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

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:

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

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

$$\nu = k[A]^a \qquad (7.2)$$

$$\log \nu = \log k + a \log[A] \qquad (7.3)$$

A plot of logν 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, ν = -d[A]/d*t,* as a function of [A]. A plot of logν vs log[A] then yields the reaction order with respect to A.

2. We can make a series of measurements of the initial rate ν_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 fs = 10^{-15} 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.

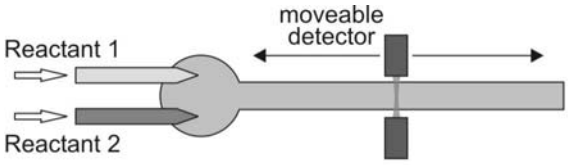
Most of the techniques we will look at are *batch techniques*, in which reaction is initiated at a single chosen time and concentrations are then followed as a function of time after initiation. We will also consider one or two examples of *continuous techniques*, in which reaction is continuously initiated 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.

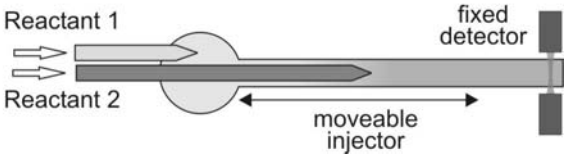
(i) Techniques for mixing the reactants and initiating reaction

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.

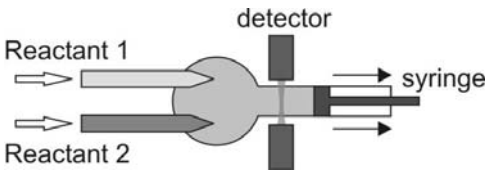
Flow techniques

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 ns = 10^{-9} 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 fs = 10^{-15} 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

$$\mathrm{A} \underset{k_{1\mathrm{r}}}{\overset{k_{1\mathrm{f}}}{\rightleftharpoons}} \mathrm{B}$$

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

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

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

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

We now increase the temperature suddenly by a few degrees. This is often done by discharging a high voltage capacitor through the solution (~10^{-7} 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 $[A]_{eq,1}$ and $[B]_{eq,1}$, but the system is not at the equilibrium composition for the higher temperature. The system relaxes back to the new equilibrium concentrations $[A]_{eq,2}$ and $[B]_{eq,2}$ at a

rate determined by the new higher-temperature rate constants k_{2f} and k_{2r}. The new concentrations are given by

$$k_{2f}[A]_{eq,2} = k_{2r}[B]_{eq,2}$$

If we define $x = [A] - [A]_{eq,2}$ as the deviation of the concentration from its new (higher temperature) equilibrium value (note that the deviation of [B] from its equilibrium value must therefore be $-x$), then during the relaxation the concentrations change as follows

$$\begin{aligned}\frac{d[A]}{dt} &= -k_{2f}[A] + k_{2r}[B] \\ &= -k_{2f}([A]_{eq,2} + x) + k_{2r}([B]_{eq,2} - x) \\ &= -(k_{2f} + k_{2r})x \qquad (\text{since } k_{2f}[A]_{eq,2} = k_{2r}[B]_{eq,2})\end{aligned}$$

Since the rate of change of [A] is the same as the rate of change of x, we can integrate the rate law to give

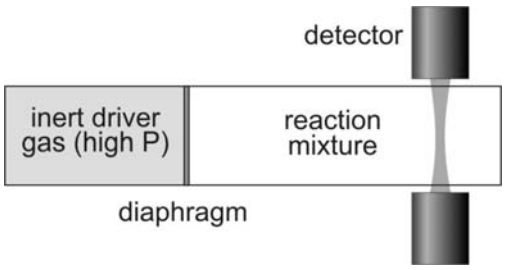
$$x = x_0 \exp(-t/\tau) \qquad \text{with} \qquad \frac{1}{\tau} = k_{2f} + k_{2r}$$

We see that the rate at which the concentrations relax to their new equilibrium values is determined by the sum of the two new rate constants. The new equilibrium constant is given by the ratio of the two rate constants, $K = k_{2f}/k_{2r}$, so together a measurement of the rate of relaxation and the equilibrium constant allows the individual reaction rate constants for the forward and reverse reaction to be determined.

The details of the kinetic equations change for more complicated reactions, but the basic principle of the technique remains the same.

Shock tubes

The shock tube method provides a way of producing highly reactive atomic or radical species through rapid dissociation of a molecular precursor, without the use of a discharge or laser pulse. The method is based on the fact that a very rapid increase in pressure (the shock) causes rapid heating of a gas mixture to a temperature of several thousand Kelvin. Since most dissociation reactions are endothermic, at high temperatures their equilibria are shifted towards products. A rapid increase in temperature therefore leads to rapid production of reactive species (the dissociation products) initiating the reaction of interest. A shock tube (shown schematically below) essentially consists of two chambers separated by a diaphragm. One chamber contains the appropriate mixture of reactants and precursor, the second an inert gas at high pressure. To initiate reaction, the diaphragm is punctured and a shock wave propagates through the reaction mixture. The temperature rise can be controlled by varying the pressure and composition of the inert gas. The composition of the reaction mixture after initiation is monitored in real time, usually spectroscopically.



The shock tube approach is often used to study combustion reactions. Suitable precursors for such studies, together with the radical species obtained on dissociation using argon as the shock gas include:

$HCN \rightarrow H + CN$	$CH_4 \rightarrow CH_3 + H$
$SO_2 \rightarrow SO + O$	$N_2O \rightarrow N_2 + O$
$CH_3 \rightarrow CH_2 + H$	$C_2H_2 \rightarrow C_2H \_ H$
$H_2S \rightarrow HS + H$	$CF_3Cl \rightarrow CF_3 + Cl$
$NO \rightarrow N + O$	$C_2H_4 \rightarrow C_2H_3 + H$
$NH_3 \rightarrow NH_2 + H$	$C_2H_4 \rightarrow C_2H_2 + H_2$