible) with a change in temperature.

A *disgusting* and *abhorrent* table below summarises the four possible scenarios:

ΔH	ΔS	ΔG	Feasibility
< 0	< 0	always < 0	All temperatures
< 0	> 0	always > 0	Never
> 0	< 0	depends	Low temperatures
> 0	> 0	depends	High temperatures

PART III

Reaction Kinetics

1 Collision Theory

The collision theory of reaction is used to represent how individual molecules of reactants actually behave in a given reaction. It models reactions as collisions between molecules, and thus there are three conditions that must be satisfied:

- A collision must occur
- The collision must occur with the molecules in the correct orientation
- The molecules must collide with sufficient speed to overcome the activation energy

Furthermore, the rate of a given reaction depends on the number of effective collisions in a given amount of time — the *effective collision frequency*.

The importance of having the correct orientation can be seen in the electrophilic addition of HBr to an alkene; the δ^+ on the H atom is attacked by the electron-rich π-bond, so naturally the HBr molecule must be oriented such that the H end is facing the alkene.

2 Activation Energy

Activation energy represents the minimum amount of energy required before a reaction can take place — this is usually manifested as the kinetic energy of colliding molecules of reactants, using the collision theory model of reaction. For most reactions, the activation energy is sufficiently high that the rate of reaction is not ridiculously fast, given that there are an enormous number of collisions between molecules at any given time.

2.1 Reaction Pathway Diagram

Activation energy is often represented in two ways; firstly, in the reaction pathway diagram as shown below. Note that even though the reaction is exothermic (it releases energy), it still requires a minimum amount of activation energy (E_a) to take place. On a side note, at the top of the energy "peak", a theoretical activated complex or transition state is formed; this cannot be isolated, and exists only for a tiny amount of time.
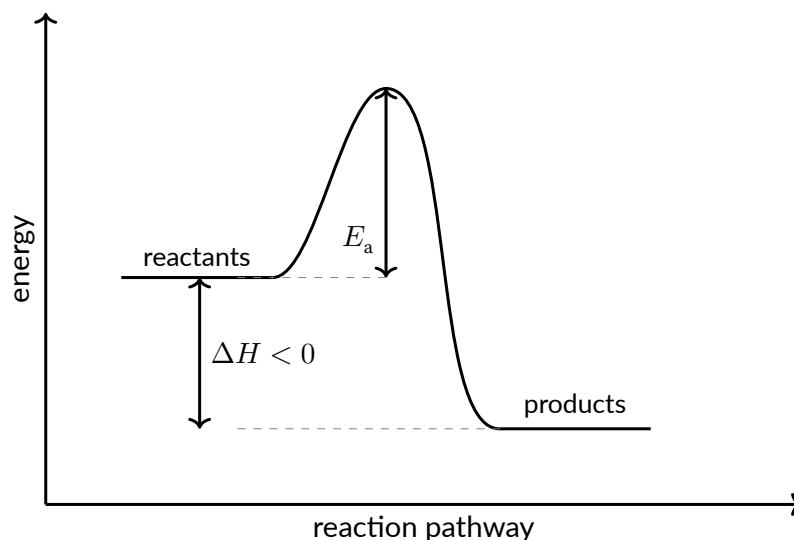
2.2 Maxwell-Boltzmann Distribution Curve

The other way that activation energy can be seen is through a Maxwell-Boltzmann distribution curve.
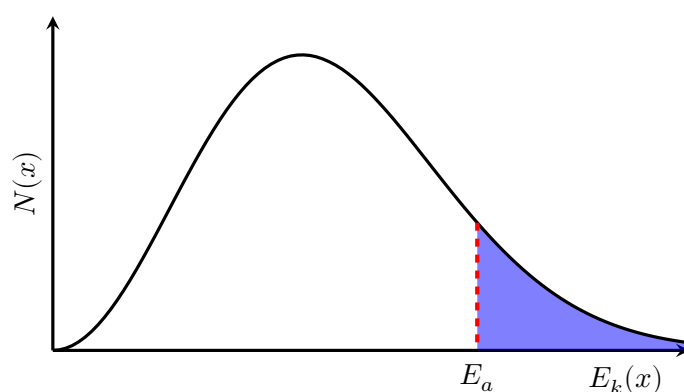
The shaded area represents the total number of molecules whose energy is greater than the activation energy, and can undergo a successful reaction. Note that the reactant molecules must still be oriented correctly for a successful reaction.

Activation energy is independent of the enthalpy change of the reaction, and instead depends on the reactants themselves; it is always positive, because bonds are always broken first before new bonds are formed.

- If reactants are similarly charged, E_a will be high — the reverse is also true
- If the bonds that need to be broken are strong, E_a will be high

Activation energy also affects the rate of a reaction; the lower the E_a, the larger the fraction of molecules that are at or above this energy. Hence, the frequency of effective collisions increase, and hence rate of reaction increases as well.

3   Rates of Reaction

The rate of a reaction is primarily determined by the rate of change of the concentrations of the reactants and products. That is, the faster the concentration of products increases, the faster the rate of reaction. Conversely, the faster the decrease of concentration of reactants, the faster the rate of reaction.
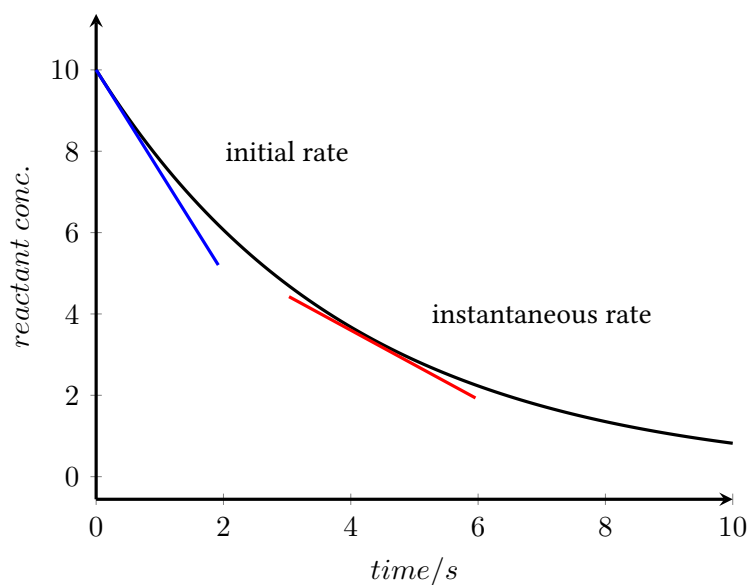
Thus, from a concentration-time graph, it is possible to determine the rate of a reaction through the measurement of the gradient. The initial rate of reaction is the gradient at $t = 0$, the rate of reaction at a given point in time is simply the gradient at that point, and the average rate of reaction is simply the rate of change of concentration across the graph.

The rate equation outlines the relationship between the concentration of a given reactant and the actual rate of the reaction. All its components must be found experimentally, through a tedious process of actually conducting an experiment. It has this general form:

$$\text{Rate} = k[A]^x[B]^y \dots [C]^z$$

R is the rate of the reaction (in $\text{mol dm}^{-3}\,\text{s}^{-1}$). k is the constant of proportionality (discussed below); *[A]*, *[B]* etc. are the concentrations of each reactant, and *x*, *y*, and *z* are the orders of reaction with respect to that reactant.

For single-direction equations (ie. not dynamic equilibrium reactions), the rate equation typically only contains the reactants, not the products. Also, the orders of reaction of each reactant are independent of the stoichiometric coefficients of those reactants in the actual equation. That is to say, an equation with "$4\,CO_2$" does not mean that the order of reaction with respect to CO_2 has to be 4. (it can be, but it's coincidental)

3.1 Order of Reaction

The order of a reaction with respect to a certain reactant determines the magnitude of the change in the rate of reaction when the concentration of that reactant is changed. Since the orders of the reaction are exponents, then it can be inferred that, the increase or decrease in the rate of reaction would be equal to the change in the concentration of a given reactant, to the power of its order.

For instance, given this reaction and its rate equation:

$$2\,NO\ (g) + 2\,H_2\ (g) \longrightarrow N_2\ (g) + 2\,H_2O\ (g)$$
$$\text{Rate} = k[NO]^2[H_2]$$
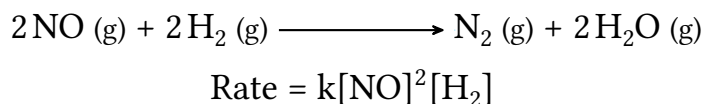
When the concentration of H_2 is doubled, the rate of the reaction will double. However, when [NO] is doubled, the rate of the reaction will increase by 4x. This also shows that the coefficients of the reactants in the chemical equation has nothing to do with the its order of reaction.

Orders of reaction are not restricted to nonzero integers, of course; if the order of reaction of a reactant is negative, then when its concentration is increased, the rate of reaction will decrease; fractional orders also exist.

If the order of reaction of a reactant is 0, it is usually omitted from the rate equation, as changing its concentration has no effect on the rate of the reaction.

The overall order of a reaction is simply the sum of the individual orders of its reactants.

3.2 Rate Constant

The rate constant k is an amalgamation of two factors; the activation energy of the reaction and the temperature of the system.

In the presence of catalysts (discussed later), the activation energy of the reaction will decrease. As the concentrations of the reactants are not affected, the increase in the rate of reaction is manifested in the increase of the rate constant. Similarly, a change in temperature will also affect the rate constant, and hence the rate of the reaction.

Since the concentration of the reactants is represented in $mol\,dm^{-3}$, and the final rate of the reaction is represented with $mol\,dm^{-3}\,s^{-1}$, the rate constant must have appropriate units to "balance" the units of the rate equation. Competent humans should be able to determine the units of the rate constant by comparing the appropriate powers.

4   Determination of Reaction Order

4.1   Initial Rates Method

A reactant's order of reaction can be determined through the measurement of its initial rate, whilst changing the initial concentration of one or more reactants.

Given the initial concentrations of all reactants and the initial rate (for two equations), a relationship between the rates can be determined. For example:

$$\frac{R_1}{R_2} = \frac{k(0.03)^x(1.0)^y(0.5)^z}{k(0.01)^x(1.0)^y(0.5)^z}$$

Given that the initial rates R_1 and R_2 are known, basic math can be applied to solve for x, y, or z. (In this case, x)

4.2   Large Excess Method

The other method of determining the order of a reaction would be to use all but one reactant in large excess. For the purposes of this method, large excess is defined as a concentration 10x or more than the usual. This means that the concentrations of the other reactants appear to be constant, making them pseudo-zero-order.

The reaction must be carried out once per reactant; an aliquot of the reaction mixture is first withdrawn, then the concentration of the reactant in question is measured, and then finally plotted in a concentration-time graph. A few things are in order:

- The withdrawn aliquot must be quenched, either by using ice (cooling), or removing the catalyst if the reaction cannot proceed without it.
- The aliquot is usually titrated with something to determine its concentration.

The order of reaction can be determined by the shape of the graph (discussed below).

5   Rate Graphs

5.1   Concentration-Time Graph

A concentration-time graph is arguably the most versatile and useful graph. In such graphs, the rate of the reaction is represented by the gradient of the graph. As such, the order of the reaction can be determined by the shape of the graph.

Concentration-time graphs are often used with the "large-excess" method, so that only the concentration of the reactant being observed appears to change.

5.1.1   Zeroth Order Reactions

For the zero-order reaction graph below, the rate of the reaction, which is the gradient, is constant even as [E] decreases. Thus, the rate is unaffected by the concentration of [E], and thus is zero order with respect to [E].
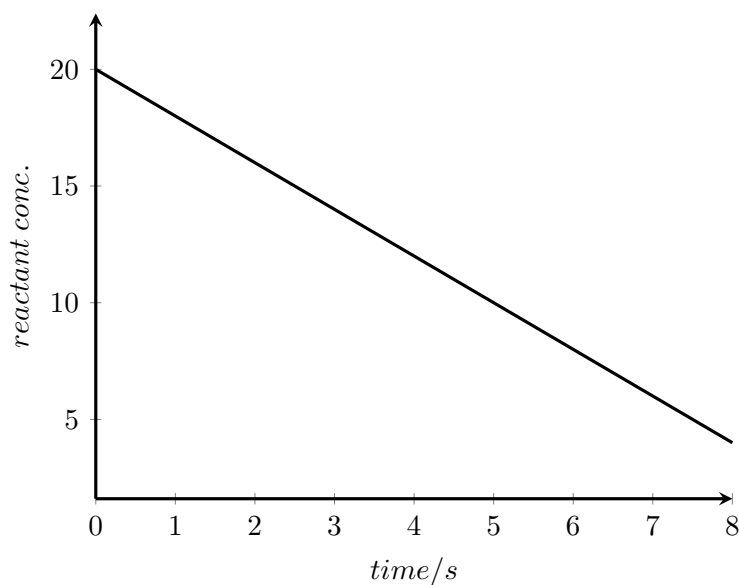
The gradient of the graph is $-kt$, and the y-intercept is the initial concentration, $[E]_0$.
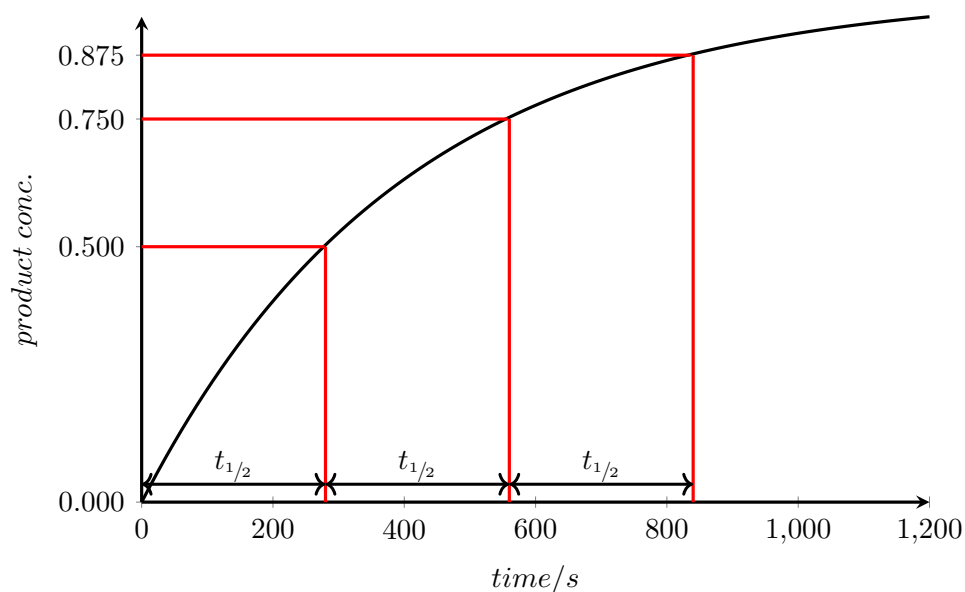
5.1.2 First Order Reactions

For first-order reactions, the concentration of the reactant decreases exponentially with time, and it has a constant half-life. This graph is a curve, because the rate of the reaction decreases as [A] decreases — however, the rate of change of this decrease constant.
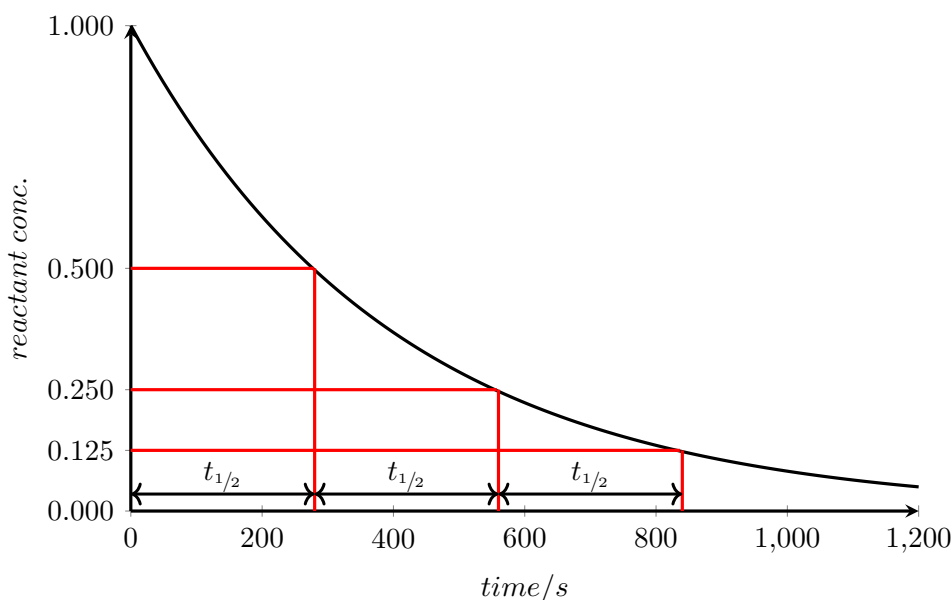
Above, $t_{1/2}$ represents the half-life. The half-life of a reaction is defined as the time taken for the concentration of a reactant to decrease to half its previous value. As it can be seen, in the graph above it goes from 0.10 to 0.05 to 0.025 to 0.0125, and so on.

Conversely, half-life can also be applied to the concentration of a product; it is the time taken for it to increase from 0 to 0.5, from 0.5 to 0.75, from 0.75 to 0.875, and so on. Note that the product concentration is just 1 - reactant concentration.

For an overall first-order reaction, the half-life can be represented with this equation:

$$t_{1/2} = \frac{ln(2)}{k}$$

This means that the half-life is independent of the concentration of any reactant or product, and is only dependent on k, the rate constant.

5.1.3 Second Order (and above) Reactions

The graph for second-order reactions has the same general exponential shape as the graph of a first-order reaction, except that the half-life is not constant. This is the key distinguishing difference between a first-order reaction and reactions of second-order and above.
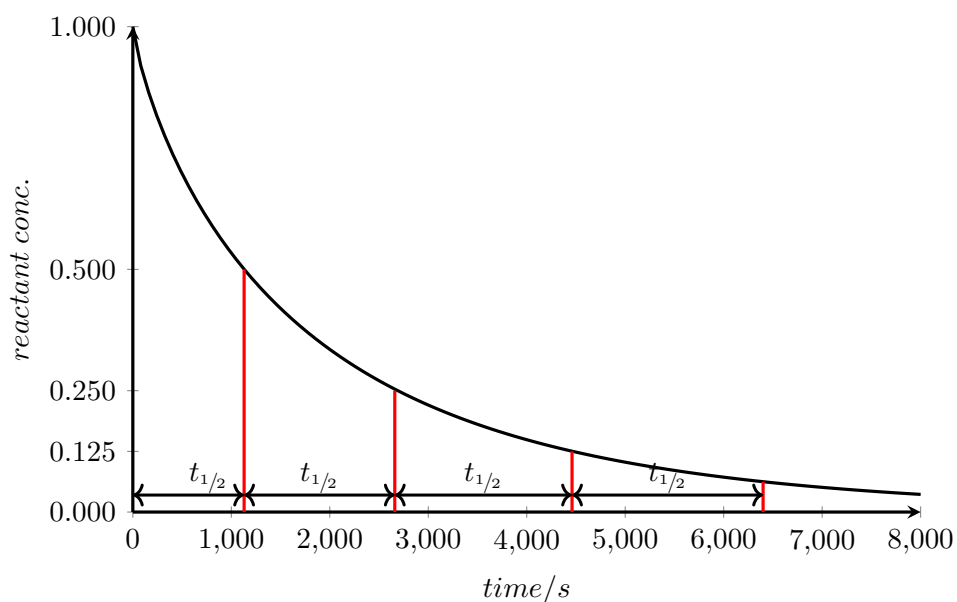
Here, the half-life increases as the concentration of A decreases, so this is not a first- order reaction. It is possible to determine the precise order of a reaction using a rate- concentration graph (below) if the half-life is not constant.
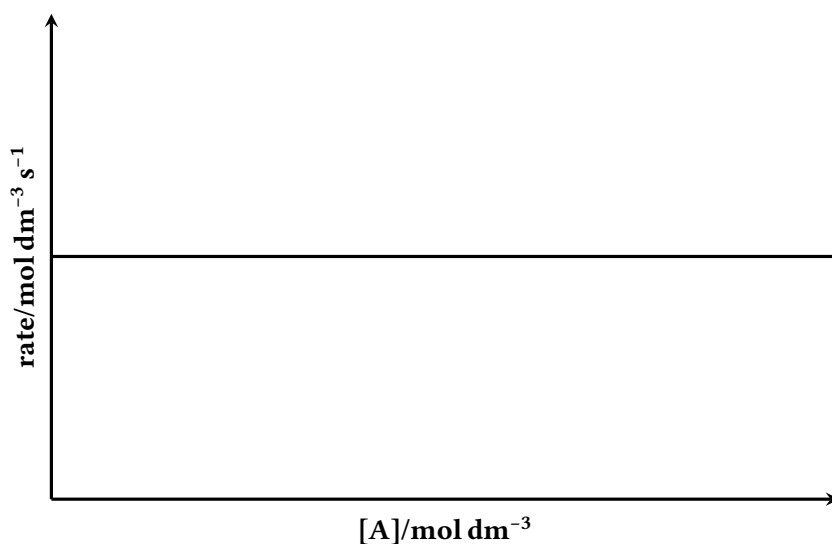
5.2 Rate-Concentration Graph

The other useful graph is a plot of rate of reaction against concentration of a given reactant. This graph can be obtained in two ways;

- Measure the gradient at intervals along the concentration-time graph (this is the rate), plotting these against the concentration of the reactant at that time
- Measuring various initial rates of reaction from changing the initial concentration of a reactant, and plotting those. Note that all but the zero-order graphs pass through the origin, as rate is 0 when [A] is 0.

5.2.1 Zeroth Order Reactions

If a reaction is zero-order with respect to a certain reactant, then the rate of reaction is independent of its concentration. Thus, since rate $= k[A]^0$, then rate $= k$, and the result is a horizontal line. The rate is constant at all values of [A].

5.2.2 First Order Reactions

For first-order reactions, the rate increases with the concentration of the reactant, in a linear manner. As such, rate $= k[A]$, which is in effect a $y = kx$ graph. Note that the graph must cut the origin, since the rate of reaction must be 0 when there is no reactant.
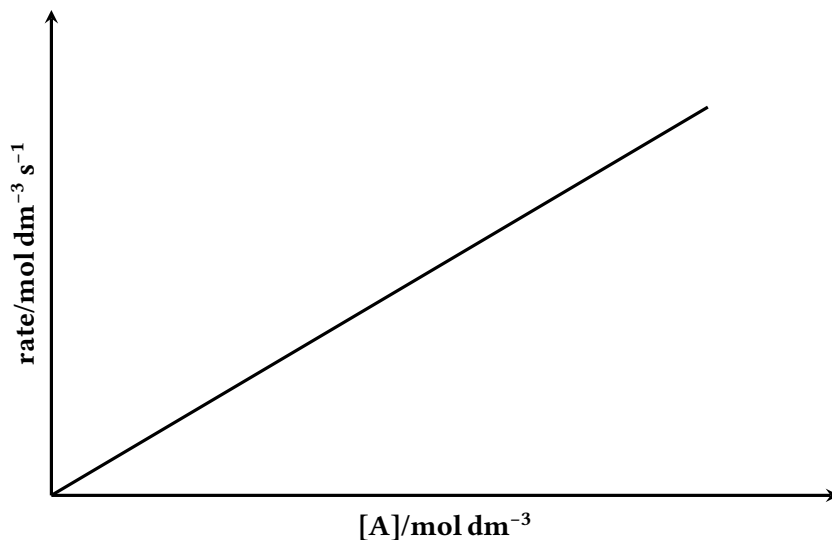
5.2.3 Second Order (and above) Reactions

Of course, for reactions that are second-order or higher, the graph simply looks like an exponentially increasing curve.
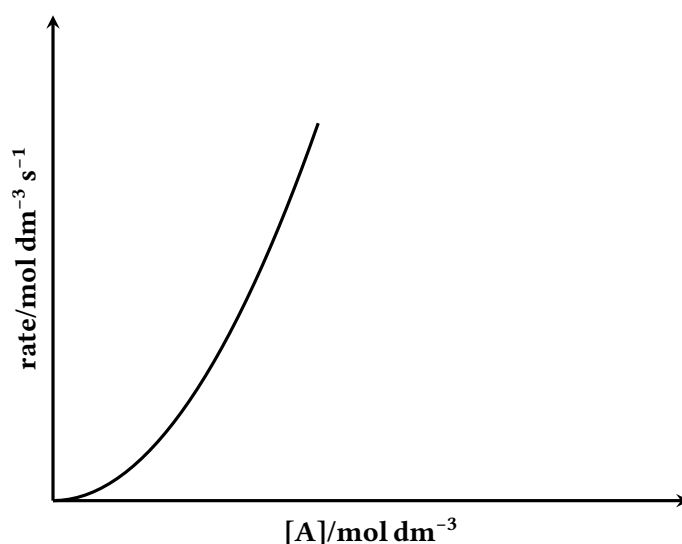
Of course, a better way to affirm the actual order of the reaction would be to plot a graph of rate against concentration squared — resulting in a linear graph. A similar concept can be applied to the third order and above, plotting $[A]^3$ or $[A]^4$ or whatever.

6   Factors Affecting Rate of Reaction

Note that all the factors below with the *exception* of concentration and pressure reflect the change in the rate of reaction through a change in the rate constant, k.

6.1   Concentration and Pressure

When the concentration or pressure (for gas) of a reactant is increased, there are *more molecules of reactant in a given volume*; thus, they are closer together, and they collide more frequently. Thus, there will be a *greater frequency of effective collisions*, resulting in an increase in the rate of reaction.

The statements above should be regurgitated to get the maximum marks. However, there is a caveat — the effect on the rate of reaction is only applicable if the reactant in question appears in the rate equation. Hence, it must be in the rate-determining step as well.

6.2   Surface Area of Solids

If the reaction involves a solid reactant, then the exposed surface area of the block is also a determining factor. With a greater surface area, there is a *greater probability* that other reactants can come into contact with the solid, thus *increasing the effective frequency of collisions*, thus increasing the rate of reaction.

As an example, a single large block of solid reactant will result in a slower rate of reaction as opposed to the use of a finely powdered solid reactant. This effects a change in k.

6.3 Temperature

Other than simply increasing the frequency of collisions, which the factors above have dealt with, a more effective method of increasing the rate of reaction is to increase the number of reactant molecules that are successful in colliding. There are two methods:

- Increasing the average energy of the collisions
- Reducing the energy barrier

By increasing the temperature, the rate constant k is also increased. From looking at the Maxwell-Boltzmann curve below, it can be seen that when the temperature of the system increases, there is a *greater proportion* of molecules that have a kinetic energy greater than the activation energy; hence, more of the collisions that occur will result in a successful reaction.
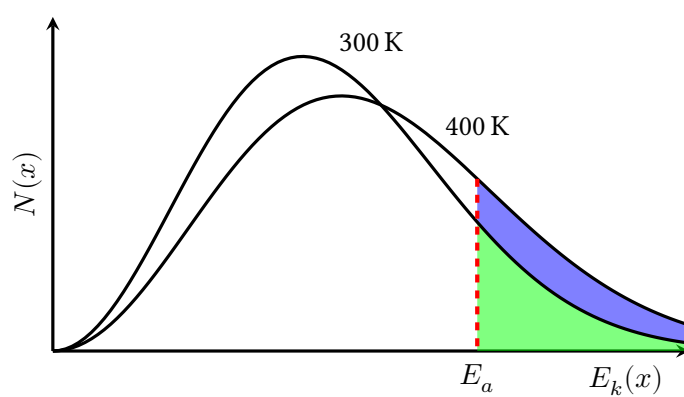
As the diagram illustrates, when the temperature is increased by $100\,\mathrm{K}$, the proportion of molecules that have a kinetic energy greater than the activation energy increases, from just the green area to the sum of the blue and green areas.

6.4 Effect of Light

Light can also have an effect. When certain molecules absorb light energy, it is manifested as kinetic energy, resulting in a greater proportion of molecules that are beyond the energy barrier of the activation energy.

6.5 Catalysts

The other method of course is to reduce the energy barrier itself. This is done by using a catalyst, which provides an *alternative pathway* to the original. This is important — it does not modify the activation energy of the actual reaction, it just provides another way to get to the products.

From the Maxwell-Boltzmann curve, this would increase the number of molecules that have a kinetic energy greater than the activation energy, since this barrier is now lower.
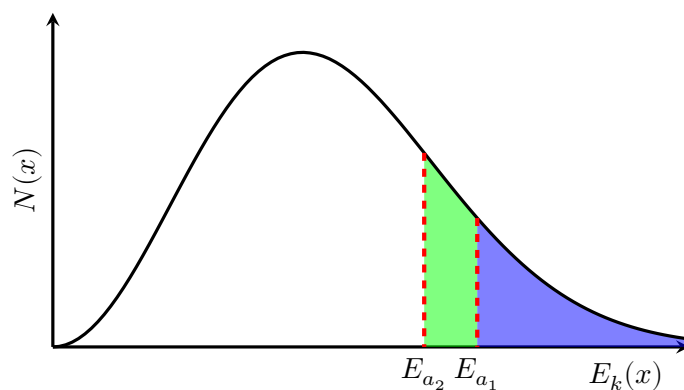
The activation energy decreases from E_{a_1} to E_{a_2}, so the number of molecules greater than the activation energy increases from just the blue area, to the sum of the blue and green areas.

This effect can also be similarly illustrated with a reaction pathway diagram — the one found on the cover page, you fool.
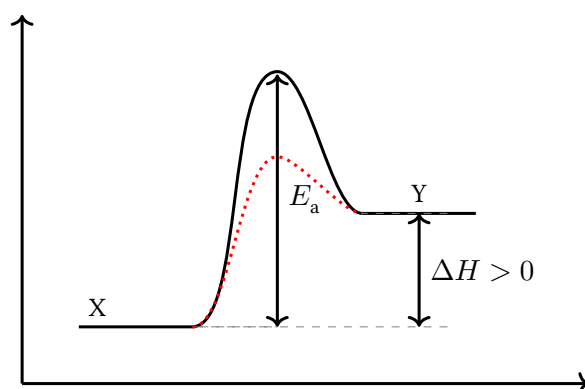
The red dotted line represents the alternative pathway that is taken. As such, the frequency of effective collisions increase, and thus rate of reaction increases.