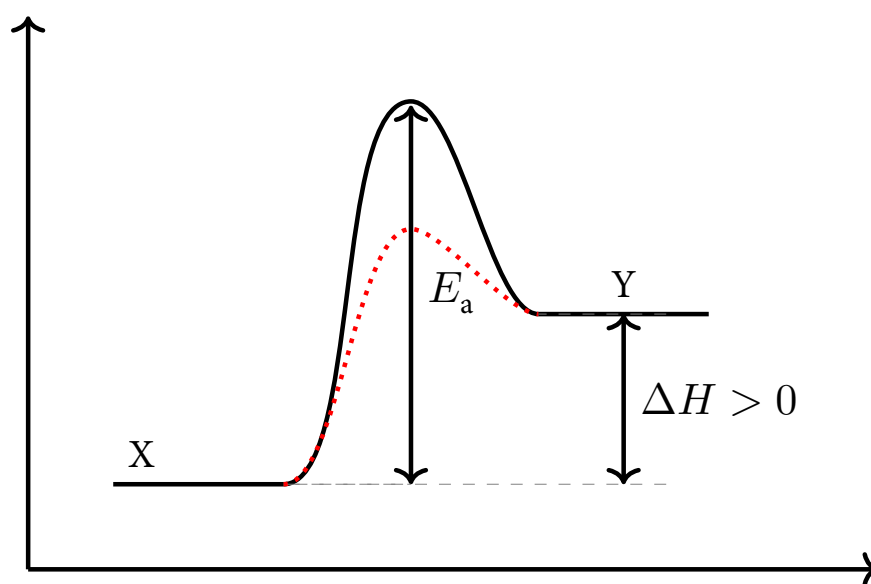


# Physical Chemistry



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

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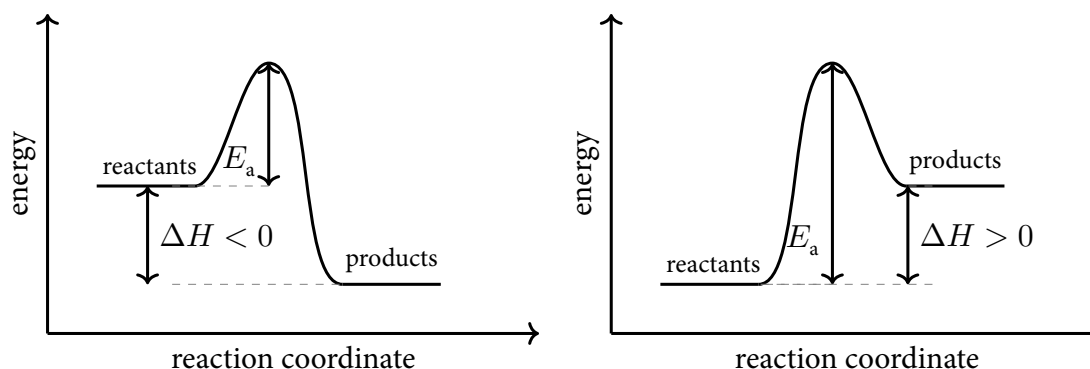
# Enthalpies

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## 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. Enthalpy change, or  $\Delta H$ , 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*;  $\Delta H > 0$ , and heat is absorbed from the surroundings to feed the reaction.

### 1.1 Activation Energy

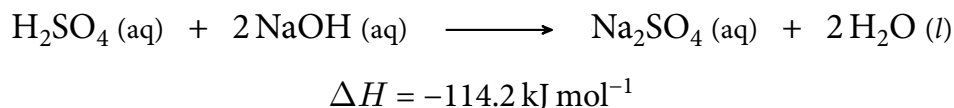
Regardless of the enthalpy change of the reaction, some energy must always be inputted, and thus the activation energy,  $E_a$ , is always positive. This is because bonds must always be broken before new bonds can be formed, requiring some amount of input energy.

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

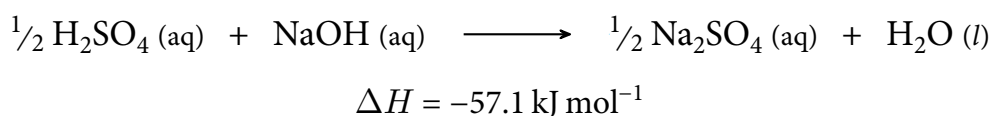


## 1.2 Thermochemical Equations

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.



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:



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<sub>4</sub> is 425 kJ mol<sup>–1</sup>, while that of the second C–H bond (in what is now CH<sub>3</sub>) is 470 kJ mol<sup>–1</sup>.

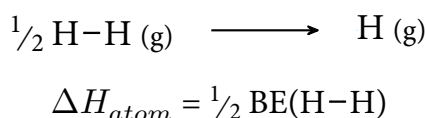
Naturally, the bond dissociation energies can vary by significant amounts between different molecules — the BDE for a C–H bond in CH<sub>4</sub> is smaller than that of the C–H bond in CH<sub>2</sub>=CH<sub>2</sub>.

## 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 ( $\Delta H_{atom}$ , below) are related: The bond energy is twice the enthalpy change of atomisation.



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) by taking the difference between the energies of the formed bonds and the broken bonds.

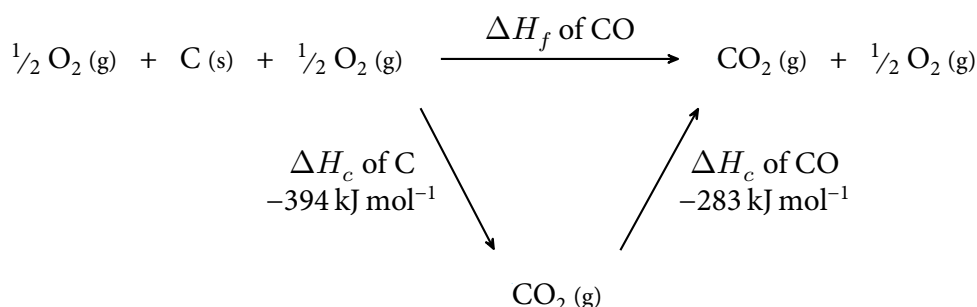
$$\Delta H_r = \Sigma \text{BE}(\text{broken}) - \Sigma \text{BE}(\text{formed})$$

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, an energy cycle diagram is typically drawn, inserting whatever intermediate reaction is required (with known enthalpies) to get to the final product.



Half a mole of  $\text{O}_2$  was added on both sides of the primary reaction to balance it.

## 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,  $\Delta H^\circ$ , 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<sub>2</sub> (l), N<sub>2</sub> (g), etc.) are assigned an enthalpy value of 0.

The unit of enthalpy change is usually kJ mol<sup>-1</sup> (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 J g <sup>-1</sup> K <sup>-1</sup> )
$\Delta T$	Change in temperature of the solution (before and after reaction)
$\Delta H$	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 temperature change.

## 1.8 Types of Enthalpy Change

### 1.8.1 Enthalpy Change of Fusion and Vaporisation

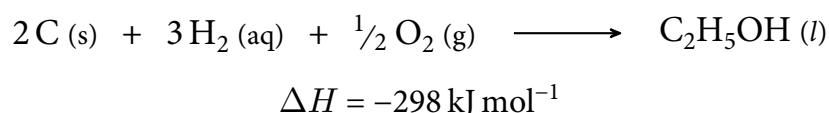
The enthalpy change of fusion is the change in enthalpy when *1 mole* of a substance in the *solid state* is heated, at a constant temperature (the melting point), until it becomes a liquid. Similarly, the enthalpy change of vaporisation is the change in enthalpy when *1 mole* of a substance in the *liquid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

### 1.8.2 Enthalpy Change of Formation

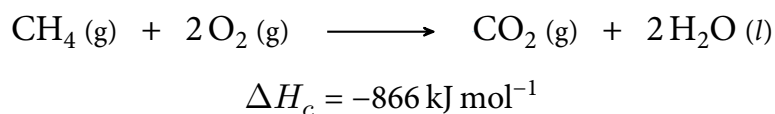
The standard enthalpy change of formation a compound is the heat evolved when *1 mole* of it is formed from its constituent elements, all in their standard states, under standard conditions. This disregards the actual method of forming the compound, and instead only accounts for simply mashing elements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



If the enthalpy change of formation of a substance,  $\Delta H_f$  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  $\Delta H_f$  of elements in their standard states is 0, by definition.

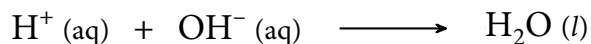
### 1.8.3 Enthalpy Change of Combustion

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.



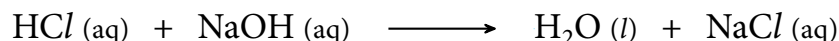
### 1.8.4 Enthalpy Change of Neutralisation

The enthalpy change of neutralisation is the heat evolved when *1 mole* of  $\text{H}_2\text{O}$  is formed when an acid and a base are reacted. Normally, it is the reaction between  $\text{H}^+$  ions and  $\text{OH}^-$  ions in aqueous solution.



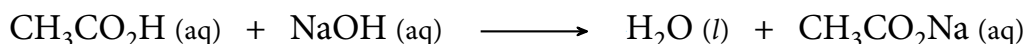
$$\Delta H_{\text{neut}} = -57.1 \text{ kJ mol}^{-1}$$

This reaction between  $\text{H}^+$  ions and  $\text{OH}^-$  ions underlies the majority of reactions between acids and bases.



$$\Delta H_{\text{neut}} = -57.1 \text{ kJ mol}^{-1}$$

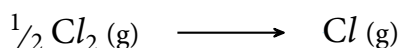
In general, the enthalpy change of neutralisation of all strong acid-base reactions will be the same, at  $-57.1 \text{ kJ mol}^{-1}$ . However, for weak acids, the  $\text{H}^+$  and  $\text{OH}^-$  ions only dissociate partially — energy is thus needed to break these partially dissociated bonds, which decreases the enthalpy change of neutralisation of weak acids and bases.



$$\Delta H_{\text{neut}} = -55.9 \text{ kJ mol}^{-1}$$

### 1.8.5 Enthalpy Change of Atomisation

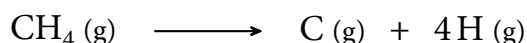
The enthalpy change of atomisation of an element is the energy required to create *1 mole* of gaseous atoms from the element in the standard state.



$$\Delta H_{\text{atom}} = +122 \text{ kJ mol}^{-1}$$

For elements that are already gaseous at their standard state, such as  $\text{F}_2 (\text{g})$ , the enthalpy change of atomisation would simply be the bond energy, in this case of the  $\text{F}-\text{F}$  bond. For elements that are monatomic gases in the standard state, such as noble gases, the  $\Delta H_{\text{atom}}$  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:



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.  $\Delta H_{hyd}$  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  $\Delta H_{sol}$  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  $\Delta H_{sol}$  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

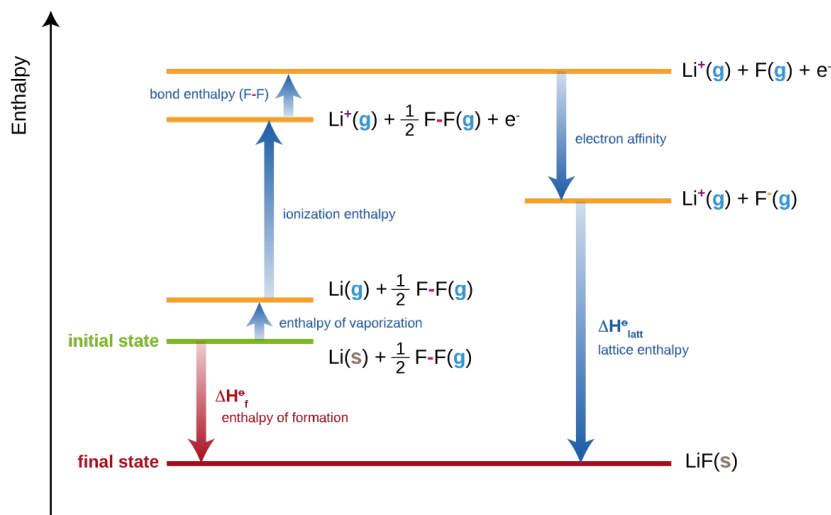
There exists no truly ionic compound — all ionic bonds will have some degree of covalent character, due to the behaviour of electrons. Naturally, some ionic bonds exhibit greater covalent character than others. This is related to the charge density of the cation and the ionic radius of the anion.

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 has 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.



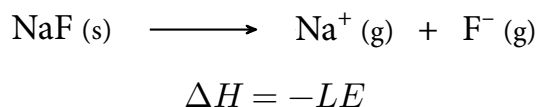
In the example above, the lattice energy of LiF,  $\Delta H_{\text{latt}}$  is being calculated indirectly using various enthalpy changes. The initial state is given an enthalpy of 0. To put into words:

1. Atoms are at their initial, standard state; Li (s) and  $\frac{1}{2} \text{F}_2$  (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  $\text{Li}^+$  (g) and  $\text{e}^-$ .  
 $\Delta H = \Delta H_{fus} + \Delta H_{vap} + \text{First IE (Li)}$ .
4. The F-F bond is broken, forming F (g).  
 $\Delta H = \Delta H_{fus} + \Delta H_{vap} + \text{First IE (Li)} + \text{BE(F-F)}$ .
5. One mole of electrons is added to F (g), forming  $\text{F}^-$  (g).  
 $\Delta H = \Delta H_{fus} + \Delta H_{vap} + \text{First IE (Li)} + \text{BE(F-F)} + \text{First EA (F)}$ .
6. LiF (s) is formed from its constituent gaseous ions,  $\text{Li}^+$  (g) and  $\text{F}^-$  (g).  
 $\Delta H = \Delta H_{fus} + \Delta H_{vap} + \text{First IE (Li)} + \text{BE(F-F)} + \text{First EA (F)} + \Delta H_{\text{latt}}$ .
7. To determine  $\Delta H_{\text{latt}}$ ,  $\Delta H_f$  is used — the enthalpy change of formation of LiF (s) from constituent elements in their standard state.
8. Thus, applying the *Law of Hess* —  $\Delta H_f = \Delta H_{fus} + \Delta H_{vap} + \text{First IE (Li)} + \text{BE(F-F)} + \text{First EA (F)} + \Delta H_{\text{latt}}$ . Rearrange to solve for  $\Delta H_{\text{latt}}$ .

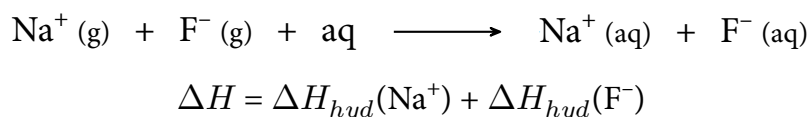


### 1.9.3 Lattice Energy, $\Delta H_{sol}$ and $\Delta H_{hyd}$

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 from the solid ionic compound:



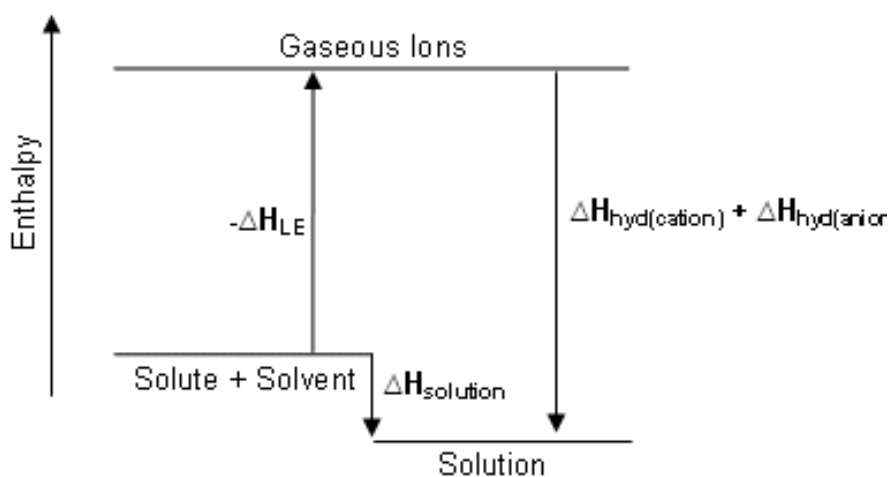
Second, the gaseous are hydrated.



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.

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

Hence, 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.



## 2 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 thus minimised 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.

### 2.1 Change in Entropy ( $\Delta S$ )

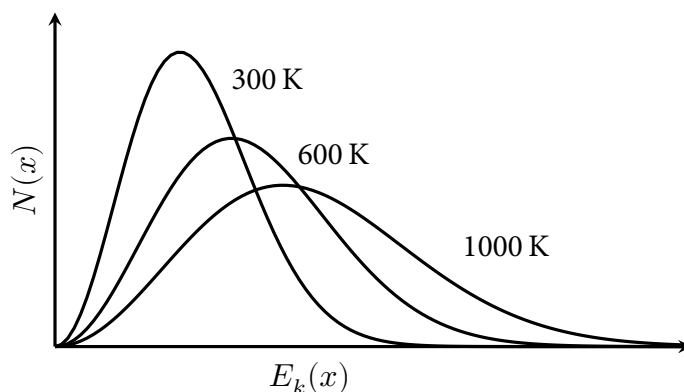
The entropy change of a given reaction or action is determined mainly by the effect on the number of ways to distribute energy in the system. The ways in which entropy is changed include changing the *temperature*, *number of moles of gas*, or the *state* of one or more compounds present in the system.

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

#### 2.1.1 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 number of ways to distribute energy in the system increases, resulting in greater entropy. ( $\Delta S > 0$ )

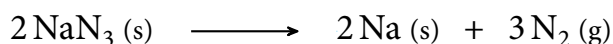


The Maxwell-Boltzmann curve illustrates the distribution of kinetic energies as across different temperatures.

## 2.1.2 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 ( $\Delta S > 0$ ).

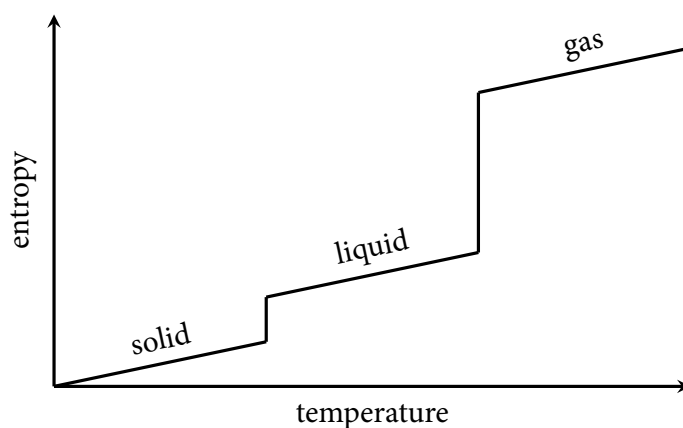
Simply put, if the reaction results in a greater number of gaseous products than reactants, then there will be a net increase in entropy. For example:



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.

## 2.1.3 Change in Phase

When a particular substance melts, boils, condenses, or freezes, the entropy of the system will change accordingly.



The entropy of a system increases as it transitions to less constrained states of matter.

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.

## 2.1.4 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.

## 2.1.5 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 ( $\Delta S > 0$ ).

### 3 Gibbs Free Energy

Since the enthalpy change ( $\Delta H$ ) and the change in entropy ( $\Delta S$ ) 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,  $\Delta G$ . 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, the enthalpy change, and the entropy change. The units of  $\Delta G$  are typically  $\text{kJ mol}^{-1}$ , and that for temperature is K.

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

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

#### 3.1 Effect of Gibbs Free Energy

Given the sign (and relative magnitude) of both  $\Delta H$  and  $\Delta S$ , it is possible to determine if  $\Delta G$  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 table below summarises the four possible scenarios:

$\Delta H$	$\Delta S$	$\Delta G$	Feasibility
$< 0$	$< 0$	always $< 0$	all temperatures
$< 0$	$> 0$	always $> 0$	never
$> 0$	$< 0$	depends	low temperatures
$> 0$	$> 0$	depends	high temperatures

# Reaction Kinetics

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## 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*.

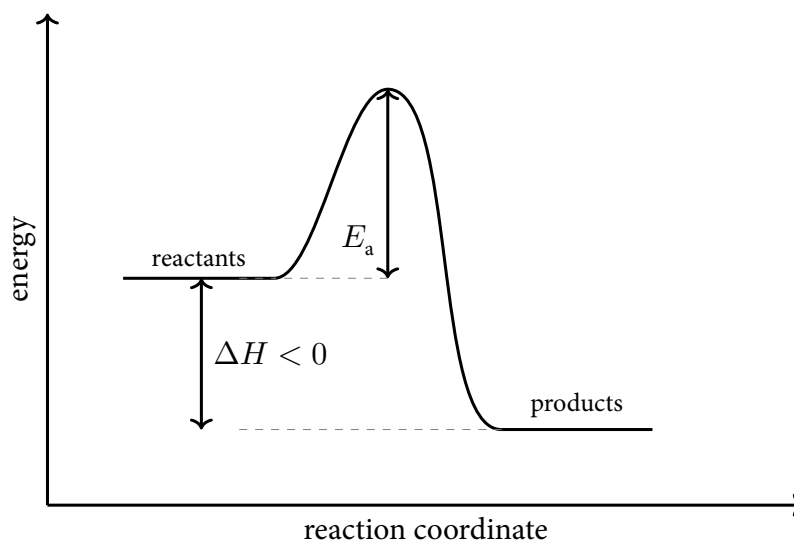
The importance of having the correct orientation can be seen in the electrophilic addition of HBr to an alkene; the  $\delta^+$  on the H atom is attacked by the electron-rich  $\pi$ -bond, so naturally the HBr molecule must be oriented such that the H end is facing the alkene.

## 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.

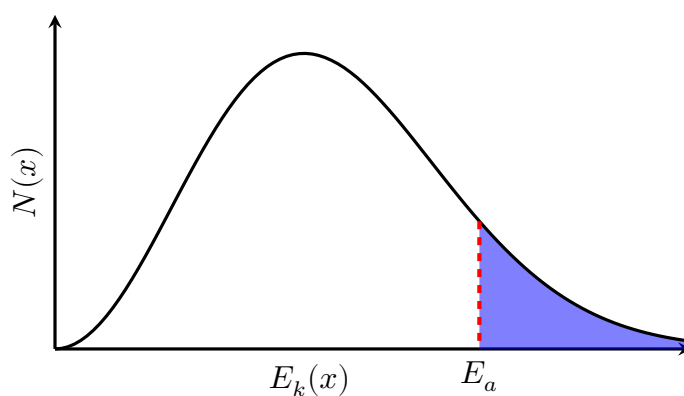
## 2.1 Energy Profile Diagram

Activation energy is often represented in two ways; firstly, in the energy profile 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.

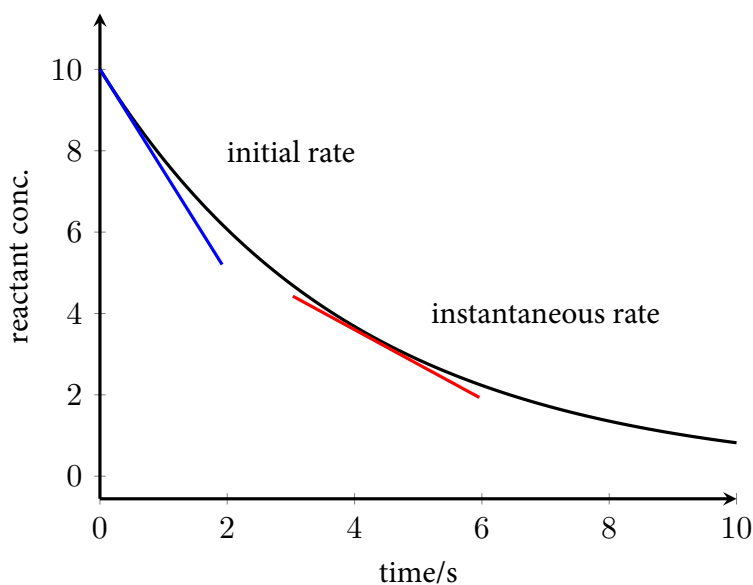
Activation energy is independent of the enthalpy change of the reaction, and instead depends on the reactants themselves; it is always positive, because bonds are always broken first before new bonds are formed.

- 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 increases, and rate of reaction increases as well.

### 3 Rates of Reaction

The rate of a reaction is primarily manifested through the rates 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. Similarly, the faster the decrease of concentration of reactants, the faster the rate of reaction.



From a concentration-time graph, it is possible to determine the rate of a reaction through measuring 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:

$$R = k[A]^x[B]^y \dots [C]^z$$

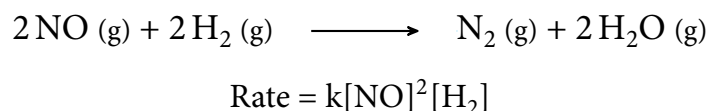
$R$  is the rate of the reaction (in  $\text{mol dm}^{-3} \text{s}^{-1}$ ).  $k$  is the constant of proportionality (discussed below);  $[A]$ ,  $[B]$  etc. are the concentrations of each reactant, and  $x$ ,  $y$  etc. are the orders of reaction with respect to that reactant. For single-direction equations (ie. not dynamic equilibrium reactions), the rate equation typically contains only the reactants and not the products.

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  $4 \text{ CO}_2$  does not mean that the order of reaction with respect to  $\text{CO}_2$  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, it can be inferred that the change 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:



When the concentration of  $\text{H}_2$  is doubled, the rate of the reaction will double. However, when  $[\text{NO}]$  is doubled, the rate of the reaction will quadruple. This also shows that the coefficients of the reactants in the chemical equation have nothing to do with the 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  $\text{mol dm}^{-3}$  and the final rate of the reaction in  $\text{mol dm}^{-3} \text{ s}^{-1}$ , the rate constant must have appropriate units to 'balance' the units of the rate equation; the units of the rate constant can be determined by simple dimensional analysis.

## 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, the unknowns ( $x$ ,  $y$ , and  $z$ ) can be found.

### 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.

## 5 Rate Graphs

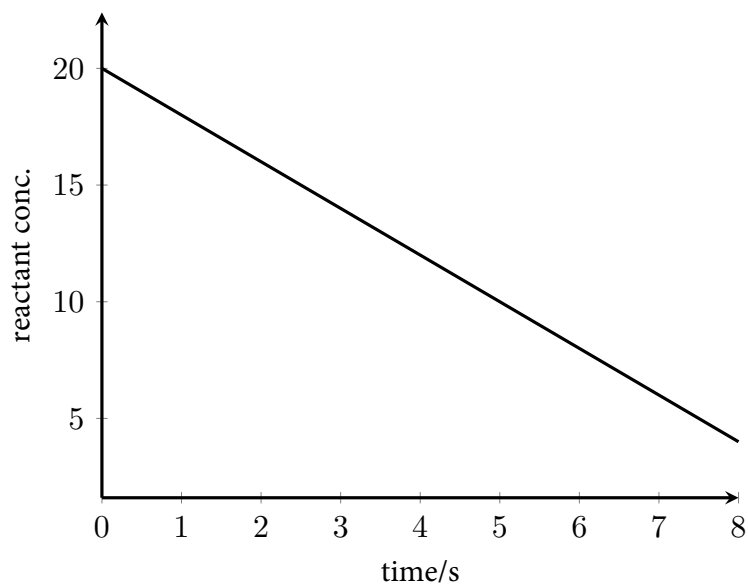
### 5.1 Concentration-Time Graph

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

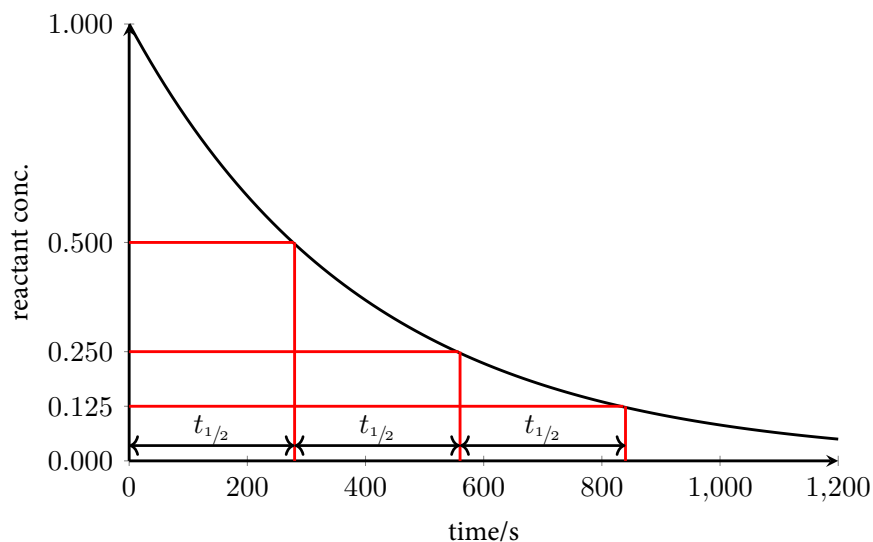
For the zero-order reaction graph below, the rate of the reaction, which is the gradient, is constant even as  $[E]$  decreases. Thus, the rate is unaffected by the concentration of  $[E]$ , and is zero order with respect to  $[E]$ .



The gradient of the graph is  $-kt$ , and the y-intercept is the initial concentration,  $[E]_0$ .

## 5.1.2 First Order Reactions

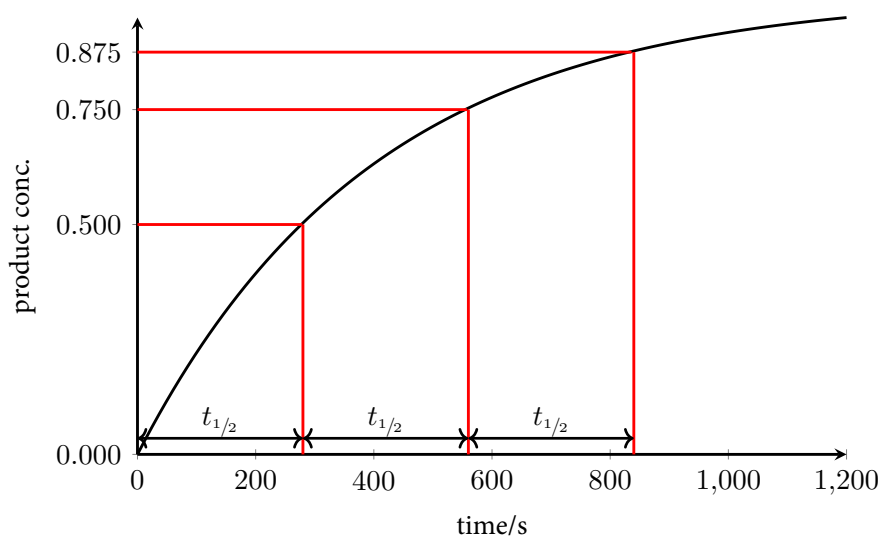
For first-order reactions, the concentration of the reactant decreases exponentially with time, and it has a constant half-life. This graph is a curve, because the rate of the reaction decreases as  $[A]$  decreases — however, the rate of change of this decrease is constant.



The half-life,  $t_{1/2}$ , is fixed.

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 the concentration decreases from 0.10 to 0.05 to 0.025 to 0.0125 and so on, every 280 seconds.

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  $1 - \text{reactant concentration}$ .



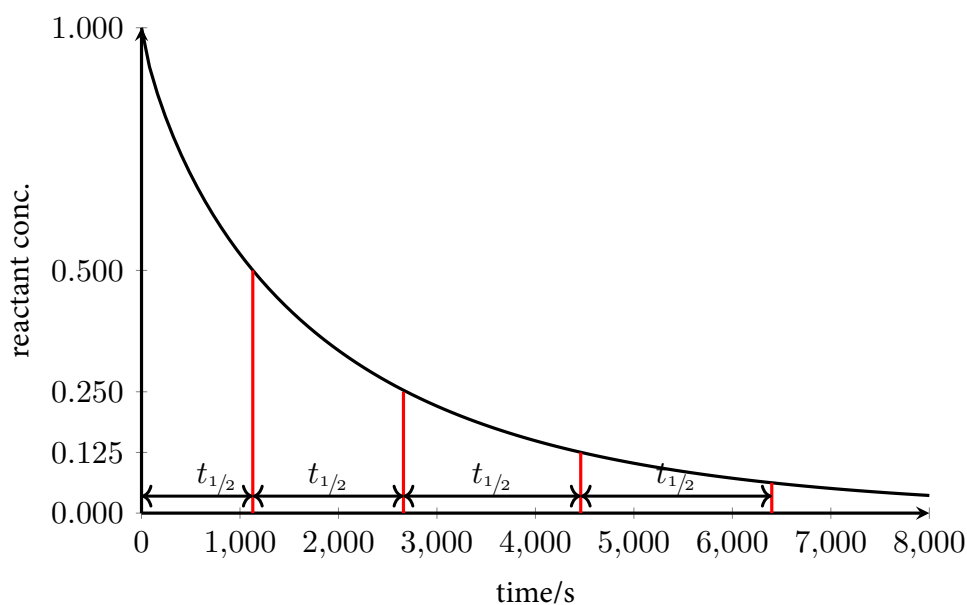
For an overall first-order reaction, the half-life can be represented with this equation:

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

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 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.

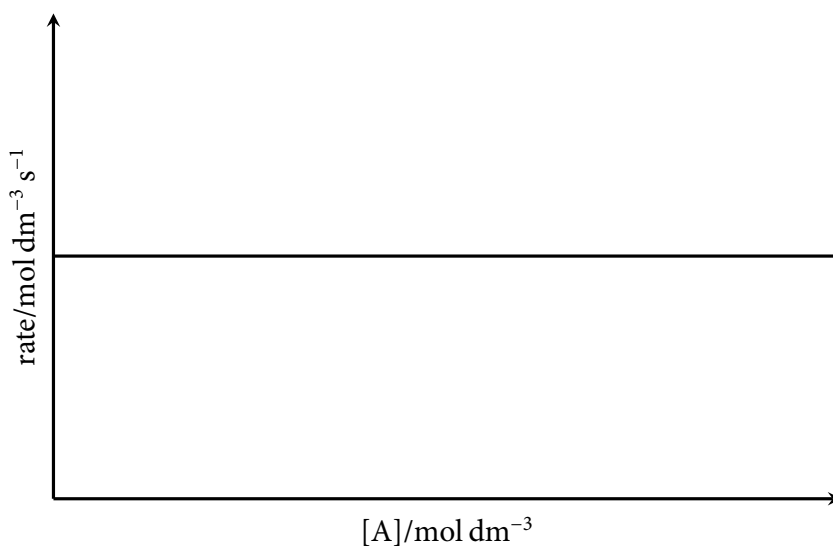
## 5.2 Rate-Concentration Graph

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.

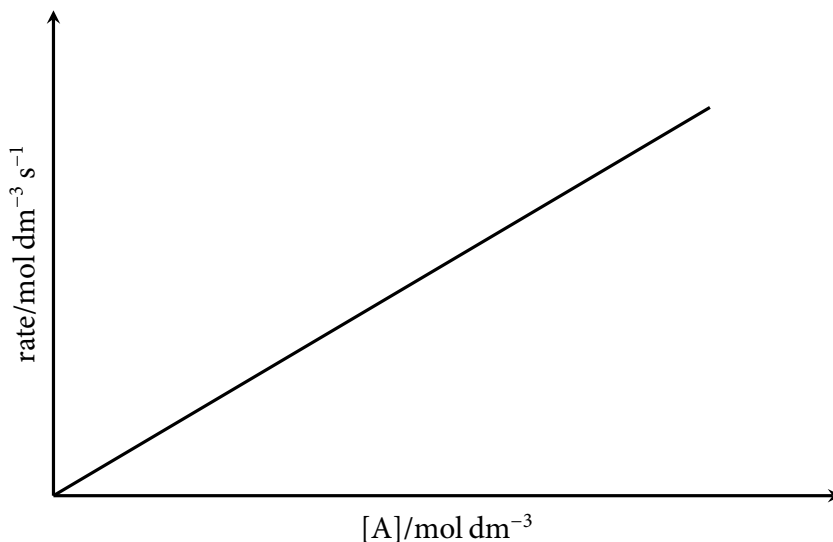
### 5.2.1 Zeroth Order Reactions

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



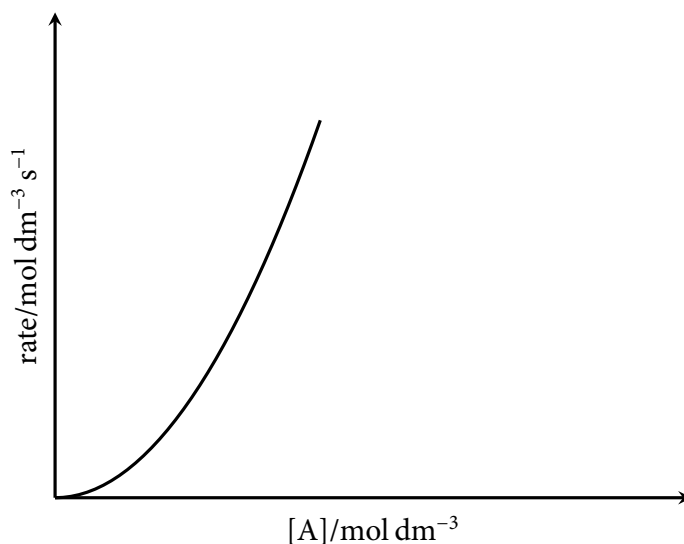
## 5.2.2 First Order Reactions

For first-order reactions, the rate increases with the concentration of the reactant in a linear manner. As such,  $\text{rate} = k[A]$ , 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

For reactions that are second-order or higher, the graph simply looks like an increasing polynomial curve.



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  $[A]^4$ .

## 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.

However, there is a caveat — there will only be an effect on the rate of reaction if the reactant in question appears in the rate equation, implying that it must be involved in the rate-determining step as well.

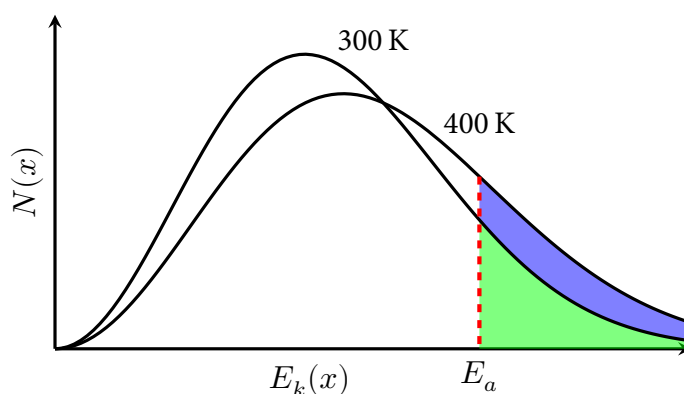
### 6.2 Surface Area of Solids

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

By increasing the temperature, the rate constant  $k$  is also increased; there is a *greater proportion* of molecules with kinetic energy greater than the activation energy. Hence, more of the collisions that occur will result in a successful reaction.



When the temperature increases, the fraction of molecules with  $\text{KE} > E_a$  increases.



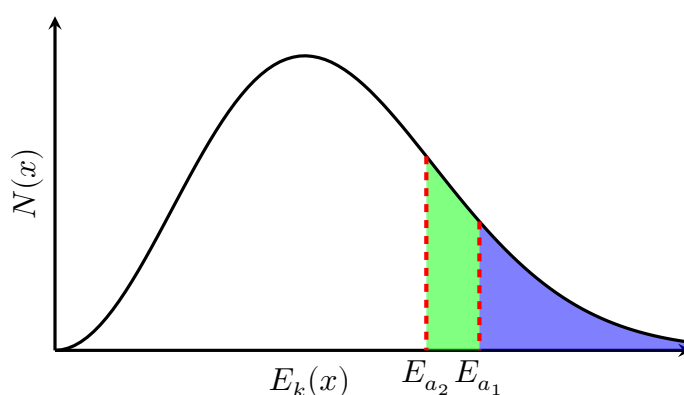
## 6.4 Effect of Light

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

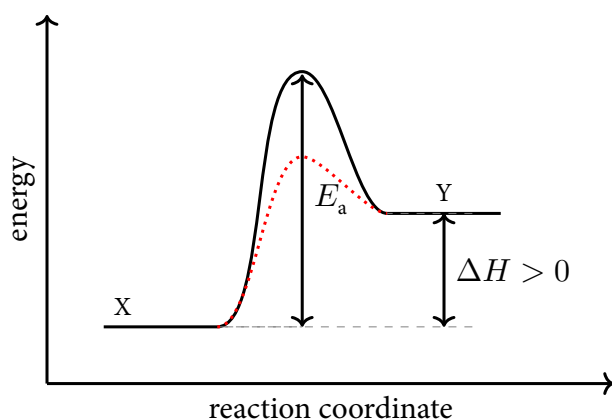
A catalyst provides an *alternative pathway* to the original, without modifying the activation energy of the original reaction.

The alternative pathway typically has a lower activation energy than the original reaction route, hence increasing the number of molecules that have a kinetic energy exceeding said activation energy.



The activation energy decreases from  $E_{a_1}$  to  $E_{a_2}$ , increasing the fraction of molecules with  $KE > E_a$ .

This effect can also be similarly illustrated with a energy profile diagram:



The dotted line represents the alternative pathway that is taken, with a lower activation energy.

# Reaction Mechanisms

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## 1 Introduction

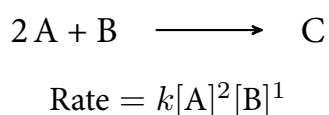
The reaction mechanism of any given reaction allows one to glean more information than usually possible from just the chemical equation. The chemical equation simply represents the overall reactants and products of the reaction; the reaction mechanism on the other hand represents the individual steps of the reaction, including which molecules collide with which other molecules, and the intermediate compounds that are formed.

The mechanism of any given reaction cannot be directly determined; they must first be hypothesised then confirmed with data from experiments.

## 2 Single-step Reactions

For single-step reactions, there is only one step, so naturally it has to be the *rate-determining*, or *slow*, step; there are no intermediates either.

Since this equation represents the entire reaction, then the stoichiometric coefficients of each reactant *will be* their respective orders of reaction. For example,



Again, note that this is only applicable to the *rate-determining* step; the orders of reaction for each reactant cannot be determined from the overall equation.

## 3 Multi-step Reactions

Even though most reactions appear to be single-step, in reality they often consist of multiple steps. The rate of reaction of the entire system is governed, naturally, by the *rate-determining step*; this step is often slow because of a high activation energy.

For multi-step reactions, the order of reaction of each reactant is determined by their stoichiometric ratio in the *rate-determining step*, not in the overall reaction.

### 3.1 Elementary Steps

In a multi-step reaction, the mechanism is often split into multiple *elementary reactions* — those that cannot be broken down further into separate steps.

- Unimolecular steps involve only one molecule.
- Bimolecular steps involve the collision of two molecules.
- Termolecular steps involve the collision of three molecules, simultaneously.

Given that termolecular reactions are already quite rare, there are no known elementary steps involving the simultaneous collision of four or more molecules.

### 3.2 Intermediates

Intermediates, distinct from transition states, are typically stable compounds that can often be isolated, and are usually formed as the product of intermediate steps in the reaction mechanism.

Intermediates must be reacted away by the end of the reaction, since they are not present in the overall equation.

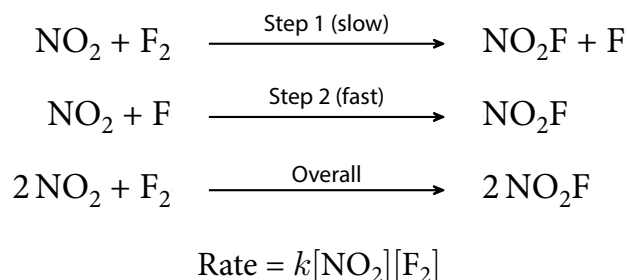
### 3.3 Mechanisms

For multi-step reactions, it is important to note that reactants in the elementary (fast) steps *before* the rate-determining step are included in the rate equation, and reactants appearing in the fast steps *after* the rate-determining step are *not* included.

Thus, there are two main cases — when the rate-determining step is the first step, and when it is not.

### 3.3.1 Rate-Determining Step is First

For example, take the reaction between nitrogen dioxide ( $\text{NO}_2$ ) and fluorine gas ( $\text{F}_2$ ):

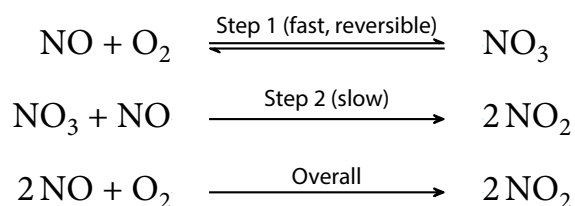


As can be seen, the orders of reaction of  $\text{NO}_2$  and  $\text{F}_2$  follow the coefficients in the rate-determining slow step, not the overall equation. This is the case for a reaction where the slow step is the first step.

### 3.3.2 Rate-Determining Step is not First

If the rate-determining step is not the first step, then the reaction most likely involves an intermediate, which must be dealt with before the final step, since it cannot appear in the overall reaction.

For example, taking the reaction for the oxidation of nitrogen monoxide ( $\text{NO}$ ),



In this situation, the intermediate species  $\text{NO}_3$  is formed in the first fast step, but is reacted away in the second, slow step. To begin with, a preliminary rate equation comprising the reactants in the slow step can be formed:

$$R = k_1[\text{NO}_3][\text{NO}]$$

The concentration of  $\text{NO}_3$  must be substituted for the concentrations of the reactants that it was created from, in this case  $\text{NO}$  and  $\text{O}_2$ . Since the first step is an equilibrium reaction, the equilibrium constant  $K_c$  can be used to calculate  $[\text{NO}_3]$  in terms of  $[\text{NO}]$  and  $[\text{O}_2]$ .

$$K_c = \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]}$$

Moving things around, the following is conceived:

$$[\text{NO}_3] = K_c[\text{NO}][\text{O}_2]$$

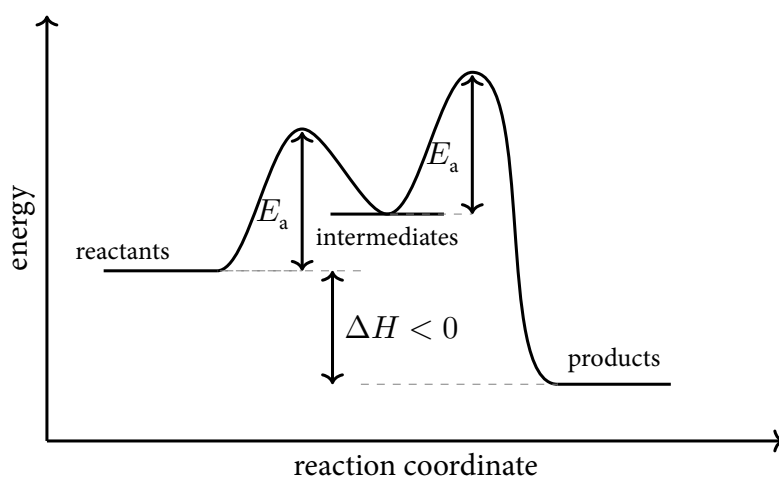
Thus, substituting this into the original, partial rate equation and refactoring  $k = k_1 \times K_c$ :

$$R = k_1 K_c [\text{NO}][\text{O}_2][\text{NO}] = k[\text{NO}]^2[\text{O}_2]$$

By looking at the reaction, it might be tempting to come to the conclusion that, because 1 mol of  $\text{NO}_3$  is formed by 1 mol of  $\text{NO}$  and  $\text{O}_2$ , it is possible to simply substitute  $[\text{NO}_3] = [\text{NO}][\text{O}_2]$  directly. This is, however, incorrect.

Don't do it.

### 3.3.3 Energy Profile Diagram



The diagram is mostly self-explanatory; there is an *intermediate compound* formed between the formation of the products. The intermediate is *not the same* as a transition state — the former is at a local energy minimum, while the latter is at a local energy maximum. Intermediates can sometimes be isolated as compounds, while transition states can never be.

## 4 Catalysis of Reactions

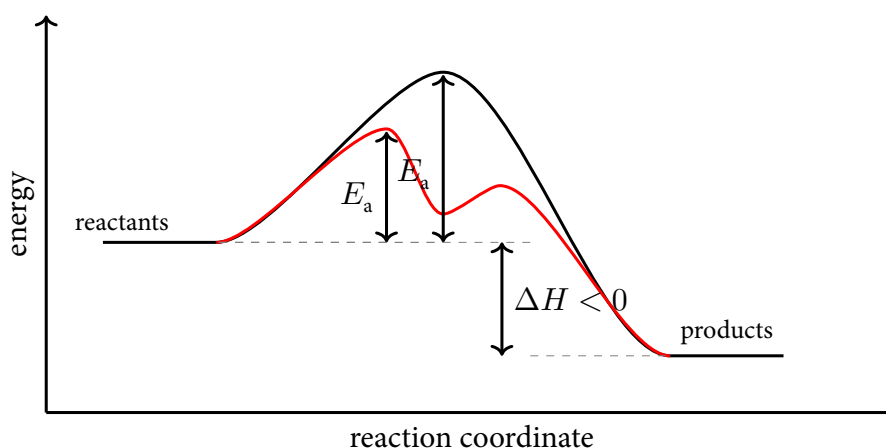
As explained previously, catalysts provide an alternative reaction pathway for the reaction, typically with a lower activation energy. There are two mechanisms of action for catalysis: homogeneous and heterogeneous.

The mechanism of action of the catalyst is determined by the phase it is in. Note that *phase* and *state* are different concepts. While each state represents a phase, an oil phase and an aqueous phase are different phases, but the same state.

Note that the concentration of a catalyst over the course of the reaction does not decrease, since it must be regenerated at the end of the reaction.

### 4.1 Homogeneous Catalysts

Homogeneous catalysts exist in the same phase as the reactants of the reaction. They are uniformly mixed in the reaction mixture, and they often form intermediates together with the reactants, before they are regenerated in the last step of the reaction.



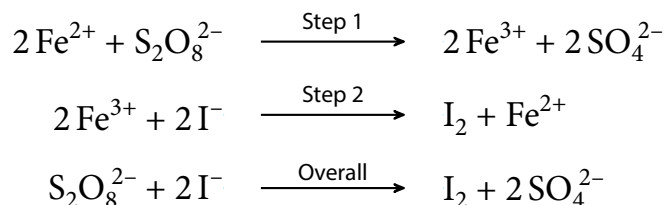
In the diagram above, the catalysed reaction is represented with the red line. It can have any number of intermediates, as long as the maximum activation energy is less than the activation energy of the original reaction.

Homogeneous catalysts must be one of the reactants in the rate-determining step for it to affect the rate of reaction. As such, it usually appears in the final rate equation (for the catalysed reaction), even though it is not part of the balanced chemical equation.

### 4.1.1 Catalysis of $\text{I}^- + \text{S}_2\text{O}_8^{2-}$ reaction with $\text{Fe}^{2+}$

$\text{Fe}^{2+}$  acts as a catalyst in the reaction of iodide ions ( $\text{I}^-$ ) with peroxodisulphate ions ( $\text{S}_2\text{O}_8^{2-}$ ), via homogeneous catalysis. The reaction of these two species involves the collision of two negatively charged ions, which has a high energy barrier and thus is infeasible. As such, the reaction occurs very slowly without a catalyst.

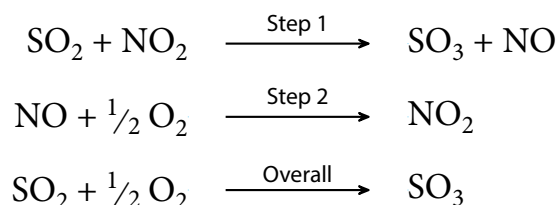
In this reaction,  $\text{I}^-$  is a reducing agent, and  $\text{S}_2\text{O}_8^{2-}$  is an oxidising agent. However, with  $\text{Fe}^{2+}$  as the catalyst, these two species do not interact directly. Instead, the positively charged  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions easily attract the negative ions, and it is oxidised and reduced by  $\text{S}_2\text{O}_8^{2-}$  and  $\text{I}^-$  respectively.



In the first step,  $\text{Fe}^{2+}$  is oxidised by  $\text{S}_2\text{O}_8^{2-}$  to form  $\text{Fe}^{3+}$ . In the second step, this  $\text{Fe}^{3+}$  is reduced again by  $\text{I}^-$  back to  $\text{Fe}^{2+}$ , regenerating the catalyst. Since this involves the reaction of oppositely charged ions, the activation energy for each step is much lower than that for the uncatalysed reaction.

### 4.1.2 Catalysis of oxidation of $\text{SO}_2$ with $\text{NO}_2$

In the atmosphere, nitrogen dioxide often catalyses the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ , thus forming acid rain (mainly  $\text{H}_2\text{SO}_4$ ). It is catalysed in two steps:



The  $\text{SO}_3$  formed reacts readily with water vapour in the atmosphere to form sulphuric acid,  $\text{H}_2\text{SO}_4$ .

## 4.2 Heterogeneous Catalysis

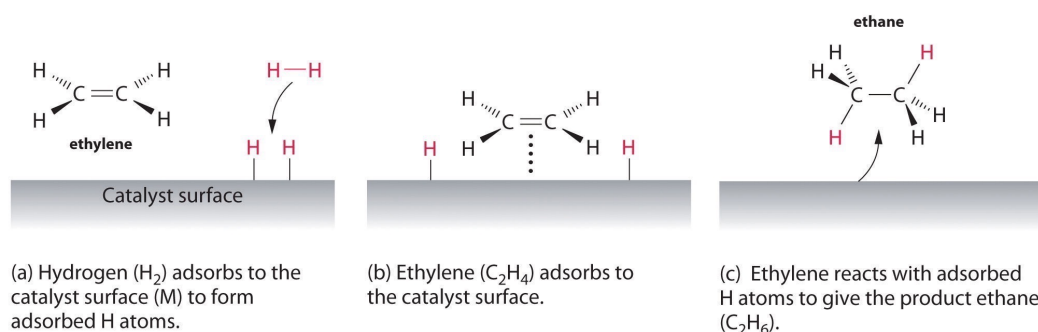
Heterogeneous catalysts catalyse the reaction from a different state or phase than the reactants in the reaction. It is most often a solid catalyst reacting with liquid or gaseous reactants. Thus, since they do not have a concentration, they do not appear in the rate equation; their effect is manifested in the rate constant  $k$ .

Most heterogeneous catalysts have the concept of *active sites*, which are areas on the surface of the solid catalyst that are available for reaction. Thus, catalysts with a larger surface area, such as wire gauze or fine powder, are preferred to increase the rate of reaction.

- Haber Process for production of  $\text{NH}_3$  (ammonia) (Fe powder or  $\text{Fe}_2\text{O}_3$ )
- Hydrogenation of alkenes (Pd, Pt, or Ni)

### 4.2.1 Mechanism of Action

Heterogeneous catalysts operate in three steps. The example below uses the hydrogenation of an alkene to demonstrate how a heterogeneous catalyst (in this reaction, either Ni (s), Pd (s) or Pt (s)) catalyses the reaction of hydrogen ( $\text{H}_2$ ) with ethene ( $\text{C}_2\text{H}_4$ ).



## Adsorption

First, the ethene molecule and the  $\text{H}_2$  molecule diffuse toward, and are adsorbed onto, the surface of the catalyst. Note that adsorb  $\neq$  absorb — adsorption is the *adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface*, while absorption implies the molecule *entering the substance*.

Adsorption occurs at the *active sites* of the catalyst through relatively weak attractive forces, which bring the reactant molecules *closer together*. Thus, the concentrations of the reactants at the surface of the catalyst are higher, resulting in a *greater frequency of collision*.

Since they are bonded to the catalyst, the bonds within the reactants are also *weakened*, resulting in a *lower activation energy*. Furthermore, most catalysts ensure that the reactant molecules are *correctly oriented*, further increasing the frequency of effective collisions.

## Desorption

Once the reaction is complete, the product desorbs from the surface of the catalyst and diffuses away. The active site is now free and available to catalyse more reactants.



## 4.2.2 Limitations of Active Sites

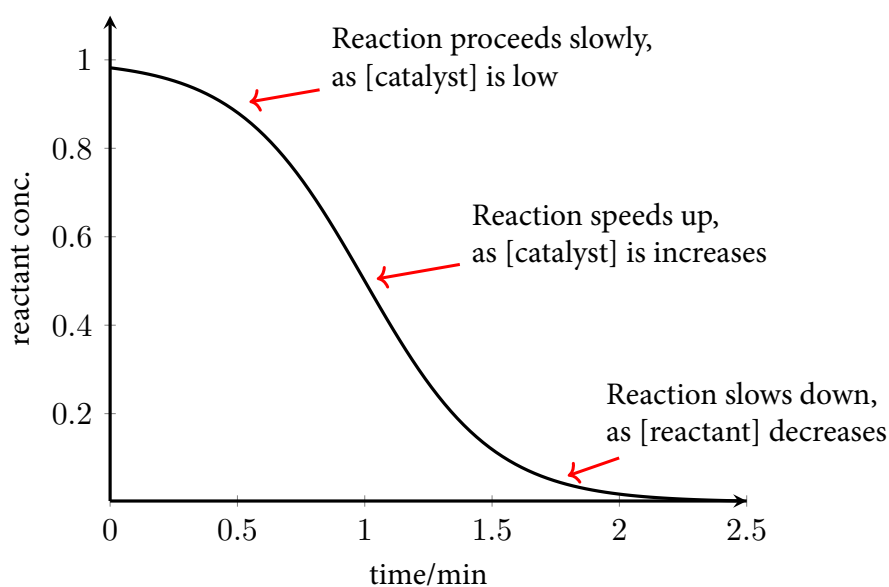
Due to the fact that the number of active sites for any given surface area of catalyst are limited, it can also be one of the limiting reagents, as it were, for the reaction.

If all the active sites are *saturated*, increasing the concentration of the reactants will not increase the rate of the reaction, as new reactants are not being catalysed. In this case, the only solution is to increase the number of active sites, usually by adding more of the catalyst.

Conversely, if the concentration of *reactants* is low, (ie. the catalyst is not saturated), then adding more of the catalyst will not significantly increase the rate of reaction.

## 4.3 Autocatalysis

Autocatalysis occurs when the product of a reaction is the catalyst for the reaction. Thus, the rate of reaction is affected by the progress of the reaction. Typically, autocatalysts are homogeneous in nature, since they directly react with the reactants.



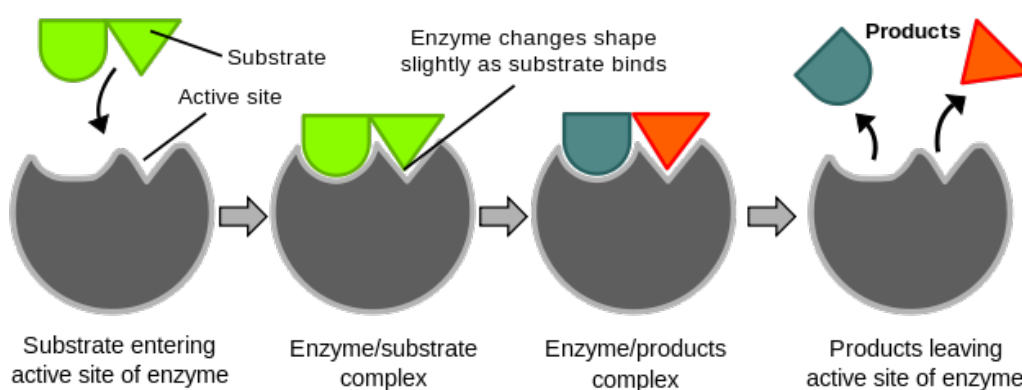
Initially, the rate of reaction is limited by the concentration of the catalyst. As the reaction progresses, more catalyst is produced, increasing the rate. Finally, when the reactants are mostly consumed, they become the limiting reactant, and the rate of reaction slows once more.

## 4.4 Biological Catalysis

Enzymes are biological catalysts that play an important role in the perpetuation of life. Given that the temperature of the reaction system is usually at or near room temperature (around 35 °C for humans), and that the concentration of reactants is usually very low, efficient catalysts are required for reactions to take place at any appreciable rate.

There are a multitude of different enzymes that perform a very specific job, because the shape of the enzyme is perfectly suited to catalyse only a very small group of molecules.

Because they are soluble in water, globular enzymes typically operate in the same phase as the reactants they catalyse. However, the mechanism of action is typical of a heterogeneous reaction, with a limited number of active sites. Thus, they have the characteristics of both homogeneous and heterogeneous catalysts.



The reactant that is being adsorbed is known as the *substrate*, and the diagram above shows the rough mechanism of the enzyme. The fast step of the reaction is almost always the adsorption of the substrate, while the slow, rate-determining step is typically the actual reaction of the complex to form the products.

### 4.4.1 Limitations of Enzymes

Due to their highly specific and biological nature, enzymes are only efficient at a certain pH and temperature. In fact, going into the extremes of these ranges will irreversibly destroy the enzyme, in a process known as denaturation.

Furthermore, enzymes, and in fact any heterogeneous catalyst, are prone to poisons — molecules that are preferentially adsorbed onto the active site (either reversibly or irreversibly). These poisons can either slow down the rate of reaction significantly if used in high concentrations, or destroy the catalyst all together.



# Chemical Equilibrium

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## 1 Overview

Most of the reactions thus far have been irreversible, or uni-directional. However, many reactions in real life are actually in an equilibrium state — at a certain stage, the rates of reaction for both the forward and backward reactions are equal, so the concentration of reactants and products do not change any further.

The *position of equilibrium* can be controlled to a certain extent, according to the principles of a man named *Le Châtelier*. Lexically, an equilibrium reaction is represented with a double-hooked arrow,  $\rightleftharpoons$ , instead of a normal arrow,  $\longrightarrow$ .

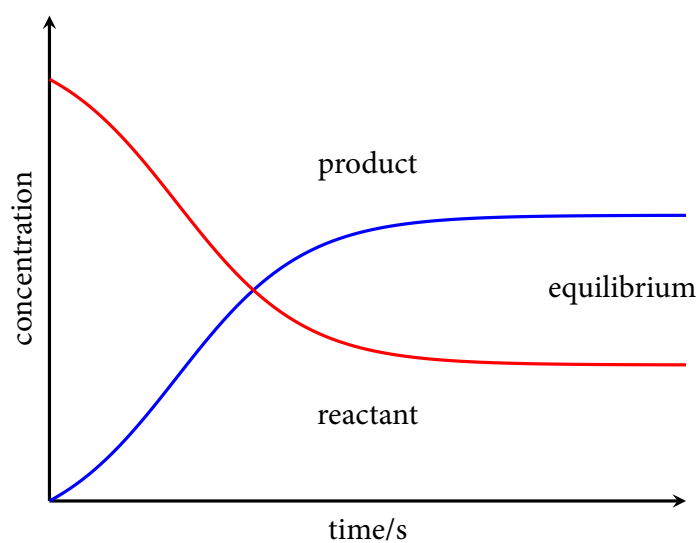
### 1.1 Dynamic Equilibrium

It is important to note that this state of equilibrium is a *dynamic* equilibrium; the rate of the forward and backward reactions are *equal* and *non-zero*. If both the rates of reaction are zero, then it is in a state of *static* equilibrium. Unless the reaction mixture is disturbed, the system will remain in this equilibrium.

The nature of equilibrium reactions means that they can be ‘started’ from either direction, beginning with only reactants or only products. The system will eventually move back into the position of equilibrium.

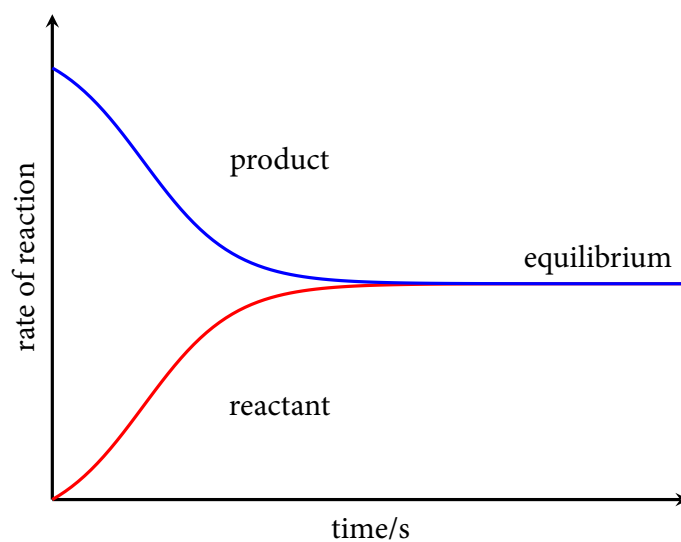
## 1.2 Graphs

### 1.2.1 Concentration-Time



Both gradients reach 0 at the equilibrium

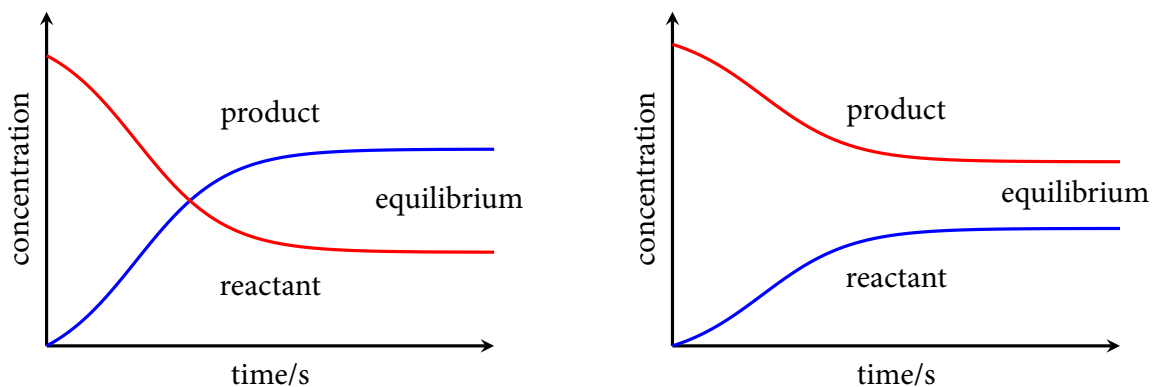
### 1.2.2 Rate-Time



The rates of reaction meet in the centre and are equal at the position of equilibrium.

### 1.3 Position of Equilibrium

From the concentration-time graph, it is possible to determine if the position of equilibrium lies more to the *left* or the *right*. The former means that the forward reaction is favoured more (reading equations from left-to-right), while the latter indicates a more favoured backwards reaction.



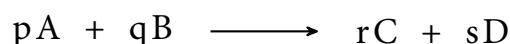
In the system on the left, the final concentration of products is greater than the final concentration of reactants; *ie.* the position of equilibrium is further to the right. Conversely, the position of equilibrium is to the left in the graph on the right.

## 2 Equilibrium Constants

There are two equilibrium constants,  $K_c$  and  $K_p$ , that serve roughly the same purpose in different contexts — the former for normal, aqueous reactions where normal concentrations apply, and the latter for gaseous systems where it is more logical to use partial pressures.

### 2.1 Equilibrium Constant $K_c$

$K_c$  is calculated using the concentrations of each product and each reactant, *at equilibrium*. For the reaction below:



The corresponding  $K_c$  would be as such:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Note that it is *products over reactants*. The power that each concentration is raised to is simply the stoichiometric coefficient of that reactant or product, nothing more — far simpler than the rate equation nonsense.

The derivation for  $K_c$  can be found in the appendix.

### 2.2 Gaseous Equilibrium Constant $K_p$

In situations where it is more convenient to use partial pressures, then it is as simple as substituting the concentrations in the original  $K_c$  equation with the corresponding partial pressures to get  $K_p$ , like so:

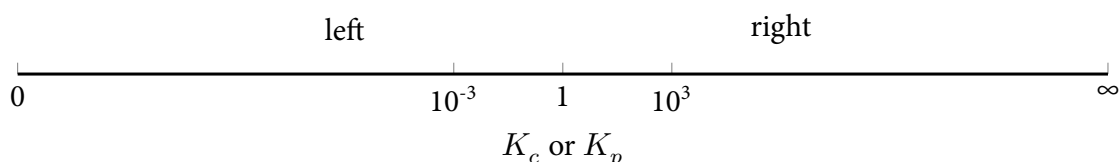
$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

This works because partial pressure is simply equivalent to the mole ratio of a particular gas to the total number of moles of gas in the system – when put together, the moles cancel, leaving what is effectively the stoichiometric coefficient.

## 2.3 Determination of Position of Equilibrium

From the equations of  $K_c$  and  $K_p$  above, it can be seen that when the numerator and denominator are equal, then the values of  $K_c$  and  $K_p$  become 1. At this point, the position of equilibrium lies perfectly in the centre, favouring neither the forward nor backward reactions.

Applying the knowledge of fractions, the larger the value of  $K_c$ , then the further forward lies the position of equilibrium. Conversely, the smaller the value, the further backward it lies.



$K_c$  values around  $1 \times 10^{-3}$  to  $1 \times 10^3$  are considered systems where the position of equilibrium is relatively centred, while values outside of that range indicate a system strongly preferring either the forward or reverse reaction.

## 2.4 Equilibrium Quotients $Q_c$ and $Q_p$

$Q_c$  and  $Q_p$  are essentially exactly the same as  $K_c$  and  $K_p$ , except the  $Q$  values represent the position of equilibrium *at that instant*. Thus, it is often useful to compare the  $Q_c$  and  $K_c$  values for a system, to determine where the *current* position of equilibrium lies, and which direction the system is currently proceeding in.

There are 3 cases, as there always are when comparing two numbers:

- $Q < K$ ; the current position is too far backward, and the system proceeds in the *forward* direction until equilibrium is achieved
- $Q = K$ ; the system is currently at equilibrium, and will remain so unless disturbed
- $Q > K$ ; the current position is too far forward, and the system proceeds in the *reverse* direction until equilibrium is achieved.

Naturally, the value of  $Q$  uses the same formula, except with the *instantaneous* values for concentration or partial pressure.



## 3 Factors Affecting Equilibrium Position

### 3.1 Le Châtelier's Principle

This man's principle governs exactly how various changes to a system at equilibrium will result in a shift in the position of said equilibrium.

*When any system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to (partially) counteract the effect of the applied change and a new equilibrium is established.*

— Henry Louis Le Châtelier

In short, the system will attempt to compensate for, and reverse, any changes made to it by an external agent, through a shift in the position of equilibrium.

### 3.2 Changes in Concentration or Partial Pressure

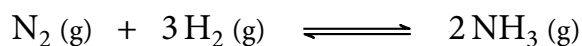
This is the most direct method to affect the system. If the concentration of one or more reactants is increased, then the concentration difference deviates from the equilibrium. Thus, the system will attempt to compensate by shifting *forwards*, in an attempt to consume the reactant and bring the concentration ratio back to an acceptable range.

The idea above applies in reverse when increasing the concentration of one or more products, and indeed applies for gaseous systems using partial pressures as well.

### 3.3 Changes in Total (System) Pressure

Unlike a change in the partial pressure of a reactant or product, changing the total pressure of the system affects both the products and reactants.

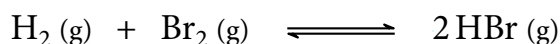
Using the reaction for the formation of ammonia,  $\text{NH}_3$ , from  $\text{H}_2$  and  $\text{N}_2$ :



The forward reaction changes the number of moles of gas from 4 (1 + 3) to 2, resulting in a net *decrease*; the backwards reaction would thus increase the number of moles of gas from 2 to 4, a net *increase*.

When the total pressure is *increased*, the system will attempt to reduce it, by reducing the number of moles of gas in the system — thus moving the position of equilibrium *to the right*, favouring the production of  $\text{NH}_3$ .

If the total number of moles of gas on either side of the reaction are the same, for example:

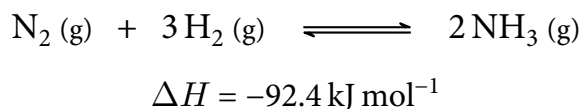


Then a change in the pressure of the system will have *no effect* on the position of equilibrium.

## 3.4 Changes in Temperature

Changes in temperature will shift the equilibrium in an attempt to reduce the change — in this case, the enthalpy change of the reaction is used, since it determines whether the reaction will result in a net release or absorption of heat.

Again, using the formation of ammonia:



The forward reaction is *exothermic* as given by the negative  $\Delta H$ . Thus, a *decrease* in temperature will make the system attempt to compensate by increasing the temperature. Since the forward reaction *releases heat*, it will be favoured, and the position of equilibrium moves to the *right*.

Naturally, the reverse applies.

## 3.5 Presence of Catalyst

This section is a red herring — adding or removing a catalyst *does not* change the position of equilibrium, since the rate of reaction for *both* the forward and backward reactions are increased or decreased by an equal amount.

Thus, catalysts only change the amount of *time taken* to reach equilibrium, not its position.

## 4 The Process of Haber-Bosch

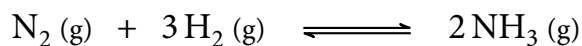
### 4.1 Overview

The *Haber Process* is an important, industrially-used process for the manufacture of ammonia (NH<sub>3</sub>), which is widely used for fertiliser.

*My name is Fritz Haber, and I maked a process. It was all me, Carl Bosch did nothing.*

— *Fritz Haber*

As shown above, the formation of NH<sub>3</sub> from H<sub>2</sub> and N<sub>2</sub> is an equilibrium, and unfortunately the position of equilibrium likes quite far to the left — hence the need for expensive industrial equipment to produce this at scale.

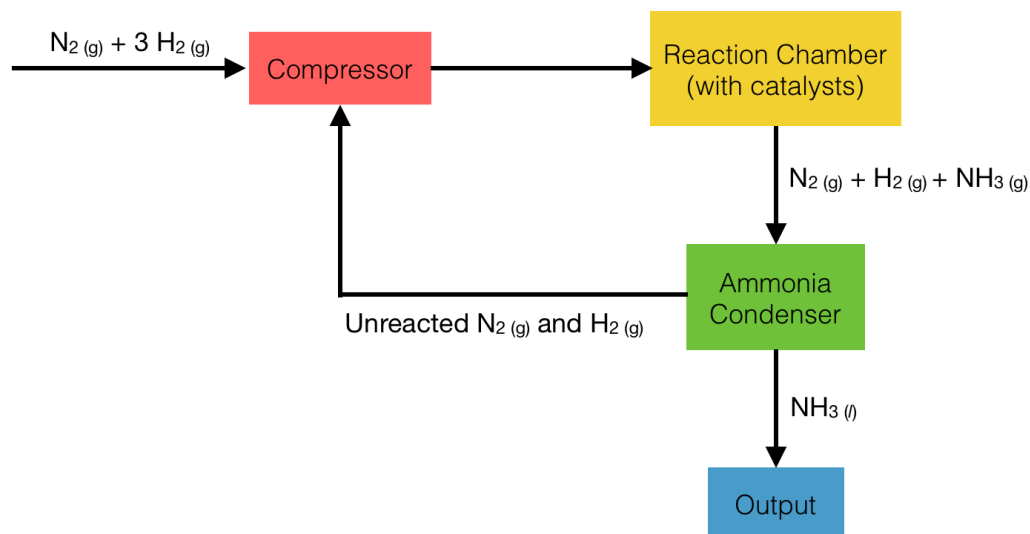


To increase the yield of ammonia, 3 techniques are used:

- The pressures of H<sub>2</sub> and N<sub>2</sub> are kept as high as practically possible
- NH<sub>3</sub> formed is removed as soon as possible, to reduce its concentration
- The rate of reaction is increased using iron powder as a catalyst

A note on the last point — while it does not move the position of equilibrium and speeds up both reactions, if the position of equilibrium is already to the right, there will be a net gain.

## 4.2 Process



The image should be fairly self-explanatory. Pure nitrogen gas is obtained from liquefied air, while hydrogen gas is obtained via methane ( $\text{CH}_4$ ) and steam, in the presence of a catalyst.

### 4.2.1 Conditions

In a rare occasion for this series, some figures must be memorised. Note that while Le Châtelier's Principle would imply low temperatures, the temperature is typically kept (relatively) high to allow for the reaction to proceed at an appreciable rate. It's one thing for the position of equilibrium to be far forward, it's another thing for the forward reaction to actually occur.

**Conditions:** 450 °C, 250 atm, Finely divided Fe catalyst.



# Solubility Equilibrium

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## 1 Overview

Ions are typically soluble in a polar solvent, but since systems always tend to approach the lowest energy level, if a solid ionic compound can be created from some of those ions, then it will precipitate out of solution.

The solubility of any given ionic compound is largely determined by  $\Delta H_{sol}$ , the enthalpy change of solution; it is the sum of the enthalpy changes of hydration of the constituent ions, minus the lattice energy of the ionic compound.

Hence, for a compound with a highly negative lattice energy, the enthalpy change of solution will be quite endothermic, and it is unlikely to be very soluble. Essentially, stronger ionic lattices are less soluble than weaker ones.

Furthermore, solubility typically increases with temperature, since the increased energy of the solvent can increase the feasibility of solution.

### 1.1 Saturation

Even for highly soluble salts, eg.  $\text{NaCl}$ , solubility is not infinite. Beyond a certain point, additional solid salt added to the solvent will no longer dissolve. At this limit, a *saturated solution* is formed.

When more solid salt is added to a saturated solution, an equilibrium is created, where ions are simultaneously being dissolved from, and precipitated into, the solid state. As with any other dynamic equilibrium, the rates of reaction of these two processes are *non-zero* and identical.

## 1.2 Solubility of Common Ionic Compounds

The solubilities of ionic compounds are often grouped by the anion, and most of them have fairly straightforward trends.

Anion	Solubility	Exceptions
$\text{NO}_3^-$	Soluble	—
$\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$	Soluble	$\text{Ag}^+$ and $\text{Pb}^{2+}$
$\text{SO}_4^{2-}$	Soluble	$\text{Ag}^+$ , $\text{Pb}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$
$\text{CO}_3^{2-}$	Insoluble	Group I cations and $\text{NH}_4^+$
$\text{OH}^-$	Insoluble	Group I cations
$\text{O}^{2-}$	Insoluble	Group I cations

Even though a certain ionic salt is said to be *insoluble*, most of the time a small amount of free ions can still be found in solution; the concentrations of these ions are just *very, very small*.

Certain salts, such as  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ , are actually *sparingly soluble* — not-insignificant amounts of ions are dissolved into solution; limewater is a saturated solution of calcium hydroxide, and the pH of a magnesium hydroxide solution is actually greater than 7.

## 2 Solubility Constants

### 2.1 Solubility

The solubility of a salt is the number of moles, or mass, of the salt that can be dissolved in a given volume of solvent to create a saturated solution at a fixed temperature.

The units of solubility are typically either  $\text{mol dm}^{-3}$  or  $\text{g dm}^{-3}$ , depending on the the scale used.

If the solubility of a certain salt, for instance  $\text{Mg}(\text{NO}_3)_2$ , is  $8.43 \text{ mol dm}^{-3}$ , then the concentration of  $\text{Mg}^{2+}$  ions in solution will be  $8.43 \text{ mol dm}^{-3}$ , and the concentration of  $\text{OH}^-$  ions will be twice that,  $16.9 \text{ mol dm}^{-3}$ .

### 2.2 Solubility Product, $K_{sp}$

The  $K_{sp}$  of a sparingly soluble salt is the molar concentrations of the constituent ions in a saturated solution raised to their stoichiometric coefficients, at a fixed temperature.

The solubility product of an ionic equilibrium is derived from the equilibrium constant,  $K_c$ . Hence, like  $K_c$ , the value of the solubility product for any salt is only valid at a certain temperature. For a given equilibrium of solution:



The equilibrium constant is this:

$$K_c = \frac{[\text{Mg}^{2+}][\text{OH}^-]^2}{[\text{Mg}(\text{OH})_2]} \quad K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

Since the ‘concentration’ of a solid, in this case  $\text{Mg}(\text{OH})_2$ , is constant, it can be factored out, giving the equation of  $K_{sp}$ . The units of  $K_{sp}$  are naturally dependent on the ions and their powers on the right side, so in this case they are  $\text{mol}^3 \text{ dm}^{-9}$ .

### 2.3 Ionic Product

The ionic product of an ionic salt is defined in the same manner as the solubility product, except the solution need not be saturated; it is most often a measure of the *current* concentration of ions in solution.

The IP can be compared with  $K_{sp}$  to determine if the solution will form a precipitate if more ions are added. If the ionic product is greater than  $K_{sp}$ , then ions will precipitate out until IP is equal to  $K_{sp}$ . If it is less, then more solid can be added until they are equal, giving a saturated solution.

The idea here is similar to the relationship between  $Q_c$  and  $K_c$ .



### 3 Factors Affecting Solubility

#### 3.1 Position of Equilibrium

One of the main factors affecting the solubility of an ionic salt is the position of equilibrium of the solution system. For a given equilibrium, for example that of  $\text{Mg}(\text{OH})_2$ :



The position of equilibrium depends solely on the concentrations of the ions, since adding or removing solids will not change its position. Any action that modifies the concentration of either ion will result in a shift in equilibrium, and hence an increase or decrease in the solubility of the salt.

For example, adding an acid like  $\text{H}_2\text{SO}_4$  to the system will cause the concentration of  $\text{OH}^{-}$  to decrease, and hence by the principle of Le Châtelier, the position of equilibrium will shift to the right, causing more of the solid to dissolve.

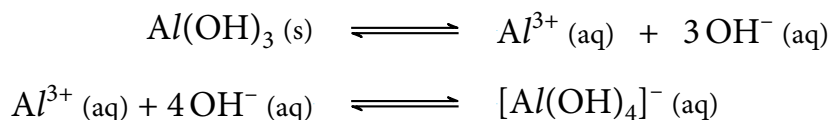
Conversely, if the concentration of  $\text{Mg}^{2+}$  were increased, for instance by adding  $\text{Mg}(\text{NO}_3)_2$ , then the position of equilibrium will shift to the left, causing less solid to dissolve, and indeed causing existing ions to precipitate out of solution.

##### 3.1.1 Common Ion Effect

The common ion effect is really just a fancy name for a special case of shifting the equilibrium by increasing the concentration of an ion; if a solution containing 'common ions' is added to an existing equilibrium, then the solubility of the sparingly soluble salt will decrease, as a result of Le Châtelier's Principle.

##### 3.1.2 Complex Formation

This is also just a special case of changing the position of equilibrium by changing concentrations. For example, given the following systems of  $\text{Al}(\text{OH})_3$  and  $[\text{Al}(\text{OH})_4]^{-}$ :



If  $\text{OH}^{-}$  ions are introduced to an aqueous solution of  $\text{Al}^{3+}$  ions, then the precipitate of  $\text{Al}(\text{OH})_3$  will form since the ionic product is greater than the solubility product.

If excess  $\text{OH}^{-}$  ions are added, however, then the complex ion  $[\text{Al}(\text{OH})_4]^{-}$  forms, which is soluble in water. This removes  $\text{Al}^{3+}$  ions from solution, and if enough complex ions form, then the position of equilibrium for the solution system will shift forward enough to dissolve the precipitate.

# Acid-Base Equilibrium

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## 1 Theory of Acids and Bases

### 1.1 Brønsted-Lowry

Fundamental to understanding this chapter is the Brønsted-Lowry theory of acids and bases... as the section header would lead you to conclude.

- Brønsted acids *donate* a proton ( $\text{H}^+$ ) to a base
- Brønsted bases correspondingly *accept* a proton ( $\text{H}^+$ ) from an acid.

Thus, there are some restrictions placed on each — acids must contain one or more atoms of H to donate, and bases must have one or more lone pairs in order to accept the  $\text{H}^+$  ion.

As such, acid-base reactions in the context of this theory involves the transfer of a proton from a Brønsted acid to a Brønsted base.

Note that, in the context of aqueous reactions,  $\text{H}^+$  can also be represented by  $\text{H}_3\text{O}^+$ , which is how it is currently theorised to exist in aqueous solutions.

### 1.2 Lewis

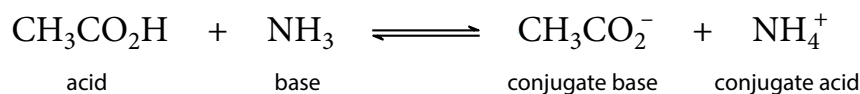
While Brønsted acids and bases are defined in terms of the transfer of protons, Lewis acids and bases are defined in terms of the transfer of electron pairs. Thus:

- Lewis acids *accept* an electron pair from a Lewis base donor.
- Lewis bases correspondingly *donate* an electron pair to a Lewis acid.

Further references to acids or bases implicitly refer to the *Brønsted* definition.

## 1.3 Conjugate Acid-Base Pairs

When an acid loses the  $\text{H}^+$  ion, an anion is naturally left — this is the conjugate base of the acid. Conversely, when a base accepts a proton, it forms the conjugate acid of the base.



It should be immediately clear that this is an *equilibrium* reaction.

In the forward reaction,  $\text{CH}_3\text{CO}_2\text{H}$  acts as the acid, donating a proton to the base,  $\text{NH}_3$ . In the reverse direction,  $\text{NH}_4^+$  is the acid, donating a proton to the base  $\text{CH}_3\text{CO}_2^-$ .

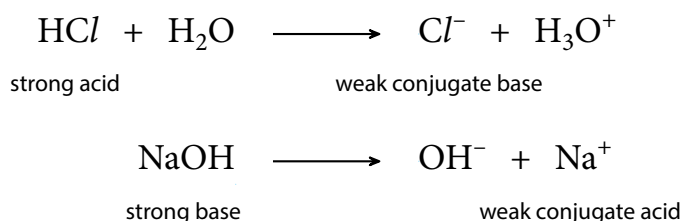
Furthermore,  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{CH}_3\text{CO}_2^-$  are *conjugate pairs*, as are  $\text{NH}_3$  and  $\text{NH}_4^+$ . Conjugate pairs always differ by a proton, and in any given acid-base reaction, there are two such pairs.

## 1.4 Strength of Acids and Bases

It is important to note that the *strength* of an acid or base is distinct from its *concentration* in solution; it is possible to have a strong, dilute acid, or a weak, concentrated base.

### 1.4.1 Strong Acids and Bases

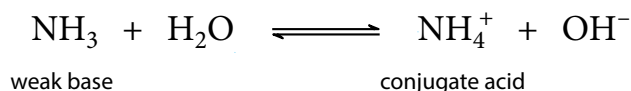
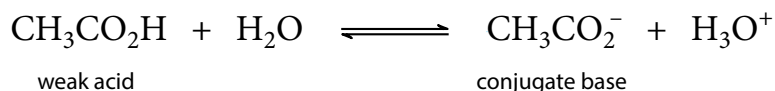
The strength of an acid or base is given as the degree of dissociation from the acid or base into ions, in solution. A strong acid or base is one that ionises *completely* in solution to give  $\text{H}^+$  or  $\text{OH}^-$  respectively.



Since they ionise *completely*, the reverse reaction is negligible, so the reaction is written with a single-headed arrow,  $\longrightarrow$ . This is because the conjugate base  $\text{Cl}^-$ , in the case of  $\text{HCl}$ , has a low tendency to accept a proton.

## 1.4.2 Weak Acids and Bases

Weak acids and bases, on the other hand, only dissociate *partially* in water to give  $\text{H}^+$  and  $\text{OH}^-$ . Thus, they are in an equilibrium with their conjugate, so the reaction is written with a double-headed arrow,  $\rightleftharpoons$ .



Since this is an equilibrium reaction, a mixture of the undissociated acid or base, as well as its dissociated ions, exist in solution.

## 2 pH, pOH, and Other Such Constants

First, the general idea of  $p$  should be stated. In essence, it is this:

$$\text{pX} = -\lg X, \quad X = 10^{-\text{pX}}$$

So, it follows pH and pOH are, respectively,

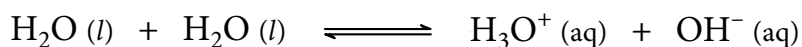
$$\begin{aligned} \text{pH} &= -\lg [\text{H}^+], & [\text{H}^+] &= 10^{-\text{pH}} \\ \text{pOH} &= -\lg [\text{OH}^-], & [\text{OH}^-] &= 10^{-\text{pOH}} \end{aligned}$$

In other words, it is a measure of the concentration of either  $\text{H}^+$  or  $\text{OH}^-$  in the solution. As you might be aware, the lower the pH, the more  $\text{H}^+$  there is. pOH is similar, although it obviously measures the concentration of  $\text{OH}^-$ .

Note that neither pH nor pOH should be used to compare acid strengths — as previously mentioned, strength is independent of concentration. It can only be used as a comparison when both acids have the same initial concentration.

## 2.1 Ionic Product of Water, $K_w$

Pure water actually *auto-ionises* to a very slight degree, giving  $\text{H}^+$  (aq) and  $\text{OH}^-$  (aq).



Since this is an equilibrium, the  $K_c$  value is as such:

$$K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Given that the extent of ionisation is minuscule, the 'concentration' of  $\text{H}_2\text{O}$  is almost constant, and so

$$K_w = K_c \times [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

Thus,  $\text{p}K_w$  becomes relatively simple, taking  $\lg$  on both sides:

$$\text{p}K_w = \text{pH} + \text{pOH}$$

Experimentally, it is found that, at  $25^\circ\text{C}$ ,  $K_w = 1.0 \times 10^{-14} \text{ mol dm}^{-3}$ , so:

- $\text{p}K_w = 14$
- $\text{pH} + \text{pOH} = 14$ .

The value of  $K_w$ , and by extension,  $\text{p}K_w$ , is affected solely by temperature, just like  $K_c$ . Thus, only at  $25^\circ\text{C}$  does  $\text{pH} + \text{pOH} = 14$  hold; at higher temperatures,  $K_w$  *increases*, so the sum is *greater than* 14.

Of course, the relationships  $\text{pH} + \text{pOH} = \text{p}K_w$  and  $K_w = [\text{H}^+][\text{OH}^-]$  always hold.

## 2.2 pH and pOH of Strong Acids and Bases

Given that strong acids and bases dissociate completely in water,  $[\text{H}^+]$  and  $[\text{OH}^-]$  simply become the initial concentration of the corresponding acid or base. If the acid in question is di- or even tri-protic, then the concentration of  $\text{H}^+$  will need to be multiplied by the appropriate ratio — the same applies for bases, of course.

If the initial concentration of the strong acid or base is smaller than  $1.0 \times 10^{-7} \text{ mol dm}^{-3}$ , the molecules of  $\text{H}^+$  or  $\text{OH}^-$  from the auto-ionisation of water must be taken into account — it is as simple as adding  $1.0 \times 10^{-7}$  to the concentration of the acid or base.

### 3 Dissociation of Acids and Bases

The acid and base dissociation constants,  $K_a$  and  $K_b$  respectively, are indicators of the degree of dissociation of the given acid or base.

Additionally, given the definitions of both  $K_a$  and  $K_b$ , the following relationships hold, for a given *conjugate acid-base pair*. Naturally it doesn't make sense to compare or relate two unrelated species.

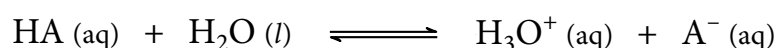
$$K_a \times K_b = K_w$$

$$\text{p}K_a + \text{p}K_b = \text{p}K_w$$

Thus, the weaker the acid, the stronger its conjugate base, and vice-versa.

#### 3.1 Acid Dissociation Constant, $K_a$

For some general weak acid HA, it dissociates partially in water:



In a dilute solution,  $[\text{H}_2\text{O}]$  is almost constant, so the equilibrium constant can be defined as such:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Naturally this is only true when the system is at equilibrium. Thus, the acid dissociation constant  $K_a$  is simply the equilibrium constant for the dissociation equilibrium, and indicates the *extent* to which the acid dissociates.

Additionally,  $\text{p}K_a$  is defined similarly to  $\text{p}K_w$ :

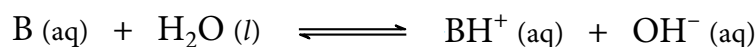
$$\text{p}K_a = -\lg K_a$$

The larger the value of  $K_a$  (and conversely, the smaller the value of  $\text{p}K_a$ ), the stronger the acid is. Thus,  $K_a$  values should be used as the basis for comparing the strength of weak acids. Naturally, the  $K_a$  values should be taken at the same temperature for a valid comparison.

Note that the  $K_a$  value for strong acids like HCl is very large, and is often irrelevant.

### 3.2 Base Dissociation Constant, $K_b$

The definitions of  $K_b$  and  $pK_b$  are essentially the mirror images of  $K_a$  and  $pK_a$ . For a given weak base B:



Thus, the base dissociation constant  $K_b$  can be defined:

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

$pK_b$  can also be defined similarly:

$$pK_b = -\lg K_b$$

As with acids, the larger the value of  $K_b$ , the stronger the base.

### 3.3 Degree of Dissociation, $\alpha$

The degree of dissociation of a given acid or base is the *ratio* of the number of moles of the substance that are ionised, to the number of unionised moles of acid or base.

$$\alpha = \frac{[\text{acid}]_{\text{dissoc}}}{[\text{acid}]_{\text{initial}}}$$

Thus, for a strong acid or base,  $\alpha$  is close to 1, while it is often much smaller than 1 for weak acids or bases.

### 3.4 Calculations involving $K_a$ and $K_b$

Calculations involving only  $K_a$  or  $K_b$  are fairly straightforward. Given the value of  $K_a$  for instance, it is trivial to find the concentration of  $\text{H}^+$  and hence pH, *assuming*:

- $[\text{H}^+] = [\text{A}^-]$ , ie. all the  $\text{H}^+$  and  $\text{A}^-$  comes from the acid
- $[\text{HA}]$  at equilibrium =  $[\text{HA}]$  initially

The first assumption will be *invalid* when there are *external sources* of  $\text{H}^+$  or  $\text{A}^-$ , as in a buffer system. The second assumption can be discarded to be more accurate, but should be used when  $[\text{H}^+] \ll 0.1$ .

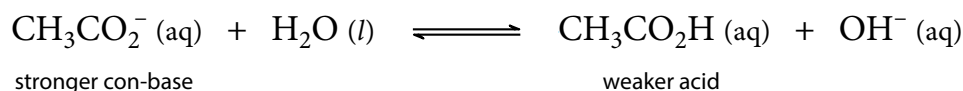
## 4 Salt Hydrolysis

Two main categories of salts undergo hydrolysis in water, forming  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions to give acidic or basic solutions respectively — ions of salts derived from weak acids or bases, and metal cations with a high charge density.

Ions of salts derived from strong acids and bases, eg.  $\text{NaCl}$  or  $\text{KNO}_3$ , will not hydrolyse, and will give a neutral solution.

### 4.1 Weak Acid, Strong Base

Examples of such salts include  $\text{CH}_3\text{CO}_2^-\text{Na}^+$ , which comes from the weak acid  $\text{CH}_3\text{CO}_2\text{H}$  and the strong base  $\text{NaOH}$ . The  $\text{Na}^+$  ion will not hydrolyse, while the  $\text{CH}_3\text{CO}_2^-$  ion will:

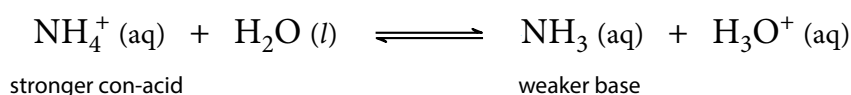


In this case, given that  $\text{CH}_3\text{CO}_2\text{H}$  is a weaker acid than water,  $\text{CH}_3\text{CO}_2^-$  is a stronger base than water; thus it is able to accept a proton — leaving  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{OH}^-$  as the products.

Since  $\text{OH}^-$  is present, the solution would be *alkaline*. However,  $\text{CH}_3\text{CO}_2^-$  is still an objectively weak base (water is a low benchmark), so the system exists in an equilibrium.

### 4.2 Strong Acid, Weak Base

$\text{NH}_4^+\text{Cl}^-$ , which comes from the weak base  $\text{NH}_3$  and the strong acid  $\text{HCl}$ , can have its  $\text{NH}_4^+$  ion undergo salt hydrolysis as well, in what is basically the mirror of the case with a strong base and weak acid:



Again,  $\text{NH}_4^+$  is a stronger acid than water, given that  $\text{NH}_3$  is weaker than water. Hence it donates a proton to  $\text{H}_2\text{O}$ , forming  $\text{H}_3\text{O}^+$  and giving an *acidic* solution that exists in an equilibrium.



### 4.3 Weak Acid and Weak Base

In this case, such as with the salt  $\text{CH}_3\text{CO}_2^-\text{NH}_4^+$ , both ions will hydrolyse — the final pH of the solution depends on the  $K_a$  and  $K_b$  values of the conjugate acid and base respectively. Generally speaking, the cation is the conjugate acid, and the anion is the conjugate base.

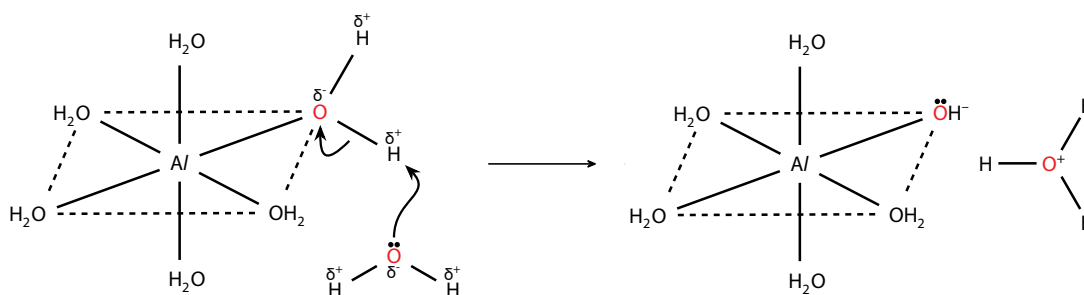
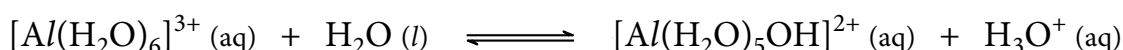
- $K_a > K_b$ ;  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$  — acidic solution
- $K_a = K_b$ ;  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$  — neutral solution
- $K_a < K_b$ ;  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$  — basic solution

### 4.4 Metal Cation With High Charge Density

There are 3 main metal cations exhibiting this property —  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Fe}^{3+}$ . As will be covered later in the *Chemistry of Transition Metals*, these ions can form complexes with  $\text{H}_2\text{O}$  ligands in aqueous solution.

Due to their high charge density, they are able to sufficiently polarise and weaken an O–H bond in one of the ligands, allowing an external  $\text{H}_2\text{O}$  molecule to gain a proton. This of course requires breaking said O–H bond, hence hydrolysis.

The  $\text{H}_3\text{O}^+$  molecule is formed, so the solution becomes acidic.



The table below shows the  $K_a$  values for the 3 cations in question:

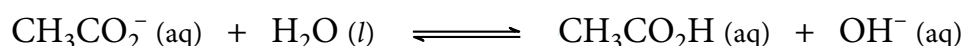
Ion	Hydrated Ion	$K_a$ / $\text{mol dm}^{-3}$ at $25^\circ\text{C}$
$\text{Fe}^{3+}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$	$6.3 \times 10^{-3}$
$\text{Cr}^{3+}$	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$	$1.6 \times 10^{-4}$
$\text{Al}^{3+}$	$[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$	$1.4 \times 10^{-5}$

## 4.5 pH of Hydrolysed Salt Solutions

Given the relevant  $K_a$  or  $K_b$  values, it is possible to find  $[H^+]$ , and hence pH, of the solution. However, if the  $K_a$  of the original weak acid is given, it is necessary to use the relationship  $K_w = K_a \times K_b$  to find the  $K_b$  value for the conjugate base.

$$K_b = \frac{K_w}{K_a} \qquad K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]}$$

Note that, in the absence of external agents,  $[CH_3CO_2H]$  and  $[OH^-]$  are equal, given that the stoichiometric ratios are also equal, in the original hydrolysis equation:



## 5 Buffer Solutions

### 5.1 Overview

All of the situations above have operated with the assumption that there are no external agents supplying ions to the solution, ie. all the ions come from the dissociation of the weak acid or base.

In a buffer solution, there is a large supply of both the undissociated acid or base, and the conjugate ion. This allows the buffer solution to react with small amounts of *both*  $H^+$  and  $OH^-$  that might be added. This allows for the system to *resist* small changes in pH.

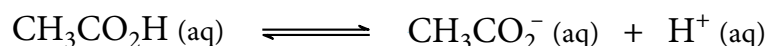
### 5.2 Method of Operation

Although the explanations below will use an acidic buffer as an example, the same principles apply for basic buffer using a weak base as a starting point.

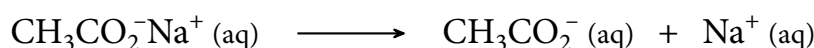
Where an acidic buffer will have a large reservoir of the undissociated weak acid and its conjugate base, an alkaline buffer will have a large reservoir of the undissociated weak base and its conjugate acid.

## 5.2.1 Creation of Buffer

The weak acid  $\text{CH}_3\text{CO}_2\text{H}$  dissociates partially in water:



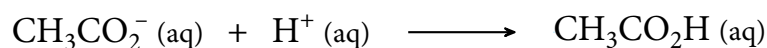
To create the buffer system, a large amount of  $\text{CH}_3\text{CO}_2^-$ , the conjugate base, is added — often using a soluble salt of that ion, for instance  $\text{CH}_3\text{CO}_2^-\text{Na}^+$ . This dissolves fully in water:



According to Le Châtelier's Principle, the position of equilibrium in the first equation (of the dissociation of the acid) shifts further to the left, suppressing the dissociation. Thus, the large supply of both  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{CH}_3\text{CO}_2^-$  is achieved.

## 5.2.2 Reaction with $\text{H}^+$

When a small amount of  $\text{H}^+$  ions are added to the buffer solution, they react with the *large reservoir* of  $\text{CH}_3\text{CO}_2^-$  molecules, the conjugate base:



The  $\text{H}^+$  ions are removed, and thus a change to the pH of the solution is resisted. From the original dissociation equation:

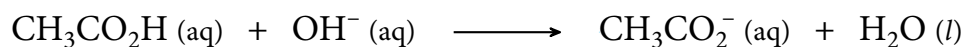
$$[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]}$$

Thus, even though  $[\text{CH}_3\text{CO}_2\text{H}]$  increases slightly and  $[\text{CH}_3\text{CO}_2^-]$  decreases slightly to neutralise the  $\text{H}^+$ , compared to the large reservoir, the change is small, and so  $[\text{H}^+]$  remains *relatively constant*, and hence so does pH.

This is the reason why a *large reservoir* is needed for a buffer solution — the larger this supply, the larger the resistance to changes in pH (ie. the more  $\text{H}^+$  or  $\text{OH}^-$  can be added before the buffer fails).

### 5.2.3 Reaction with $\text{OH}^-$

Similarly, a buffer solution reacts with added  $\text{OH}^-$  ions using the large supply of the unionised weak acid present:



As evident, the added  $\text{OH}^-$  ions are removed, and the pH of the solution remains constant — the existing  $\text{H}^+$  ions in the equilibrium are not neutralised.

Note that the *action reactions* of the buffer system are written with a single-directional arrow, as it is not directly part of the equilibrium.

## 5.3 pH of Buffer Solutions

Since the dissociation of the weak acid or base is *not* the only source of  $\text{H}^+$  or  $\text{OH}^-$  ions in the solution, the calculation of the pH of a buffer solution becomes more complex. Of course, beginning with the basic (*pun intended*) equation, for the weak acid  $\text{CH}_3\text{CO}_2\text{H}$  and the weak base  $\text{NH}_3$ :

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-]_{eqm}[\text{H}^+]_{eqm}}{[\text{CH}_3\text{CO}_2\text{H}]_{eqm}} \quad K_b = \frac{[\text{NH}_4^+]_{eqm}[\text{OH}^-]_{eqm}}{[\text{NH}_3]_{eqm}}$$

As stated above, adding the conjugate of the acid or base moves the position of equilibrium of the dissociation reaction to the left, reducing the amount of  $\text{CH}_3\text{CO}_2^-$  or  $\text{NH}_4^+$  that comes from the acid or base. Hence, the following approximations can be made:

- $[\text{CH}_3\text{CO}_2\text{H}]_{initial} = [\text{CH}_3\text{CO}_2\text{H}]_{eqm}$ , since very little  $\text{CH}_3\text{CO}_2\text{H}$  dissociates
- $[\text{CH}_3\text{CO}_2^-]_{salt} = [\text{CH}_3\text{CO}_2^-]_{eqm}$ , since almost all of the conjugate comes from the salt

Or, for the base:

- $[\text{NH}_3]_{initial} = [\text{NH}_3]_{eqm}$ , since very little  $\text{NH}_3$  dissociates
- $[\text{NH}_4^+]_{salt} = [\text{NH}_4^+]_{eqm}$ , since almost all of the conjugate comes from the salt

Hence, performing the appropriate replacements:

$$K_a = \frac{[\text{H}^+]_{eqm}[\text{salt}]}{[\text{acid}]} \quad K_b = \frac{[\text{OH}^-]_{eqm}[\text{salt}]}{[\text{base}]}$$

$$[\text{H}^+]_{eqm} = K_a \times \frac{[\text{acid}]}{[\text{salt}]} \quad [\text{OH}^-]_{eqm} = K_b \times \frac{[\text{base}]}{[\text{salt}]}$$

Thus the pH and pOH can be found, given the concentrations of the acid and salt used to create the buffer solution.

### 5.3.1 Equation of Henderson and Hasselbalch

These two people made an equation apparently — simply perform a  $-lg$  on both sides of the equations above:

$$\text{pH} = \text{p}K_a + lg \frac{[\text{salt}]}{[\text{acid}]} \quad \text{pOH} = \text{p}K_b + lg \frac{[\text{salt}]}{[\text{base}]}$$

Note that the fraction inside the logarithm is *flipped*, because math works that way.

## 5.4 Buffer Capacity

The capacity of a buffer is determined by the initial concentration of [salt], and [acid] or [base]. Furthermore, the most effective buffer solution has equal concentration of the salt to the acid or base:

$$\frac{[\text{salt}]}{[\text{acid}]} = 1 \quad \frac{[\text{salt}]}{[\text{base}]} = 1$$

Thus, it can be shown that, at the maximum capacity:

$$\text{pH} = \text{p}K_a \quad \text{pOH} = \text{p}K_b$$

When a buffer is at maximum capacity, it is able to resist the greatest changes in pH, ie. the addition of  $\text{H}^+$  or  $\text{OH}^-$  ions. The further away it is from this maximum, the less effective it becomes.

## 5.5 Effective Buffer Range

As  $\text{H}^+$  ions are added, the capacity of the buffer is *used up*, so to speak, as the ions or molecules in the buffer are consumed. This causes a change in the ratio of [salt] to [acid] or [base], since one is consumed and the other is generated.

Since the maximum capacity exists when this ratio is 1, the further away it strays, the less effective the buffer becomes, and it is less able to resist the addition of  $\text{H}^+$  or  $\text{OH}^-$  ions.

In practice, these are the limits for the effectiveness of a buffer solution:

$$0.1 < \frac{[\text{salt}]}{[\text{acid}]} < 10$$

Or, in other words, the ratio between the acid or base and its conjugate must not deviate by more than a factor of 10. Alternatively, in terms of pH and pOH:

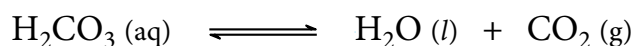
$$\text{pH range} = \text{p}K_a \pm 1 \quad \text{pOH range} = \text{p}K_b \pm 1$$

## 5.6 Biological Purpose of Buffer Systems

Curiously, chemistry seems to delve into the realms of physics and biology — *they are dark and full of terrors*. Anyway, one important function of buffers is in regulating the pH of human blood, to maintain the effectiveness of enzymes, and of course, preserve life.

In fact, blood contains a large reservoir of  $\text{H}_2\text{CO}_3$ , a weak acid which is actually dissolved aqueous  $\text{CO}_2$  and its conjugate base  $\text{HCO}_3^-$ .

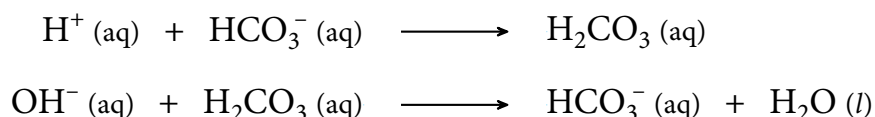
First,  $\text{H}_2\text{CO}_3$  exists in an equilibrium:



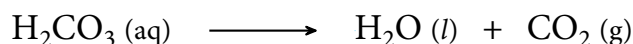
Since  $\text{H}_2\text{CO}_3$  is part of the buffer system in the blood, the following buffer equilibrium exists as well:



Thus, if the pH becomes too high, the excess  $\text{OH}^-$  will react with the  $\text{H}_2\text{CO}_3$ ; if pH becomes too low, the excess  $\text{H}^+$  reacts with the  $\text{HCO}_3^-$  in the buffer:



If the amount of  $\text{H}_2\text{CO}_3$  in the blood becomes too high, the lungs do the job of exhaling the  $\text{CO}_2$ :



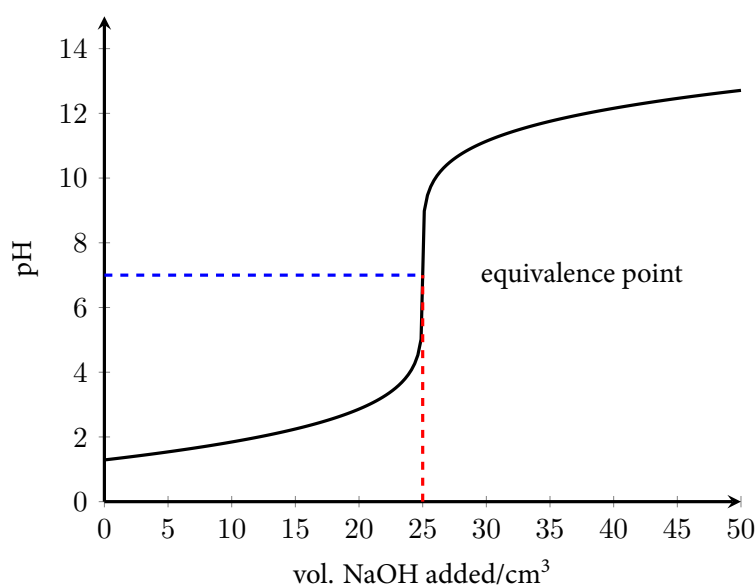
## 6 Titration of Weak Acids and Bases

In titrating acids and bases, there are  $2^2$  cases — strong acid against strong base, strong acid against weak base, weak acid against strong base, and weak acid against weak base.

Each of these cases will be covered below; all assume that the initial concentration of the acid and the base are identical, the acid is in the flask and the base in the burette, and  $25\text{ cm}^3$  of the acid is used.

### 6.1 Strong Acid and Strong Base

Here, the titration of  $\text{HCl}$  against  $\text{NaOH}$ .

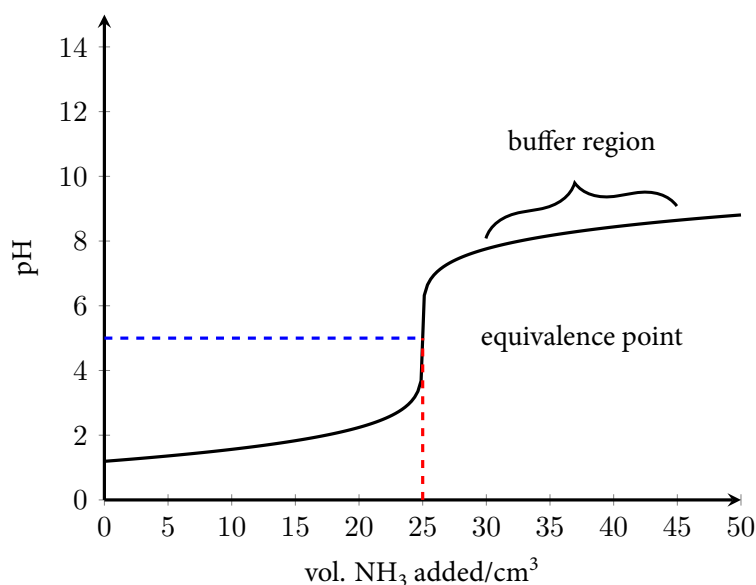


- $V = 0\text{ cm}^3$       $\text{pH} = [\text{acid}]$ , since only the strong acid exists.
- $V < 25\text{ cm}^3$       $\text{pH} < 7$ , but increases as more acid is neutralised.  
No salt hydrolysis or buffer, since there is no weak acid or base.
- $V = 25\text{ cm}^3$       $\text{pH} = 7$  at the equivalence point.  
No  $\text{H}^+$  or  $\text{OH}^-$  is present, so the solution is neutral.
- $V > 25\text{ cm}^3$       $\text{pH} > 7$  as  $[\text{OH}^-]$  increases, due to the addition of more  $\text{NaOH}$ .

*Phenolphthalein*, *methyl orange* or *thymol blue* can be used as indicators. Of note is the sharp pH change at the equivalence point in the titration curve.

## 6.2 Strong Acid, Weak Base

Here, the titration of HCl against  $\text{NH}_3$ .



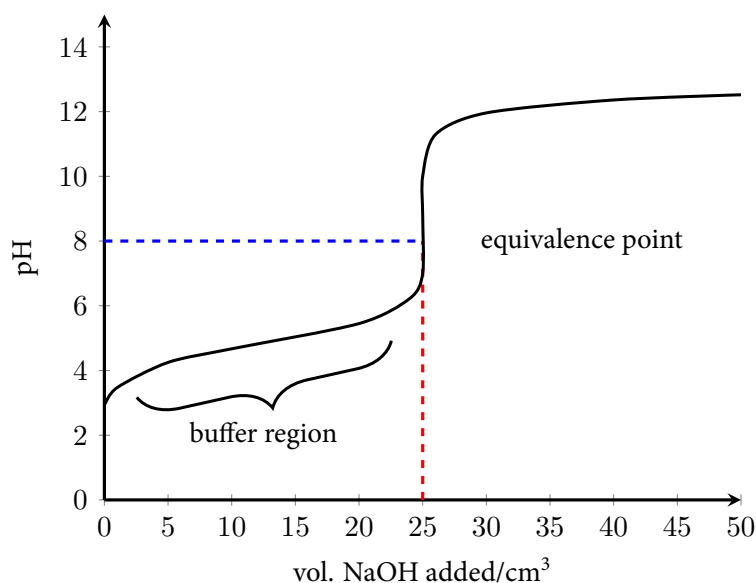
- $V = 0 \text{ cm}^3$       $\text{pH} = [\text{acid}]$ , since only the strong acid exists.
- $V < 25 \text{ cm}^3$       $\text{pH} < 7$ , but increases as more acid is neutralised.  
No salt hydrolysis or buffer, since there is no weak acid or base.
- $V = 25 \text{ cm}^3$       $\text{pH} < 7$  at the equivalence point.  
Even though no  $\text{H}^+$  or  $\text{OH}^-$  is present,  $\text{NH}_4^+$  in the salt hydrolyses, forming acid:  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$ .
- $V > 25 \text{ cm}^3$       $\text{pH} > 7$  as  $[\text{OH}^-]$  increases, due to the addition of more base.  
A buffer forms, since there is  $\text{NH}_3$  and its conjugate acid  $\text{NH}_4^+$ .

*Methyl orange* can be used as the indicator, since its working range is within the sharp pH change.



### 6.3 Weak Acid, Strong Base

Here, the titration of  $\text{CH}_3\text{CO}_2\text{H}$  against  $\text{NaOH}$ .

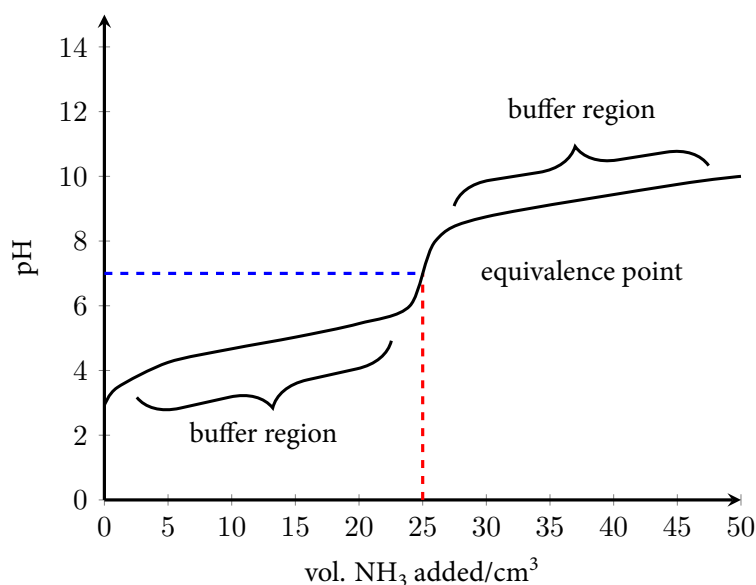


- $V = 0 \text{ cm}^3$   $pH > [\text{acid}]$ , since the acid is weak.
- $V < 25 \text{ cm}^3$   $pH < 7$ , but increases as more acid is neutralised.  
A buffer forms; there is  $\text{CH}_3\text{CO}_2\text{H}$  and its conjugate base  $\text{CH}_3\text{CO}_2^-$ .
- $V = 25 \text{ cm}^3$   $pH > 7$  at the equivalence point.  
Even though no  $\text{H}^+$  or  $\text{OH}^-$  is present,  $\text{CH}_3\text{CO}_2^-$  in the salt hydrolyses, forming base:  $\text{CH}_3\text{CO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}_2\text{H} + \text{OH}^-$ .
- $V > 25 \text{ cm}^3$   $pH > 7$  as  $[\text{OH}^-]$  increases, due to the addition of more base.  
No buffer; there is no  $\text{CH}_3\text{CO}_2\text{H}$  left, only its conjugate  $\text{CH}_3\text{CO}_2^-$ .

*Phenolphthalein* or *thymol blue* can be used as the indicator, since their working ranges lie within the sharp pH change.

## 6.4 Weak Acid, Weak Base

Here, the titration of  $\text{CH}_3\text{CO}_2\text{H}$  against  $\text{NH}_3$ .



- $V = 0 \text{ cm}^3$      $\text{pH} > [\text{acid}]$ , since the acid is weak.
- $V < 25 \text{ cm}^3$      $\text{pH} < 7$ , but increases as more acid is neutralised.  
A buffer forms; there is  $\text{CH}_3\text{CO}_2\text{H}$  and its conjugate base  $\text{CH}_3\text{CO}_2^-$ .
- $V = 25 \text{ cm}^3$      $\text{pH} \approx 7$  at the equivalence point.  
Both the conjugate base and conjugate acid hydrolyse:  

$$\text{CH}_3\text{CO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}_2\text{H} + \text{OH}^-$$

$$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$$
 The exact pH depends on the  $K_a$  and  $K_b$  values of the conjugates.
- $V > 25 \text{ cm}^3$      $\text{pH} > 7$  as  $[\text{OH}^-]$  increases, due to the addition of more base.  
A buffer forms; there is  $\text{NH}_3$  and its conjugate acid  $\text{NH}_4^+$ .

No suitable indicator can be used, since there is no sharp pH change at all. A pH meter can be used instead. Note that the pH at the equivalence point is not necessarily 7 — following the situation of simultaneous salt hydrolysis of a weak acid and base:

- $K_a > K_b$     —     $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ ;    acidic solution
- $K_a = K_b$     —     $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ ;    neutral solution
- $K_a < K_b$     —     $[\text{H}_3\text{O}^+] < [\text{OH}^-]$ ;    basic solution

In this case, the  $K_a$  and  $K_b$  of  $\text{NH}_3^+$  and  $\text{CH}_3\text{CO}_2\text{H}$  are almost equal ( $1.8 \times 10^{-5} \text{ mol dm}^{-3}$ ), so the  $K_b$  and  $K_a$  of their conjugates will be as well.

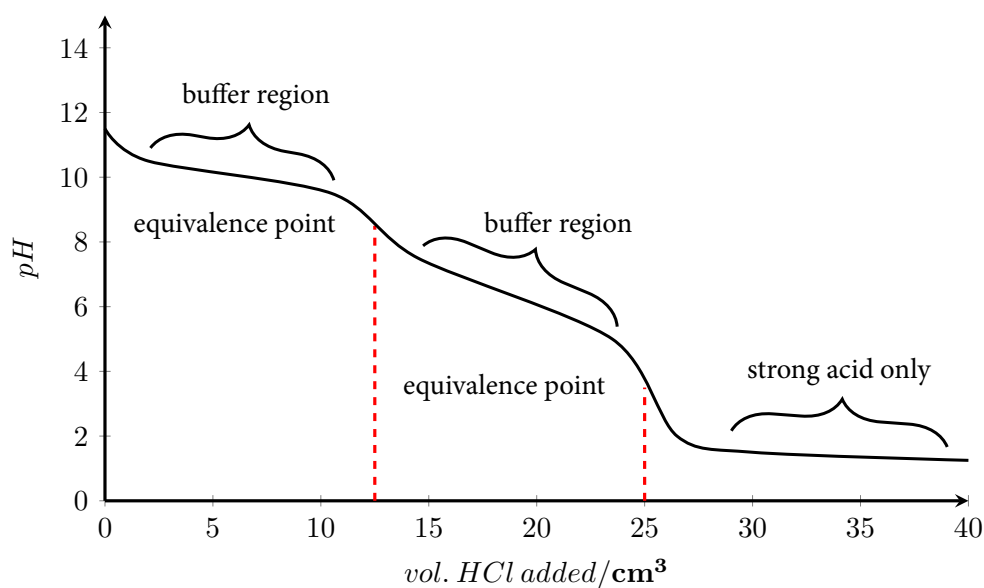
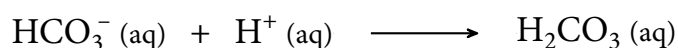
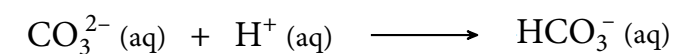
## 6.5 Titration of Polyprotic Acids or Bases

Polyprotic acids are acids with multiple ionisable protons; conversely polybasic bases are those that can accept more than one proton.

$\text{H}_2\text{CO}_3$  is a polyprotic acid with a weak second acid  $\text{HCO}_3^-$ , while  $\text{H}_2\text{SO}_4$  is a strong polyprotic acid with a strong first acid and a weak second acid  $\text{HSO}_4^-$ . Often times the  $K_a$  of the first proton is much larger than that of subsequent ones.

When analysing polyprotic things, it is often convenient and apt to assume that every molecule of acid will first lose one proton, before starting to lose the second.

Thus, a distinct titration curve can be seen, in this case using the example of  $\text{CO}_3^{2-}$ , which is the conjugate base of the weak acid polyprotic  $\text{H}_2\text{CO}_3$ :



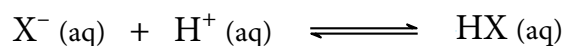
There are two distinct equivalence points here, and they should be observed separately with two indicators — *phenolphthalein* for the first equivalence point at  $\text{pH} = 8.5$ , and *methyl orange* for the second one at  $\text{pH} = 3.5$ .

*Methyl orange* should only be added to the solution after the first equivalence point is observed, if not the first point will be obscured since methyl orange exhibits no colour change at that point.

## 7 pH Indicators

### 7.1 Working Range

Indicators exist in an equilibrium with  $H^+$ ; the colour of the indicator depends on the ratio of the concentration of one ion to the other. For instance, taking an arbitrary indicator species  $X^-$  and its conjugate  $HX$ :



Following the general formula for  $K_a$ , and manipulating slightly:

$$K_X = \frac{[H^+][X^-]}{[HX]} \quad pH = pK_X + \lg \frac{[X^-]}{[HX]}$$

For the colour change to be visible, the concentration of the dominant ion must be greater than the less dominant one by a factor of 10, so the working range of an indicator is as such:

$$pH = pK_X \pm 1$$

## 7.2 Appropriate Indicator Selection

When selecting which indicator to use, the most obvious consideration is that the colour change will occur at the equivalence point of the reaction — if not it is pointless. For any indicator to be used at all, there should be a sharp change at said equivalence point; titrations involving at least one *strong* acid or base (or both) will exhibit such a sharp change.

The working pH ranges for a number of common indicators, and their uses, are summarised below:

Indicator	Working Range (pH)	Colour (Low/High)
Methyl Orange	3.1 to 4.4	Red / Yellow
Phenolphthalein	8.0 to 9.6	Colourless / Pink
Thymol Blue	8.0 to 9.6	Yellow / Blue

Next, according to their working pH ranges, a summary of the suitable indicators for each kind of titration:

Situation	Sharp pH Change	Indicators
Strong Acid, Strong Base	3.0 to 11.0	Any
Strong Acid, Weak Base	3.0 to 7.0	Methyl Orange
Weak Acid, Strong Base	7.0 to 11.0	Phenolphthalein, Thymol Blue
Weak Acid, Weak Base	<i>none</i>	<i>none</i>

# Electrochemical Cells

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## 1 Overview

Electrochemical cells are typically composed from two half-cells, each with their own redox reaction occurring and each having an electrode that is typically inert to prevent it from interfering. As the name might suggest, electrochemical cells generate some amount of *emf*, depending on the difference between the electrode potentials of the half-cells.

### 1.1 Electrodes

Consistent across both electrolytic cells and electrochemical cells, is the designation of the cathode and anode, in terms of redox reactions:

- Oxidation occurs at the *anode*
- Reduction occurs at the *cathode*

This comes in useful since the direction of electron flow, and hence the polarity of each electrode, will change between the two systems.

## 2 Standard Reduction Potential, $E^\ominus$

The standard reduction potential,  $E^\ominus$  is defined for a half redox reaction — either reduction or oxidation. However, per convention, the *values* for  $E^\ominus$  are always quoted for the reduction reaction. Hence, if the  $E^\ominus$  for oxidising Zn to  $\text{Zn}^{2+}$  is +0.76 V, the quoted  $E^\ominus$  value will be −0.76 V.

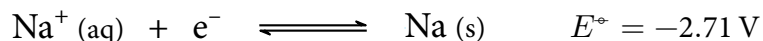
As its name would imply, the *standard* reduction potential is measured using a *standard hydrogen cell*, which is an electrochemical cell (covered later), with these properties:

- 1.0 mol dm<sup>−3</sup> of  $\text{H}^+$  ions in an aqueous solution
- Temperature of 298 K
- Hydrogen gas at 1 atm bubbling over a *platinised platinum* (how obtuse) electrode

The potential on the surface of the platinum electrode is assigned a value of 0 by convention, and all standard electrode potentials are measured relative to this value of 0.

This standard allows for the comparison of different half-equations — the more positive the value of  $E^\ominus$ , the more feasible the redox reaction. Since it is defined as such, that means the given substance is easier to *reduce*.

Conversely, if the value of  $E^\ominus$  for a certain equation is highly negative, like this:



This means that it is far more feasible for the equation to proceed in the *reverse direction* (note that these are written with reversible arrows when the direction of progress is still indeterminate), aka. the oxidation of Na instead.

## 2.1 Comparing $E^\ominus$ Values

Standard reduction potential values of different species can be used as a judge of their reduction or oxidation strength. If the  $E^\ominus$  value of a species is very high — the  $E^\ominus$  value of Li is  $-3.04 \text{ V}$  for instance — it is very spontaneously *oxidised*, making it a very powerful *reducing agent*.

Conversely, with  $\text{F}_2$ , the  $E^\ominus$  value is  $+2.87 \text{ V}$ , implying that it is very likely to be *reduced*, and hence making it a very powerful *oxidising agent*.

## 3 Standard Cell Potentials, $E^\ominus_{\text{cell}}$

Given that electrochemical cells are often made of two half-cells, or at the very least always have two redox half-reactions, the  $E^\ominus_{\text{cell}}$  represents the *total* potential of the two half-cells, otherwise known as the *standard cell potential*.

This standard cell potential is also the output *emf* of the electrochemical cell, and can be measured with a voltmeter connected between the two electrodes.  $E^\ominus_{\text{cell}}$  is simply defined as the difference between the  $E^\ominus$  of the reduction half cell, and the  $E^\ominus$  of the oxidation half cell, like so:

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$

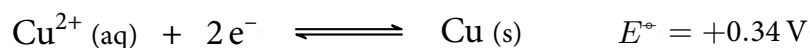
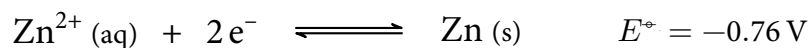
However, with some sign manipulation, it can be also expressed as the sum of the standard electrode potential of the reduction half-equation, and the *oxidation potential* of the oxidation half-equation.

While  $E^\ominus_{\text{cell}}$  is a measure of the output *emf* of the cell, if it is negative to begin with, the required redox reactions are unfeasible, and there will be no *emf* produced at all, and no reaction occurring. This is often used to predict the feasibility of a spontaneous redox reaction between two species, even if the produced *emf* is not the primary goal.

### 3.1 Calculating Standard Cell Potentials

While the definition of  $E_{cell}^{\ominus}$  might be simple, figuring out which values to use for each  $E^{\ominus}$  is not quite so simple. To put it concisely, each species in the reaction mixture will react in the most feasible way it can.

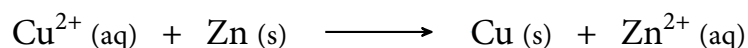
For example, given the following half-equations:



The first objective should be to identify the half-equation at the cathode, or where reduction is taking place. Comparing the two  $E^{\ominus}$  values for the reduction of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ , the  $E^{\ominus}$  of the reduction of copper is *more positive* than that for the reduction of  $\text{Zn}^{2+}$  — hence copper will be reduced at the cathode.

Thus the other half-reaction must occur at the anode, and in this case zinc is oxidised.

Combining the two, the overall reaction is determined, as well as the cell potential,  $+0.34 - (-0.76) = +1.10$ .



$$E_{\text{cell}}^{\ominus} = +1.10 \text{ V}$$

### 3.2 Relation to Gibbs Free Energy

Given that both the standard cell potential and Gibbs Free Energy predict the feasibility and spontaneity of a reaction, they can be related by an equation:

$$\Delta G^{\ominus} = -nFE_{\text{cell}}^{\ominus}$$

$F$  is the Faraday constant, which is  $9.648 \times 10^5 \text{ C mol}^{-1}$ , and  $n$  is the number of moles of electrons transferred in the redox reaction.



### 3.3 Predicting Redox Feasibility with Cell Potentials

Since an  $E_{cell}^\circ$  value  $< 0$  will not result in any reaction, it can be used to predict the feasibility of arbitrary redox reactions, to determine whether they will occur spontaneously when the reactants are mixed.

Unfortunately there are limitations that prevent cell potential from being a perfect gauge of a reaction's feasibility.

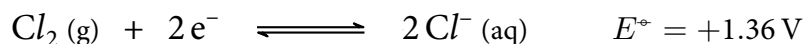
#### 3.3.1 Rate of Reaction

$E_{cell}^\circ$  only serves to show that the reaction is feasible, and says nothing about the *rate of reaction*; the most common cause of this is a high activation energy for the reaction.

#### 3.3.2 Conditions

The entire system of values for  $E^\circ$  and hence  $E_{cell}^\circ$  are defined only for *standard conditions* — pressure, temperature, etc. However, given that each half-reaction is actually an equilibrium, our old friend Le Châtelier's Principle can predict the direction that the position of equilibrium will shift in.

For example, given the reduction of chlorine:



If the pressure of the system were to increase, then by Le Châtelier's Principle, the position of equilibrium would shift to the right, favouring the *reduction of chlorine*. Hence, the value of  $E$  (note, not  $E^\circ$  since it's not standard any more) would *increase*.

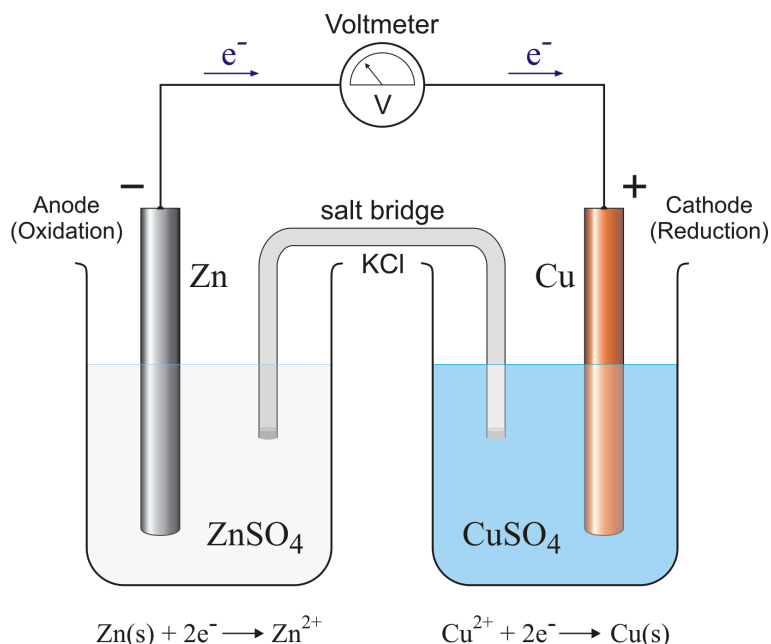
#### 3.3.3 Ion Concentration

Again, by Le Châtelier's Principle, changing the concentration of ions can also move the position of equilibrium changing the value of  $E$ . This can be exploited by connecting two half-cells of the same ion, but at different concentrations. The difference in  $E$  values will create a net positive  $E_{cell}^\circ$  that can be measured.

## 4 Electrochemical Cells

### 4.1 Overview

Now that all the crucial terms have been defined, electrochemical cells are simply a combination of two half-cells that can be linked together with a *salt bridge* to produce a usable voltage and current.



Electrochemical cell with copper and zinc

### 4.2 Electrode and Electrolyte Choice

Referring back to the diagram, electrodes and electrolytes should be chosen to make life easier. Firstly the choices need to be able to supply the relevant reactants for the reaction, and the ions that are not participating in the reaction (ie.  $\text{SO}_4^{2-}$  above) should... be inert.

For the cathode half-reaction,  $\text{Cu}^{2+}(\text{aq})$  is reduced to  $\text{Cu}(\text{s})$ . Hence, there needs to be a source of  $\text{Cu}^{2+}$  ions, in this case provided by the  $\text{CuSO}_4(\text{aq})$  electrolyte. Note that while a copper electrode is used, it is not necessary — any inert electrode can be used as well.

For the anode half-reaction,  $\text{Zn}(\text{s})$  is oxidised to  $\text{Zn}^{2+}(\text{aq})$ . Hence, there needs to be a source of  $\text{Zn}(\text{s})$  atoms, in this case provided by the anode — the anode will slowly reduce in mass as the reaction proceeds. While the electrolyte used is  $\text{ZnSO}_4$ , again there is no need for it to actually contain  $\text{Zn}^{2+}(\text{aq})$  ions.

Finally, even though the electrolyte and electrodes need not contain the species being reduced or oxidised, the standardised nature of  $E_{\text{cell}}^\ominus$  requires fixed concentrations of ions; while the cell will function with different reactants, the measured value of  $E$  will likely differ from  $E_{\text{cell}}^\ominus$  in such cases.

## 4.3 Salt Bridge

A preliminary knowledge of electricity will tell you that circuits need to be closed for electricity to flow. This is one of the purposes of the salt bridge, to connect the two half-cells so that current will flow.

The other purpose is to balance the electrical charge in each half-cell. At the anode half-cell, electrons are lost and  $\text{Zn}^{2+}$  is added to the solution, creating a net positive charge; at the cathode,  $\text{Cu}^{2+}$  ions are removed from solution and electrons are added, creating a net negative charge.

Without a salt bridge, this imbalance would grow unchecked. Eventually, the *potential difference* due to the difference in charge of the two cells would overpower the  $E_{\text{cell}}^{\circ}$  of the redox reactions, and no more electrons would flow.

The salt bridge typically contains ions that do not react with the electrodes or electrolytes, in this case  $\text{K}^+$  and  $\text{Cl}^-$ . If the electrolyte contains  $\text{Pb}^{2+}$  for instance, then obviously  $\text{Cl}^-$  cannot be used in the salt bridge.

As the positive charge in the anode half-cell increases,  $\text{Cl}^-$  ions from the salt bridge flow in to counteract the positive charge, and vice-versa for  $\text{K}^+$  ions and the cathode half-cell.

### 4.3.1 Ion Migration Rates

An alternative to a salt bridge is simply a porous membrane between the two cells, that reduces the mixing of electrolytes. Due to the different migration rates (depending on charge and size) of the ions in the electrolytes, there may be a net potential difference, which can impact the performance and  $E_{\text{cell}}^{\circ}$  of the overall cell.

Hence, the ions chosen to fill the salt bridge need to have similar migration rates; examples include  $\text{K}^+$  and  $\text{NO}_3^-$ , or as above,  $\text{K}^+$  and  $\text{Cl}^-$ .

## 5 Applications of Electrochemical Cells

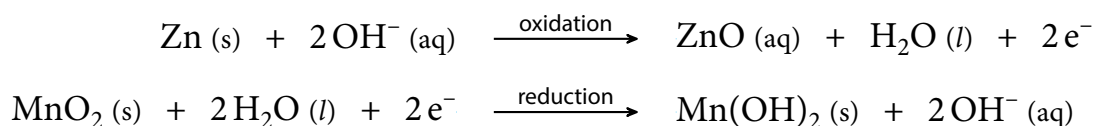
### 5.1 Batteries

Hmm... a reaction that produces an *emf*, what could it be used for...

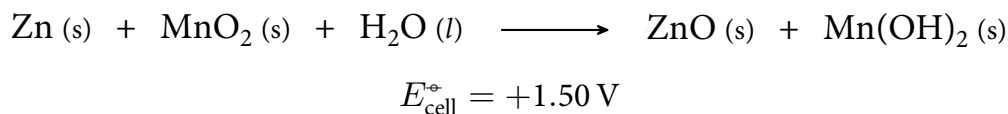
Clearly, the most common use for an electrochemical cell is... in a battery. Or rather, a battery is an electrochemical cell. The sections below detail some of the more commonly seen varieties of batteries.

#### 5.1.1 Alkaline

Quite possibly the most common battery, non-rechargeable alkaline batteries are commonplace in everyday devices. They typically employ a *graphite cathode*, and a *zinc anode*. The electrolyte is usually  $\text{MnO}_2$  in  $\text{KOH}$  paste — the  $\text{OH}^-$  in the paste is used for the oxidation of zinc.

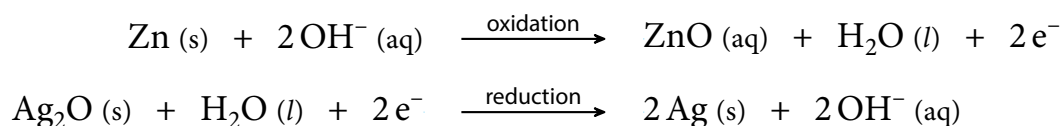


The overall reaction is as such:

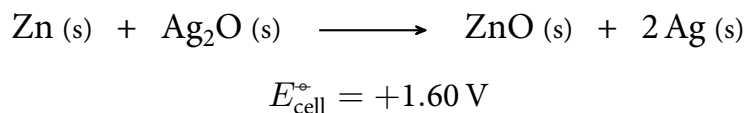


#### 5.1.2 Silver

Silver button cells are commonly used for small devices, and employ a zinc anode and a silver oxide ( $\text{Ag}_2\text{O}$ ) cathode. The electrolyte is, again, some alkaline paste, for example  $\text{KOH}$  or  $\text{NaOH}$ .

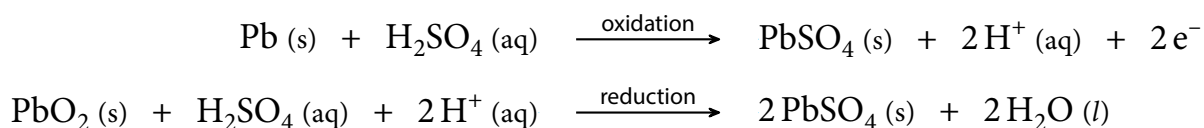


The overall reaction is as such:

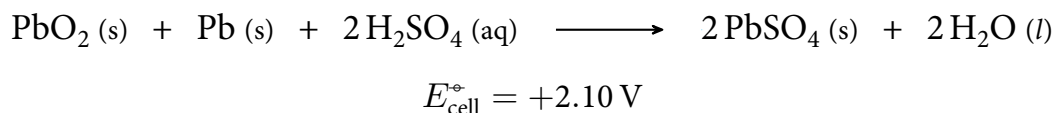


### 5.1.3 Lead-Acid

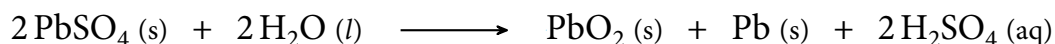
Lead-acid batteries are commonly found in cars, and have the nice property of being rechargeable.



The overall reaction is as such:



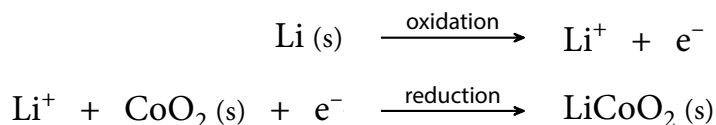
When the battery is recharged, it functions like an electrolytic cell, and the half-reactions above are simply reversed. Then, the overall equation is reversed as well:



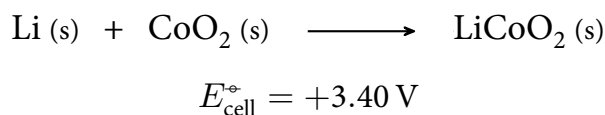
### 5.1.4 Lithium-Ion

Again, lithium ion batteries are rechargeable. They commonly use a graphite anode — the hexagonal layers are able to bind to the relatively small  $\text{Li}^+$  ions, as well as Li atoms. The cathode is typically made of a transition metal oxide, in this case  $\text{CoO}_2$ , which can also bind to  $\text{Li}^+$  ions in its structure.

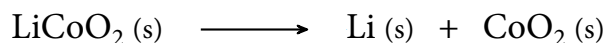
Note that aqueous solvents (containing water) cannot be used in the battery, because of the high reactivity of lithium metal; organic solvents are usually used.



The overall reaction is as such:



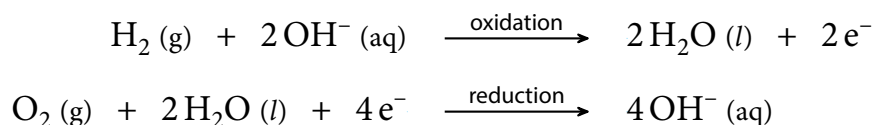
Again, the process for recharging is simply electrolysis, and involves reversing the equations above.



## 5.2 Fuel Cells

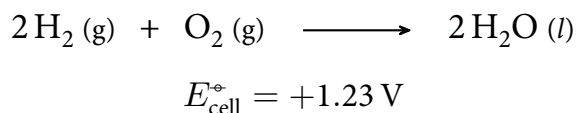
Fuel cells are basically batteries where the reactants are constantly replenished. Of note is the hydrogen-oxygen fuel cell, which basically involves the oxidation of hydrogen gas into water. The electrolyte is basically  $\text{OH}^-$  (aq), typically heated to increase the rate of reaction.

The main attraction of a hydrogen fuel cell is to enable the direct conversion of the  $\text{H}_2$  (g) fuel into electricity, instead of using the typical burn-the-gas-and-heat-water-to-make-steam-that-turns-a-turbine-that-turns-a-generator-that-finally-makes-electricity design — this enables much higher levels of efficiency, up to 70%, over the 40-odd% of typical generators.



At the anode,  $\text{H}_2$  gas diffuses through the porous graphite electrode and comes into contact with the KOH electrolyte; at the cathode,  $\text{O}_2$  gas does the same.  $\text{H}_2$  is oxidised, and  $\text{O}_2$  is reduced.

The overall equation forms water only, which is a selling point of this design since the product is clean.





# Electrolysis

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## 1 Overview

Electrolysis is, simply put, the reverse of an electrochemical cell — now current is *supplied*, and the half-reactions on either side are simply reversed.

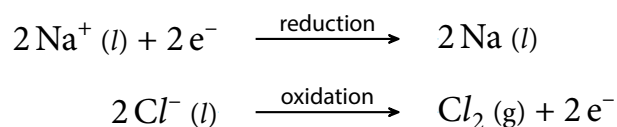
One difference is that there will often be different ions in solution, and certain ions will be *selectively discharged*, which depends on a number of factors — mostly their  $E^\ominus$  value.

Note that while oxidation still occurs at the anode and reduction still occurs at the cathode, the *polarity* of each electrode has been reversed; the external battery removes electrons from the anode causing it to be *positive*, while supplying electrons to the cathode causing it to be *negative*.

## 2 Electrolysis of Pure Molten Salts

The electrolysis of a pure molten salt is very straightforward — there are only two substances in the electrolyte to consider, so one will always be oxidised, and the other reduced.

If it isn't already obvious, the anion is oxidised and the cation is reduced. For example, with the electrolysis of molten NaCl:



When the current in the circuit flows, the electrode connected to the negative terminal of the battery will be the cathode — it supplies electrons, and *reduces* the  $\text{Na}^+$  ions.

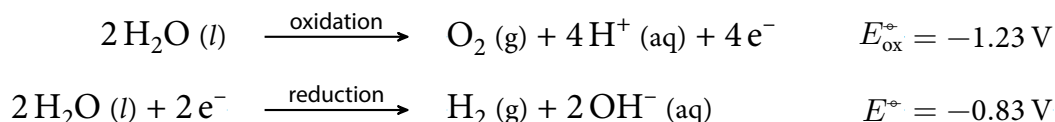
Because the cathode is negatively charged (due to the electrons),  $\text{Na}^+$  ions will be attracted to it, and migrate there. The reverse is true for the anode — and  $\text{Cl}^-$  ions migrate to it.

Note that each half-equation has its own  $E^\ominus$  value, and so the supply voltage (emf) of the battery must be greater than the total  $E_{\text{cell}}^\ominus$  of the system for the reaction to occur.



### 3 Electrolysis of Aqueous Ion Solutions

This is more complicated, because apart from the ions from whatever salt is dissolved, water can also be oxidised and reduced — the reaction that occurs at each electrode depends on the  $E^\ominus$  of the relevant half-equations.



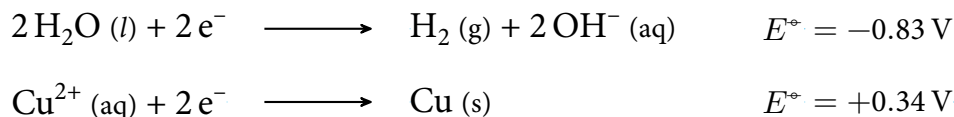
The half-equations for the reduction and oxidation of water are shown above. These are always the half-equations for oxidation and reduction of water, in any solution.

#### 3.1 Factors Affecting Selective Discharge

##### 3.1.1 $E^\ominus$ of Half-Reactions

The most direct and common way to identify the correct half-equation is by comparing  $E^\ominus$  values. The electrolysis of  $\text{CuBr}_2 (\text{aq})$  will be used as an example here, using inert platinum electrodes.

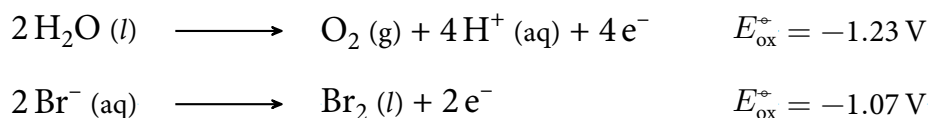
##### Cathode Reactions



Note that the equations are written with a single-arrow, since it is known that reduction is occurring.

Comparing the two half-equations, the  $E^\ominus$  value for the reduction of  $\text{Cu}^{2+}$  is larger than that of the reduction of water. Hence,  $\text{Cu}^{2+}$  will be *preferentially reduced*, depositing solid Cu metal at the cathode.

##### Anode Reactions



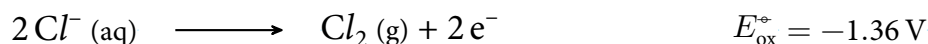
Comparing the two half-equations, the  $E_{\text{ox}}^\ominus$  value for the oxidation of  $\text{Br}^-$  is greater than that for the oxidation of water, so  $\text{Br}^-$  is *preferentially oxidised* at the anode, and  $\text{Br}_2 (\text{aq})$  forms around the anode.

Note that, in this case, the values of  $E_{\text{ox}}^\ominus$  instead of  $E^\ominus$  were used — the former is the standard oxidation potential, which is simply the reverse of the reduction potential. Hence, the *greater* value of  $E_{\text{ox}}^\ominus$  is used.

### 3.1.2 Concentration of Ions

The concentration of ions in solution can also affect the products of electrolysis. As covered in a previous chapter, ion concentrations can, as determined by Le Châtelier's Principle, increase or decrease the value of  $E^\ominus$  by moving the position of equilibrium.

The most common application of this is in the electrolysis of brine, or concentrated  $\text{NaCl}$  (aq). In a dilute solution, the anode candidates are as follows:



The  $E_{\text{ox}}^\ominus$  value for the oxidation of water is larger than for the oxidation of  $\text{Cl}^-$ , so water is preferentially oxidised.

However, when the concentration of  $\text{Cl}^-$  is increased, the position of equilibrium in the half-reaction shifts to the right, thus increasing the value of  $E_{\text{ox}}^\ominus$ .

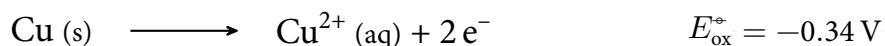
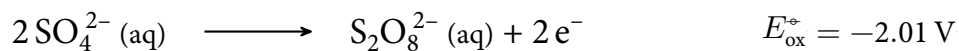
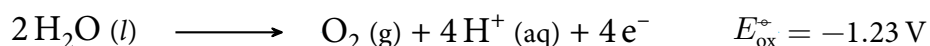
Since the difference between  $E_{\text{ox}}^\ominus$  for water and for chlorine is quite small, high concentrations of  $\text{Cl}^-$  can allow its  $E_{\text{ox}}^\ominus$  value to 'surpass' that of water, allowing chlorine gas to be preferentially discharged.

At the cathode, nothing new happens — water is still reduced, because the difference between the  $E^\ominus$  values of  $\text{Na}^+$  and  $\text{H}_2\text{O}$  are too great, at  $-2.71 \text{ V}$  and  $-0.83 \text{ V}$  respectively — something a change in concentration cannot overcome.

### 3.1.3 Electrode Reactions

Electrolysis typically uses inert electrodes, such as platinum or graphite. However, it is sometimes useful to have the electrode provide a source of reactants — this is typically the anode, since the metal atoms can be oxidised to ions.

For example, in the electrolysis of  $\text{CuSO}_4$  (aq), a copper anode is often used. Now, at the anode there are three competing half-reactions:



The last equation is only relevant because of Cu atoms being introduced by the copper anode. Since its  $E_{\text{ox}}^\ominus$  value is the greatest among the 3, copper is preferentially oxidised to  $\text{Cu}^{2+}$  ions in solution.

One final note — while graphite is typically considered inert in many cases for ionic electrolysis, if  $\text{O}_2$  (g) is formed and comes into contact with the graphite,  $\text{CO}_2$  and CO is often formed.

## 4 Electrolytic Calculations

### 4.1 Overview

*The number of moles of a substance that undergoes oxidation or reduction at each electrode is directly proportional to the quantity of charge that passes through the cell.*

— Michael Faraday

Faraday's Law of Electrolysis can be applied, along with some other physics formulae, to derive various relationships. Note that the number of moles of electrons passed depends on its mole ratio with the number of moles of product formed.

Faraday also has a constant — the aptly named Faraday Constant, that is the ratio of charge to number of moles of electrons; the quantity of charge carried per mole of electrons is 1 Faraday.

### 4.2 Formulae

$$Q = I \times t$$

$Q$ : the quantity of charge passed, in coulombs (C)

$I$ : the current provided, in amperes (A)

$t$ : the time in seconds

$$Q = n(e) \times F$$

$Q$ : the quantity of charge passed, in coulombs (C)

$n(e)$ : the number of moles of electrons passed during electrolysis

$F$ : Faraday Constant (approx. 96 500 C mol<sup>-1</sup>)

$$F = L \times e$$

$F$ : Faraday Constant (approx. 96 500 C mol<sup>-1</sup>)

$L$ : Avogadro Constant (approx.  $6.02 \times 10^{23}$ )

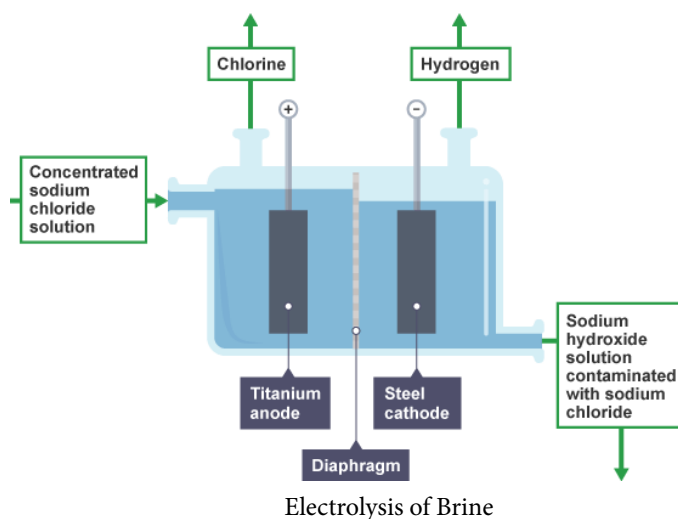
$e$ : The charge of one electron (approx.  $1.60 \times 10^{-19}$  C)

Note that this last formula is only used when the question requires calculating either  $F$ ,  $L$  or  $e$  from experimental data.

## 5 Applications of Electrolysis

### 5.1 Electrolysis of Brine

As discussed above, electrolysis of *concentrated*  $\text{NaCl}$  (aq) yields  $\text{Cl}_2$  (g), which is an industrially important compound. It also creates  $\text{H}_2$  (g) and  $\text{NaOH}$  (aq), which are also useful products.



Of note is the fact that the level of solution on the left is higher than on the right — this is important to ensure that the  $\text{OH}^-$  ions formed at the cathode do not flow back to the anode to be re-oxidised and contaminate the reactants.

### 5.2 Anodising of Aluminium

Aluminium metal naturally forms a thin layer of  $\text{Al}_2\text{O}_3$  at its surface that protects it from corrosion. Anodising the object increases the thickness of this layer, which provides more protection.

The object to be anodised is used as the... anode, and an inert cathode is used, together with a dilute acid electrolyte to conduct electricity.

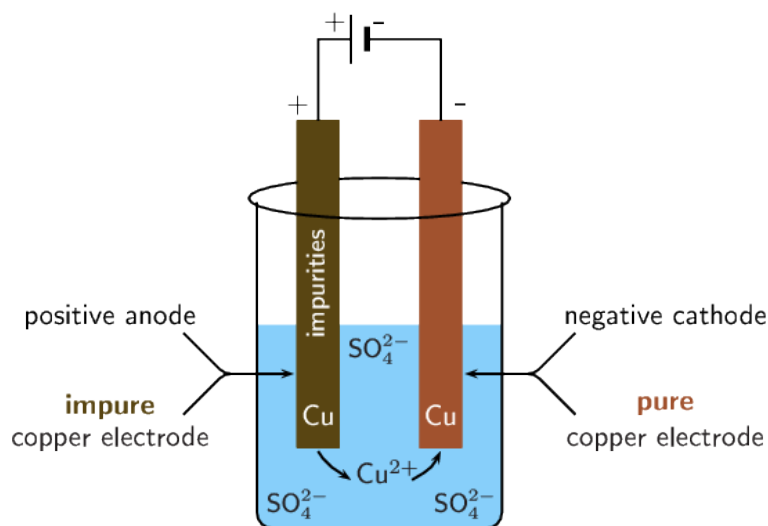
The reaction at the cathode is unimportant — the water is reduced to hydrogen gas, and is released. At the anode however, both water and aluminium are oxidised (for some **STRANGE**, unexplainable reason), forming the  $\text{Al}_2\text{O}_3$ .

The structure of this oxide layer is somewhat porous, allowing it to accept dyes more easily than a smooth metal surface.

### 5.3 Electrolytic Purification of Copper

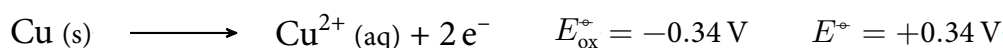
Copper minerals often contain small amounts of other metals, like zinc and silver. After a process of oxidation followed by reduction, the purely metallic form of these atoms can be obtained — including the silver and zinc impurities.

Electrolytic purification takes advantage of the different  $E^\ominus$  values between copper and the impurities, to preferentially oxidise and reduce only the wanted ions.



Electrolytic Purification of Copper

The relevant half-equations, and more importantly  $E^\ominus$  and  $E_{ox}^\ominus$  values, for each metal are shown below:



At the anode, the  $E_{ox}^\ominus$  of zinc is greater than that for copper, so it will be preferentially oxidised into  $\text{Zn}^{2+}$ . However, it only exists in small amounts, and once all the Zn has been oxidised, the next highest  $E_{ox}^\ominus$  metal is oxidised — in this case copper. As the copper is oxidised into aqueous ions, the unreacted Ag collects as *anode sludge* below the anode.

At the cathode, both  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  are present. Looking at the  $E^\ominus$  values however, copper is preferentially reduced due to its higher  $E^\ominus$  value, and  $\text{Zn}^{2+}$  ions remain in solution.

Water is also present at both electrodes, but looking at the values for  $E^\ominus$ , it is irrelevant.

A pure copper cathode is used, such that the newly-pure copper collects on already-pure copper — the impure copper is used as the anode. The electrolyte is typically  $\text{CuSO}_4 \text{ (aq)}$ .

## 5.4 Electroplating of Chromium

The process for electroplating some metal object with chromium (to increase shiny-ness) is similar to the process for purifying copper. However, to allow for a gradual and ~~modest appreciation~~ even coating of the object,  $\text{Cr}^{3+}$  is only supplied from the electrolyte, and is only present at low concentrations.

The electrolyte thus consists mainly of  $\text{CrO}_4^{2-}$  ions, and a small amount of  $\text{Cr}^{3+}$  ions. Like with copper, the object to be coated is used as the cathode;  $\text{Cr}^{3+}$  reduces to  $\text{Cr (s)}$  that coats the object, while  $\text{CrO}_4^{2-}$  is reduced to  $\text{Cr}^{3+}$ , which replenishes the ions that were consumed.