**CHEMICAL KINETICS**

**Introduction to Reaction Rate**

Chemical reaction kinetics deals with the rates of chemical processes. Any chemical process may be broken down into a sequence of one or more single-step processes known either as elementary processes, elementary reactions, or elementary steps. Elementary reactions usually involve either a single reactive collision between two molecules, which we refer to as a bimolecular step, or dissociation/isomerisation of a single reactant molecule, which we refer to as a unimolecular step. Very rarely, under conditions of extremely high pressure, a termolecular step may occur, which involves simultaneous collision of three reactant molecules. An important point to recognise is that many reactions that are written as a single reaction equation in actual fact consist of a series of elementary steps. This will become extremely important as we learn more about the theory of chemical reaction rates.

As a general rule, elementary processes involve a transition between two atomic or molecular states separated by a potential barrier. The potential barrier constitutes the activation energy of the process, and determines the rate at which it occurs. When the barrier is low, the thermal energy of the reactants will generally be high enough to surmount the barrier and move over to products, and the reaction will be fast. However, when the barrier is high, only a few reactants will have sufficient energy, and the reaction will be much slower. The presence of a potential barrier to reaction is also the source of the temperature dependence of reaction rates.

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**Rate laws**

The rate law is an expression relating the rate of a reaction to the concentrations of the chemical species present, which may include reactants, products, and catalysts. Many reactions follow a simple rate law, which takes the form

ν = *k* [A]*a*[B]*b*[C]*c*...

i.e. the rate is proportional to the concentrations of the reactants each raised to some power. The constant of proportionality, k, is called the rate constant. The power a particular concentration is raised to is the order of the reaction with respect to that reactant. Note that the orders do not have to be integers. The sum of the powers is called the overall order. Even reactions that involve multiple elementary steps often obey rate laws of this kind, though in these cases the orders will not necessarily reflect the stoichiometry of the reaction equation.

For example,

H2 + I2 → 2HI ν = *k* [H2][I2].

**The units of the rate constant**

The constant of proportionality, k, is called the rate constant. A point which often seems to cause endless confusion is the fact that the units of the rate constant depend on the form of the rate law in which it appears i.e. a rate constant appearing in a first order rate law will have different units from a rate constant appearing in a second order or third order rate law. This follows immediately from the fact that the reaction rate always has the same units of concentration per unit time, which must match the overall units of a rate law in which concentrations raised to varying powers may appear. The good news is that it is very straightforward to determine the units of a rate constant in any given rate law. Below are a few examples.

(i) Consider the rate law ν = *k*[H2][I2]. If we substitute units into the equation, we obtain

(mol dm-3 s-1) = [*k*] (mol dm-3) (mol dm-3 )

where the notation [*k*] means ‘the units of *k*’. We can rearrange this expression to

find the units of the rate constant, *k*.

[*k*] = (mol dm-3 s-1)

(mol dm-3) (mol dm-3) = mol-1 dm3 s1 or L mol-1 s1 or M-1 s-1

(ii) We can apply the same treatment to a first order rate law, for example

ν = *k* [CH3N2CH3].

(mol dm-3 s-1) = [*k*] (mol dm-3)

[*k*] = (mol dm-3 s-1)

(mol dm-3 ) = s-1

(iii) As a final example, consider the rate law ν = *k* [CH3CHO]3/2.

(mol dm-3 s-1) = [*k*] (mol dm-3)3/2

[*k*] = (mol dm-3 s-1)

(mol dm-3)3/2 = mol-1/2 dm3/2 s-1

An important point to note is that it is meaningless to try and compare two rate constants unless they have the same units.

For third order, [*k*] = (mol dm-3 s-1)

(mol dm-3) (mol dm-3) (mol dm-3) = mol-2 dm2 s-1 or L2 mol-2 s-1 or M-2 s-1

**Rate of reaction**

The rate of a chemical reaction which also refers to the velocity or speed of a reaction is the rate at which reactants are used up, or equivalently the rate at which products are formed with respect to time. The rate therefore has units of concentration per unit time, mol dm-3 s-1 . (for gas phase reactions, alternative units of concentration are often used, usually units of pressure – Torr or Pa). To measure a reaction rate, we simply need to monitor the concentration of one of the reactants or products as a function of time.

There is one slight complication to our definition of the reaction rate so far, which is to do with the stochiometry of the reaction. The stoichiometry simply refers to the number of moles of each reactant and product appearing in the reaction equation. For example, the reaction equation for the well-known Haber process, used industrially to produce ammonia, is:

N2 + 3H2 ↔ 2NH3

N2 has a stochiometric coefficient of 1, H2 has a coefficient of 3, and NH3 has a coefficient of 2.

We could determine the rate of this reaction in any one of three ways, by monitoring the changing concentration of N2, H2, or NH3. Say we monitor N2, and obtain a rate of -d[N2]/d*t* = *x* mol dm-3 s-1.

Since for every mole of N2 that reacts, we lose three moles of H2, if we had monitored H2 instead of N2 , we would have obtained a rate -d[H2]/d*t* = 3*x* mol dm-3 s-1. Similarly, monitoring the concentration of NH3 would yield a rate of 2*x* mol dm-3 s-1. Clearly, the same reaction cannot have three different rates, so we appear to have a problem. The solution is actually very simple: the reaction rate is defined as the rate of change of the concentration of a reactant or product divided by its stochiometric coefficient.

For the above reaction, the rate (usually given the symbol ν) is therefore

ν = -d[N2] = -1d[H2] = 1d[NH3]

dt 3 d*t* 2 dt

Note that a negative sign appears when we define the rate using the concentration of one of the reactants. This is because the rate of change of a reactant is negative (since it is being used up in the reaction), but the reaction rate needs to be a positive quantity.

**Factors Affecting Reaction Rates**

**Rates of reaction depends basically on**:

* [Reactant](http://www.answers.com/topic/reagent) concentrations, which usually make the reaction happen at a faster rate if raised through increased collisions per unit time,
* [Surface area](http://www.answers.com/topic/surface-area-1) available for contact between the reactants, in particular solid ones in heterogeneous systems. Larger surface area leads to higher reaction rates.
* [Pressure](http://www.answers.com/topic/pressure), by increasing the pressure, you decrease the volume between molecules. This will increase the frequency of collisions of molecules.
* [Activation energy](http://www.answers.com/topic/activation-energy), which is defined as the amount of energy required to make the reaction start and carry on spontaneously. Higher activation energy implies that the reactants need more energy to start than a reaction with lower activation energy.
* [Temperature](http://www.answers.com/topic/temperature), which hastens reactions if raised, since higher temperature increases the energy of the molecules, creating more collisions per unit time,
* The presence or absence of a [catalyst](http://www.answers.com/topic/catalysis). Catalysts are substances which change the pathway (mechanism) of a reaction which in turn increases the speed of a reaction by lowering the [activation energy](http://www.answers.com/topic/activation-energy) needed for the reaction to take place. A catalyst is not destroyed or changed during a reaction, so it can be used again.
* For some reactions, the presence of [electromagnetic radiation](http://www.answers.com/topic/electromagnetic-radiation), most notably [ultraviolet](http://www.answers.com/topic/ultraviolet), is needed to promote the breaking of bonds to start the reaction. This is particularly true for reactions involving [radicals](http://www.answers.com/topic/radical-chemistry).

**Temperature dependence of reaction rates**

***The Arrhenius equation and activation energies***

It is found experimentally that the rate constants for many chemical reactions follow the Arrhenius equation.

*k* = *A* exp(-*E*a/*RT*) or equivalently ln*k* = ln*A* – *E*a/*RT*

where *A* is the pre-exponential factor and *E*a is the activation energy. These parameters may be determined from experimental rate data by plotting ln*k* against 1/*T*. This is known as an Arrhenius plot, and has an intercept of ln*A* and a slope of –*E*a/*R*.

**The effect of a change of temperature**

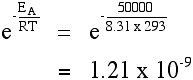
You can use the Arrhenius equation to show the effect of a change of temperature on the rate constant - and therefore on the rate of the reaction. If the rate constant doubles, for example, so also will the rate of the reaction. Look back at the rate equation if you aren't sure why that is.

What happens if you increase the temperature by 10°C from, say, 20°C to 30°C (293 K to 303 K)?

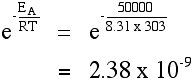
The frequency factor, A, in the equation is approximately constant for such a small temperature change. We need to look at how e-(EA / RT) changes - the fraction of molecules with energies equal to or in excess of the activation energy.

Let's assume an activation energy of 50 kJ mol-1. In the equation, we have to write that as 50000 J mol-1. The value of the gas constant, R, is 8.31 J k-1 mol-1.

At 20°C (293 K) the value of the fraction is:



By raising the temperature just a little bit (to 303 K), this increases:



You can see that the fraction of the molecules able to react has almost doubled by increasing the temperature by 10°C. That causes the rate of reaction to almost double. This is the value in the rule-of-thumb often used in simple rate of reaction work.

There are a few observations that follow from the equation.

1. The higher the activation energy, the stronger the temperature dependence of the

rate constant.

2. A reaction with no temperature dependence has an activation energy of zero (this is

common in ion-molecule reactions and radical-radical recombinations)

3. A negative activation energy implies that the rate decreases as the temperature increases, and always indicates a complex reaction mechanism.

**Orders of Reactions**

The order of a reaction is the power a particular concentration is raised to with respect to the reactants, such that the sum of the partial orders for all reactants gives the overall order of the reaction

## Zero-order reactions

A zero-order reaction has a rate which is independent of the concentration of the reactant(s). Increasing the concentration of the reacting species will not speed up the rate of the reaction. Zero-order reactions are typically found when a material that is required for the reaction to proceed, such as a surface or a catalyst, is saturated by the reactants. The rate law for a zero-order reaction is

\ r = k

where r is the reaction rate, and k is the reaction rate coefficient with units of concentration/time. If, and only if, this zero-order reaction 1) occurs in a closed system, 2) there is no net build-up of intermediates, and 3) there are no other reactions occurring, it can be shown by solving a Mass balance for the system that:

 r = -\frac{d[A]}{dt}=k

If this [differential equation](http://en.wikipedia.org/wiki/Differential_equation) is [integrated](http://en.wikipedia.org/wiki/Integral) it gives an equation which is often called the integrated zero-order rate law.

\ [A]_t = -kt + [A]_0

where \ [A]_trepresents the concentration of the chemical of interest at a particular time, and \ [A]_0 represents the initial concentration.

A reaction is zero order if concentration data are plotted versus time and the result is a straight line. The slope of this resulting line is the negative of the zero order rate constant k.

The half-life of a reaction describes the time needed for half of the reactant to be depleted (same as the [half-life](http://en.wikipedia.org/wiki/Half-life) involved in [nuclear decay](http://en.wikipedia.org/wiki/Nuclear_decay), which is a first-order reaction). For a zero-order reaction the half-life is given by

\ t_ \frac{1}{2} = \frac{[A]_0}{2k}

Example of a Zero-order reaction

* Reversed [Haber process](http://en.wikipedia.org/wiki/Haber_process): 2NH_3 (g) \rightarrow \; 3H_2 (g) + N_2 (g)

It should be noted that the order of a reaction cannot be deduced from the chemical equation of the reaction.

## First-order reactions

A first-order reaction depends on the concentration of only one reactant (a unimolecular reaction). Other reactants can be present, but each will be zero-order. The rate law for an elementary reaction that is first order with respect to a reactant A is

\ r  = -\frac{d[A]}{dt} = k[A]

*k* is the first order rate constant, which has units of 1/time.

The integrated first- order rate law is

\ \ln{[A]} = -kt + \ln{[A]_0}

A plot of ln[*A*] vs. time *t* gives a straight line with a slope of − *k*.

The half life of a first-order reaction is independent of the starting concentration and is given by \ t_ \frac{1}{2} = \frac{\ln{(2)}}{k}.

Examples of reactions that are first-order with respect to the reactant:

* \mbox{H}_2 \mbox{O}_2 (l) \rightarrow \; \mbox{H}_2\mbox{O} (l) + \frac{1}{2}\mbox{O}_2 (g)
* \mbox{SO}_2 \mbox{Cl}_2 (l) \rightarrow \; \mbox{SO}_2 (g) + \mbox{Cl}_2 (g)
* 2\mbox{N}_2 \mbox{O}_5 (g) \rightarrow \; 4\mbox{NO}_2 (g) + \mbox{O}_2 (g)

SO2Cl2- sulfuryl chloride

N2O5- dinitrogen pentoxide

An alternative view of first order kinetics

The integrated first- order rate law

\ \ln{[A]} = -kt + \ln{[A]_0}

is usually written in the form of the exponential decay equation

A=A_0e^{-kt}\,

## Second-order reactions

A **second-**order **reaction** depends on the concentrations of one second-orderreactant, or two first-order reactants.

For a second order reaction, its reaction rate is given by:

\ r = k[A]^2or \ r = k[A][B]or \ r = k[B]^2

The integrated second-order rate laws are respectively

\frac{1}{[A]} = kt + \frac{1}{[A]_0} 

or

\frac{[A]}{[B]} = \frac{[A]_0}{[B]_0} e^{([A]_0 - [B]_0)kt}

[A]0 and [B]0 must be different to obtain that integrated equation.

The half-life equation for a second-order reaction dependent on one second-order reactant is \ t_ \frac{1}{2} = \frac{1}{k[A]_0}.

For a second-order reaction half-lives progressively double.

Another way to present the above rate laws is to take the log of both sides: \ln{}r = \ln{}k + 2\ln\left[A\right] 

Examples of a Second-order reaction

* 2\mbox{NO}_2(g) \rightarrow \; 2\mbox{NO}(g) + \mbox{O}_2(g)

NO2-nitrogen dioxide, NO-nitric oxide

**Third-order reactions**

A number of reactions are found to have third order kinetics. An example is the oxidation of NO, for which the overall reaction equation and rate law are given below.

2NO + O2 → 2NO2

d[NO2]

d*t* = *k* [NO]2[O2]

One possibility for the mechanism of this reaction would be a three-body collision (i.e. a true

termolecular reaction). However, such collisions are exceedingly rare, and certainly too unlikely to explain the observed rate at which this reaction proceeds. An added complication is that the rate of this reaction is found to decrease with increasing temperature, an indication of a complex mechanism.

The overall rate is

ν =1d[NO2]

2 d*t* = *k*2[(NO)2][O2]

**Integrated rate laws**

A rate law is a differential equation that describes the rate of change of a reactant (or product) concentration with time. If we integrate the rate law then we obtain an expression for the concentration as a function of time, which is generally the type of data obtained in an experiment. In many simple cases, the rate law may be integrated analytically. Otherwise, numerical (computer-based) techniques may be used. Four of the simplest rate laws are given below in both their differential and integrated form.

Reaction Order Differential form Integrated form

A → P zeroth d[A]/d*t* = -*k* [A] = [A]0 - *kt*

A → P first d[A]/d*t* = -*k* [A] ln[A] = ln[A]0 - *kt*

A + A → P second 1d[A]

2d*t* = -*k* [A]2 1/[A] =1/[A]0+ 2*kt*

A + B → P second d[A]/d*t* = -*k* [A][B] *kt* =1 ln[B]0[A]

[B]0-[A]0[A]0[B]

In the above [A]0 and [B]0 represent the initial concentrations of A and B i.e. their concentrations at the start of the reaction.

**Half lives**

The half life, *t*1/2, of a substance is defined as the time it takes for the concentration of the

substance to fall to half of its initial value. Note that it only makes sense to define a half life for a substance not present in excess at the start of the reaction. We can obtain equations for the halflives for reactions of various orders by substituting the values *t* = *t*1/2 and [A] = ½ [A]0 into theintegrated rate laws. We obtain

Zeroth order reaction *t*1/2 =[A]0/2*k*

Successive half lives will decrease by a factor of two for every Ao/2

First order reaction *t*1/2 =ln2/*k*

There is no dependence of the half life on concentration, so *t*1/2 is constant for a first order reaction.

Second order reaction *t*1/2 =1/*k*[A]0

The inverse dependence on concentration means that successive half lives will double for a

second order reaction.

# Catalysis

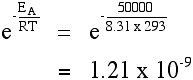
Catalysis is the increase in the rate of a chemical reaction by the addition of a catalyst, that is not itself consumed. The catalyst works by opening up a route between starting material and product with a lower activation barrier than the uncatalyzed process.

**The effect of a catalyst**

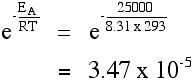
A catalyst will provide a route for the reaction with a lower activation energy thereby increasing the fraction of molecules that reacts and speeding up the reaction. We can demonstrate this by determining the fraction of molecules in the Arrhenius equation using two different activation energies.

Suppose in the presence of a catalyst that the activation energy falls from 50 kJ mol-1 to 25 kJ mol-1 at 20°C (293 K, R= 8.31 J K-1 mol-1).

Doing the calculation using 50 kJ mol-1 at 20°C gives the fraction as,



Redoing the calculation at 25 kJ mol-1 gives the fraction as:



If you compare that with the corresponding value where the activation energy was 50 kJ mol-1, you will see that there has been a massive increase in the fraction of the molecules which are able to react. There are almost 30000 times more molecules which can react in the presence of the catalyst compared to having no catalyst (using our assumptions about the activation energies). It's no wonder catalysts speed up reactions!

**Types of catalytic reactions**

Catalysts can be divided into two main types - heterogeneous and homogeneous. In a heterogeneous reaction, the catalyst is in a different phase from the reactants. In a homogeneous reaction, the catalyst is in the same phase as the reactants.

**Heterogeneous catalysis**

This involves the use of a catalyst in a different phase from the reactants. Typical examples involve a ***solid*** catalyst with the reactants as either ***liquids or gases***.

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| **How the heterogeneous catalyst works (in general terms)**  Most examples of heterogeneous catalysis go through the same stages:  One or more of the reactants are adsorbed (sticking to the surface) on to the surface of the catalyst at active sites. An active site is a part of the surface which is particularly good at adsorbing things and helping them to react.  There is some sort of interaction between the surface of the catalyst and the reactant molecules which makes them more reactive. This might involve an actual reaction with the surface, or some weakening of the bonds in the attached molecules. The product molecules are desorbed (product molecules breaking away) leaving the active site available for a new set of molecules to attach to and react.  A good catalyst needs to adsorb the reactant molecules strongly enough for them to react, but not so strongly that the product molecules stick more or less permanently to the surface. Silver, for example, isn't a good catalyst because it doesn't form strong enough attachments with reactant molecules. Tungsten, on the other hand, isn't a good catalyst because it adsorbs too strongly.  Metals like platinum and nickel make good catalysts because they adsorb strongly enough to hold and activate the reactants, but not so strongly that the products can't break away.  **Examples of heterogeneous catalysis**  **The hydrogenation of a carbon-carbon double bond**  The simplest example of this is the reaction between ethene and hydrogen in the presence of a nickel catalyst.  http://www.chemguide.co.uk/physical/catalysis/padding.gifhttp://www.chemguide.co.uk/physical/catalysis/ethh2eqn.gif  One important industrial use is in the hydrogenation of vegetable oils to make margarine, which also involves reacting a carbon-carbon double bond in the vegetable oil with hydrogen in the presence of a nickel catalyst.  http://www.chemguide.co.uk/physical/catalysis/padding.gifhttp://www.chemguide.co.uk/physical/catalysis/contact1.gif  This is done by passing sulphur dioxide and oxygen over a solid vanadium (V) oxide catalyst.  **Catalytic converters**  Catalytic converters change poisonous molecules like carbon monoxide and various nitrogen oxides in car exhausts into more harmless molecules like carbon dioxide and nitrogen. They use expensive metals like platinum, palladium and rhodium as the heterogeneous catalyst.  The metals are deposited as thin layers onto a ceramic honeycomb. This maximises the surface area and keeps the amount of metal used to a minimum. Catalytic converters can be affected by catalyst poisoning. This happens when something which isn't a part of the reaction gets very strongly adsorbed onto the surface of the catalyst, preventing the normal reactants from reaching it. Lead is a familiar catalyst poison for catalytic converters. It coats the honeycomb of expensive metals and stops it working.  In the past, lead compounds were added to petrol (gasoline) to make it burn more smoothly in the engine. But you can't use a catalytic converter if you are using leaded fuel. So catalytic converters have not only helped remove poisonous gases like carbon monoxide and nitrogen oxides, but have also forced the removal of poisonous lead compounds from petrol.  **Homogeneous catalysis**  This has the catalyst in the same phase as the reactants. Typically everything will be present as a gas or contained in a single liquid phase.  **Examples of homogeneous catalysis**  **The reaction between persulphate ions and iodide ions**  http://www.chemguide.co.uk/physical/catalysis/padding.gifhttp://www.chemguide.co.uk/physical/catalysis/persulph1.gif  The catalyst can be either Iron (II) or Iron (III) ions which are added to the same solution.  **The destruction of atmospheric ozone**  This is a good example of homogeneous catalysis where everything is present as a gas.  Ozone, O3, is constantly being formed and broken up again in the high atmosphere by the action of ultraviolet light. Ordinary oxygen molecules absorb ultraviolet light and break into individual oxygen atoms. These have unpaired electrons, and are known as free radicals. They are very reactive.  http://www.chemguide.co.uk/physical/catalysis/padding.gifhttp://www.chemguide.co.uk/physical/catalysis/ozoneeq1.gif  The oxygen radicals can then combine with ordinary oxygen molecules to make ozone.  http://www.chemguide.co.uk/physical/catalysis/padding.gifhttp://www.chemguide.co.uk/physical/catalysis/ozoneeq2.gif  Ozone can also be split up again into ordinary oxygen and an oxygen radical by absorbing ultraviolet light.  http://www.chemguide.co.uk/physical/catalysis/padding.gifhttp://www.chemguide.co.uk/physical/catalysis/ozoneeq3.gif   |  | | --- | | **Autocatalysis**  In autocatalysis, the reaction is catalysed by one of its products. One of the simplest examples of this is in the oxidation of a solution of ethanedioic acid (oxalic acid) by an acidified solution of potassium manganate(VII) (potassium permanganate).  http://www.chemguide.co.uk/physical/catalysis/padding.gifhttp://www.chemguide.co.uk/physical/catalysis/autocateq.gif  The reaction is very slow at room temperature. It is used as a titration to find the concentration of potassium manganate (VII) solution and is usually carried out at a temperature of about 60°C. Even so, it is quite slow to start with.  The reaction is catalysed by manganese (II) ions. There obviously aren't any of those present before the reaction starts, and so it starts off extremely slowly at room temperature. However, if you look at the equation, you will find manganese (II) ions amongst the products. More and more catalyst is produced as the reaction proceeds and so the reaction speeds up.  You can measure this effect by plotting the concentration of one of the reactants as time goes on. You get a graph quite unlike the normal rate curve for a reaction.  Most reactions give a rate curve which looks like this:  http://www.chemguide.co.uk/physical/catalysis/autocatgr1.gif  Concentrations are high at the beginning and so the reaction is fast - shown by a rapid fall in the reactant concentration. As things get used up, the reaction slows down and eventually stops as one or more of the reactants are completely used up.  An example of autocatalysis gives a curve like this:  http://www.chemguide.co.uk/physical/catalysis/autocatgr2.gif  You can see the slow (uncatalysed) reaction at the beginning. As catalyst begins to be formed in the mixture, the reaction speeds up - getting faster and faster as more and more catalyst is formed. Eventually, of course, the rate falls again as things get used up. | | |
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