

Reaction Kinetics

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First year, Hilary term

Suggested Reading

Physical Chemistry, P. W. Atkins
Reaction Kinetics, M. J. Pilling and P. W. Seakins
Chemical Kinetics, K. J. Laidler
Modern Liquid Phase Kinetics, B. G. Cox

Course synopsis

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1. Introduction

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, which we will cover in more detail in Section 19.

The huge variety of chemical species, types of reaction, and the accompanying potential energy surfaces involved means that the timescale over which chemical reactions occur covers many orders of magnitude, from very slow reactions, such as iron rusting, to extremely fast reactions, such as the electron transfer processes involved in many biological systems or the combustion reactions occurring in flames.

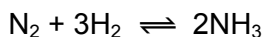
A study into the kinetics of a chemical reaction is usually carried out with one or both of two main goals in mind:

1. Analysis of the sequence of elementary steps giving rise to the overall reaction. i.e. the *reaction mechanism*.
2. Determination of the absolute rate of the reaction and/or its individual elementary steps.

The aim of this course is to show you how these two goals may be achieved.

2. Rate of reaction

When we talk about the rate of a chemical reaction, what we mean is the rate at which reactants are used up, or equivalently the rate at which products are formed. The rate therefore has units of concentration per unit time, $\text{mol dm}^{-3} \text{s}^{-1}$ (for gas phase reactions, alternative units of concentration are often used, usually units of pressure – Torr, mbar 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 stoichiometry 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:



N_2 has a stoichiometric coefficient of 1, H_2 has a coefficient of 3, and NH_3 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 N_2 , H_2 , or NH_3 . Say we monitor N_2 , and obtain a rate of $-\frac{d[\text{N}_2]}{dt} = x \text{ mol dm}^{-3} \text{ s}^{-1}$. Since for every mole of N_2 that reacts, we lose three moles of H_2 , if we had monitored H_2 instead of N_2 we would have obtained a rate $-\frac{d[\text{H}_2]}{dt} = 3x \text{ mol dm}^{-3} \text{ s}^{-1}$. Similarly, monitoring the concentration of NH_3 would yield a rate of $2x \text{ mol dm}^{-3} \text{ s}^{-1}$. 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 stoichiometric coefficient*. For the above reaction, the rate (usually given the symbol v) is therefore

$$v = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

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.

3. Rate laws

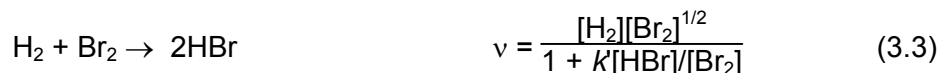
The rate law is an expression relating the rate of a reaction to the concentrations of the chemical species present, which may include reactants, products, and catalysts. Many reactions follow a *simple rate law*, which takes the form

$$v = k [\text{A}]^a [\text{B}]^b [\text{C}]^c \dots \quad (3.1)$$

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,



Other reactions follow *complex rate laws*. These often have a much more complicated dependence on the chemical species present, and may also contain more than one rate constant. Complex rate laws *always* imply a multi-step reaction mechanism. An example of a reaction with a complex rate law is

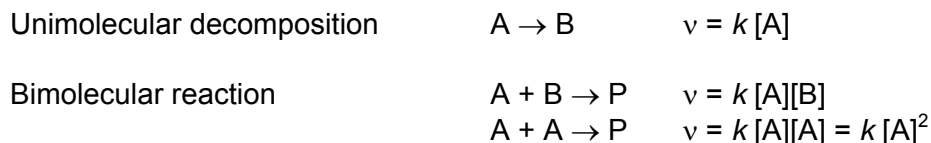


In the above example, the reaction has order 1 with respect to $[\text{H}_2]$, but it is impossible to define orders with respect to Br_2 and HBr since there is no direct proportionality between their concentrations and the reaction rate. Consequently, it is also impossible to define an overall order for this reaction.

To give you some idea of the complexity that may underlie an overall reaction equation, a slightly simplified version of the sequence of elementary steps involved in the above reaction is shown below. We will return to this reaction later when we look at chain reactions in Section 17.



As well as having rate laws for overall reactions, we can of course also write down individual rate laws for elementary steps. Elementary processes always follow simple rate laws, in which the order with respect to each reactant reflects the *molecularity* of the process (how many molecules are involved). For example,



Multi-step processes may follow simple or complex rate laws, and as the above examples have hopefully illustrated, the rate law generally does not follow from the overall reaction equation. This makes perfect sense, since the overall reaction equation for a multi-step process is simply the net result of all of the elementary reactions in the mechanism. The ‘reaction’ given in the overall reaction equation never actually takes place! However, even though the rate law for a multi-step reaction cannot immediately be written down from the reaction equation as it can in the case of an elementary reaction, the rate law *is* a direct result of the sequence of elementary steps that constitute the reaction mechanism. As such, it provides our best tool for determining an unknown mechanism. As we will find out later in the course, once we know the sequence of elementary steps that constitute the reaction mechanism, we can quite quickly deduce the rate law. Conversely, if we do not know the reaction mechanism, we can carry out experiments to determine the orders with respect to each reactant (see Sections 7 and 8) and then try out various ‘trial’ reaction mechanisms to see which one fits best with the experimental data. At this point it should be emphasised again that *for multi-step reactions, the rate law, rate constant, and order are determined by experiment*, and the orders are not generally the same as the stoichiometric coefficients in the reaction equation.

A final important point about rate laws is that *overall* rate laws for a reaction may contain reactant, product and catalyst concentrations, *but must not contain concentrations of reactive intermediates* (these will of course appear in rate laws for individual elementary steps).

4. The units of 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 $v = k[H_2][I_2]$. If we substitute units into the equation, we obtain

$$(\text{mol dm}^{-3} \text{ s}^{-1}) = [k] (\text{mol dm}^{-3}) (\text{mol dm}^{-3})$$

where the notation $[k]$ means ‘the units of k ’. We can rearrange this expression to find the units of the rate constant, k .

$$[k] = \frac{(\text{mol dm}^{-3} \text{ s}^{-1})}{(\text{mol dm}^{-3}) (\text{mol dm}^{-3})} = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

- (ii) We can apply the same treatment to a first order rate law, for example $v = k [\text{CH}_3\text{N}_2\text{CH}_3]$.

$$(\text{mol dm}^{-3} \text{ s}^{-1}) = [k] (\text{mol dm}^{-3})$$

$$[k] = \frac{(\text{mol dm}^{-3} \text{ s}^{-1})}{(\text{mol dm}^{-3})} = \text{s}^{-1}$$

(iii) As a final example, consider the rate law $v = k [\text{CH}_3\text{CHO}]^{3/2}$.

$$(\text{mol dm}^{-3} \text{ s}^{-1}) = [k] (\text{mol dm}^{-3})^{3/2}$$

$$[k] = \frac{(\text{mol dm}^{-3} \text{ s}^{-1})}{(\text{mol dm}^{-3})^{3/2}} = \text{mol}^{-1/2} \text{ dm}^{3/2} \text{ s}^{-1}$$

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

5. 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
$A \rightarrow P$	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \rightarrow P$	first	$\frac{d[A]}{dt} = -k[A]$	$\ln[A] = \ln[A]_0 - kt$
$A + A \rightarrow P$	second	$\frac{1}{2} \frac{d[A]}{dt} = -k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
$A + B \rightarrow P$	second	$\frac{d[A]}{dt} = -k[A][B]$	$kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$

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.

6. 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 half lives for reactions of various orders by substituting the values $t = t_{1/2}$ and $[A] = \frac{1}{2} [A]_0$ into the integrated rate laws from Section 5. We obtain

$$\text{Zeroth order reaction} \quad t_{1/2} = \frac{[A]_0}{2k} \quad (6.1)$$

$$\text{First order reaction} \quad t_{1/2} = \frac{\ln 2}{k} \quad (6.2)$$

$$\text{Second order reaction} \quad t_{1/2} = \frac{1}{k[A]_0} \quad (6.3)$$

7. Determining the rate law from experimental data

A kinetics experiment consists of measuring the concentrations of one or more reactants or products at a number of different times during the reaction. We will review some of the experimental techniques used to make these measurements in Section 8. In the present section, we will look at the methods that allow us to use the experimental data to determine the reaction orders with respect to each reactant, and therefore the rate law.

(i) Isolation method

The isolation method is a technique for simplifying the rate law in order to determine its dependence on the concentration of a single reactant. Once the rate law has been simplified, the differential or integral methods discussed in the following subsections may be used to determine the reaction orders.

The dependence of the reaction rate on the chosen reactant concentration is isolated by having all other reactants present in a large excess, so that their concentration remains essentially constant throughout the course of the reaction. As an example, consider a reaction $A + B \rightarrow P$, in which B is present at a concentration 1000 times greater than A. When all of species A has been used up, the concentration of B will only have changed by 1/1000, or 0.1%, and so 99.9% of the original B will still be present. It is therefore a good approximation to treat its concentration as constant throughout the reaction.

This greatly simplifies the rate law since the (constant) concentrations of all reactants present in large excess may be combined with the rate constant to yield a single *effective rate constant*. For example, the rate law for the reaction considered above will become:

$$v = k [A]^a [B]^b \approx k [A]^a [B]_0^b = k_{\text{eff}} [A]^a \quad \text{with} \quad k_{\text{eff}} = k [B]_0^b \quad (7.1)$$

When the rate law contains contributions from a number of reactants, a series of experiments may be carried out in which each reactant is isolated in turn.

(ii) Differential methods

When we have a rate law that depends only on the concentration of one species, either because there is only a single species reacting, or because we have used the isolation method to manipulate the rate law, then the rate law may be written

$$v = k[A]^a \quad (7.2)$$

$$\log v = \log k + a \log[A] \quad (7.3)$$

A plot of $\log v$ against $\log[A]$ will then be a straight line with a slope equal to the reaction order, a , and an intercept equal to $\log k$. There are two ways in which to obtain data to plot in this way.

1. We can measure the concentration of the reactant $[A]$ as a function of time and use this data to calculate the rate, $v = -d[A]/dt$, as a function of $[A]$. A plot of $\log v$ vs $\log[A]$ then yields the reaction order with respect to A.
2. We can make a series of measurements of the initial rate v_0 of the reaction with different initial concentrations $[A]_0$. These may then be plotted as above to determine the order, a . This is a commonly used technique known as the *initial rates method*.

(iii) Integral methods

If we have measured concentrations as a function of time, we may compare their time dependence with the appropriate integrated rate laws. Again, this is most straightforward if we have simplified the rate law so that it depends on only one reactant concentration. The differential rate law given in Equation (7.2) will give rise to different integrated rate laws depending on the value of a , some of which were given in Section 5. The most commonly encountered ones are:

Zeroth order integrated rate law: $[A] = [A]_0 - kt$
A plot of $[A]$ vs t will be linear, with a slope of $-k$.

First order integrated rate law: $\ln[A] = \ln[A]_0 - kt$
A plot of $\ln[A]$ vs t will be linear with a slope of $-k$.

Second order integrated rate law: $\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
A plot of $\frac{1}{[A]}$ vs t will be linear with a slope of $2k$.

If none of these plots result in a straight line, then more complicated integrated rate laws must be tried.

(iv) Half lives

Another way of determining the reaction order is to investigate the behaviour of the half life as the reaction proceeds. Specifically, we can measure a series of successive half lives. $t = 0$ is used as the start time from which to measure the first half life, $t_{1/2}^{(1)}$. Then $t_{1/2}^{(1)}$ is used as the start time from which to measure the second half life, $t_{1/2}^{(2)}$, and so on.

Zeroth order $t_{1/2} = \frac{[A]_0}{2k}$

Since at $t_{1/2}^{(1)}$, the new starting concentration is $\frac{1}{2}[A]_0$, successive half lives will decrease by a factor of two for a zeroth order reaction.

First order $t_{1/2} = \frac{\ln 2}{k}$

There is no dependence of the half life on concentration, so $t_{1/2}$ is constant for a first order reaction.

Second order $t_{1/2} = \frac{1}{k[A]_0}$

The inverse dependence on concentration means that successive half lives will double for a second order reaction.

8. Experimental techniques

Experimental techniques have been developed to monitor reactions over timescales varying from hours or days all the way down to a few femtoseconds ($1 \text{ fs} = 10^{-15} \text{ s}$). While it is relatively simple to monitor the kinetics of a slow reaction (occurring over minutes to hours or longer), highly specialised techniques are required in order to study fast reactions, some of which will be considered here.

Whatever the details of the experimental arrangement, any kinetics experiment essentially consists of mixing the reactants and initiating reaction on a timescale that is negligible relative to that of the reaction, and then monitoring the concentration(s) of one or more reactants and/or products as a

function of time. Because rate constants vary with temperature (see Section 19), it is also important to determine and control accurately the temperature at which the reaction occurs.

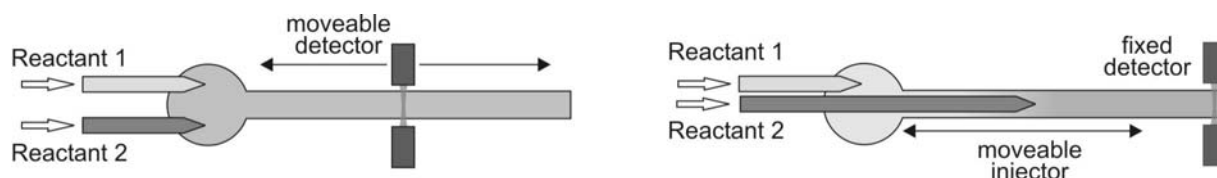
Most of the techniques we will look at are *batch techniques*, in which reaction is initiated at a single chosen time and concentrations are then followed as a function of time after initiation. We will also consider one or two examples of *continuous techniques*, in which reaction is continuously initiated and the time dependence of the reaction mixture composition is inferred from, for example, the concentrations in different regions of the reaction vessel. The continuous flow method outlined in the next section is an example of such a technique.

(i) Techniques for mixing the reactants and initiating reaction

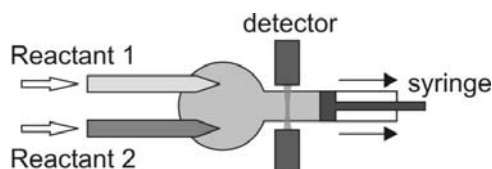
For slow reactions, occurring over minutes to hours, reaction is usually initiated simply by mixing the reactants together by hand or with a magnetic stirrer or other mechanical device. For fast reactions, a wide range of techniques have been developed.

Flow techniques

Flow techniques are typically used to study reactions occurring on timescales of seconds to milliseconds. In the simplest flow method, shown schematically on the left below, reactants are mixed at one end of a flow tube, and the composition of the reaction mixture is monitored at one or more positions further along the tube. If the flow velocity along the tube is known, then measurements at different positions provide information on concentrations at different times after initiation of reaction. In a variation on this method, shown on the right below, the detector may be in a fixed position, but a moveable injector may be used to inject one of the reactants into the flow tube at different positions relative to the detector in order to study the time dependence of the reaction mixture composition. Reactions of atomic or radical species may be studied using the discharge flow method, in which the reactive species is generated by a microwave discharge immediately prior to injection into the flow tube.



Continuous flow methods have the disadvantages that relatively large quantities of reactants are needed, and very high flow velocities are required in order to study fast reactions. These problems may be avoided by using a *stopped flow technique*. In this method, a fixed volume of reactants are rapidly flowed into a reaction chamber and mixed by the action of a syringe fitted with an end stop (see figure below). The composition of the reaction mixture is then monitored spectroscopically as a function of time after mixing at a fixed position in the reaction chamber.



Experimental systems may be designed to allow measurements to be made on very small sample volumes, making the stopped flow method popular for the study of biochemical kinetics e.g. enzyme action (see Section 15).

All flow techniques share the common problem that contributions from heterogeneous reactions at the walls of the flow tube can complicate the experiments. These can be minimised by coating the inner surface of the flow tube with an unreactive substance such as teflon or halocarbon wax, and the relative contributions from the process under study and reactions involving the walls may be quantified by varying the diameter of the flow tube (and therefore the ratio of volume to surface area).

Flash photolysis and laser pump probe techniques

In flash photolysis, reaction is initiated by a pulse of light (the 'flash') that dissociates a suitable precursor molecule in the reaction mixture to produce a reactive species, thereby initiating reaction. The concentration of the reactive species is then monitored as a function of time, usually spectroscopically using absorption spectroscopy or fluorescence techniques (see later). The shortest timescale over which reactions may be studied using this technique is determined by the duration of the 'flash'. Originally, the flash was provided by a discharge lamp, with durations in the region of tens of microseconds to several milliseconds. However, in most modern experiments the flash is provided by a laser pulse, typically with a duration of a few nanoseconds ($1 \text{ ns} = 10^{-9} \text{ s}$). For studying extremely fast reactions, such as some of the electron transfer processes involved in photosynthesis, laser pulses as short as a few tens of femtoseconds ($1 \text{ fs} = 10^{-15} \text{ s}$) may be used.

Flash photolysis has the advantage that because reactants are produced from well-mixed precursors, there is no mixing time to reduce the time resolution of the technique. Also, because the reactants are generated and monitored in the centre of the reaction cell, there are no wall reactions to worry about as there are in flow methods.

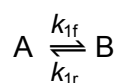
Pulse radiolysis is a variation on flash photolysis in which a short pulse of high energy electrons (10^{-9} to 10^{-6} s in duration) is passed through the sample in order to initiate reaction.

For very fast processes, the 'pump-probe' technique is often used, in which pulsed lasers are employed both to initiate reaction (the 'pump') and to detect the products via a pulsed spectroscopic technique (the 'probe'). The time separation between the two pulses can be varied either electronically or with an optical delay line down to a resolution of around 10 femtoseconds (10^{-14} s)

Relaxation methods

If we allow a chemical system to come to equilibrium and then perturb the equilibrium in some way, the rate of relaxation to a new equilibrium position provides information about the forward and reverse rate constants for the reaction. Since a system at chemical equilibrium is already well-mixed, relaxation methods overcome the mixing problems associated with many flow methods.

As an example, we will investigate the effect of a sudden increase in temperature on a system at equilibrium, an experiment known as a 'temperature jump'. Consider a simple equilibrium



where k_{1f} and k_{1r} are the rate constants for the forward and reverse reactions at the initial temperature T_1 . The rate of change of A is

$$\frac{d[A]}{dt} = -k_{1f} [A] + k_{1r} [B]$$

At equilibrium, the concentration of A is constant, and so

$$k_{1f}[A]_{\text{eq},1} = k_{1r}[B]_{\text{eq},1}$$

We now increase the temperature suddenly by a few degrees. This is often done by discharging a high voltage capacitor through the solution ($\sim 10^{-7} \text{ s}$), or by employing a UV or IR laser pulse or microwave discharge. After the temperature jump, the concentrations of A and B are initially at the values $[A]_{\text{eq},1}$ and $[B]_{\text{eq},1}$, but the system is not at the equilibrium composition for the higher temperature. The system relaxes back to the new equilibrium concentrations $[A]_{\text{eq},2}$ and $[B]_{\text{eq},2}$ at a