1 Differential Equations: Rate Laws

Many problems in chemistry can be formulated as differential equations. A general method for solving differential equations does not exist and for most practical problems an analytical solution has not been found. It is therefore very important to know how to make use of computers to solve differential equations numerically. We will see how this can be done by studying three example problems directly relevant to chemistry: (1) rate laws describing rates of chemical reactions, (2) the Schrödinger equation for wavefunctions, and (3) Newton's equations for classical dynamics. First of all, we will explore the power of programs (Mathematica, for example), that can analytically solve some differential equations and secondly, we will see how numerical solutions can be obtained in a simple way.

1.1 Chemical reaction rates

The average rate of change of the concentration of a chemical, A, over a time interval h is

$$\frac{[A](t+h) - [A](t)}{h} \tag{1.1}$$

where $[A](t)$ is the concentration at time t. In order to find the instantaneous rate of change at time t, one can imagine letting the time interval over which the average is calculated become infinitesimally small. The rate of change of the concentration then becomes the derivative of the function $[A](t)$

$$[A]'(t) = \lim_{h \to 0} \frac{[A](t+h) - [A](t)}{h} \tag{1.2}$$

If, for example, the reaction is a very simple one

$$A \to X \tag{1.3}$$
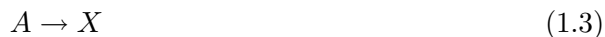
then the rate of the reaction can be described either in terms of the increase of the product X or as the rate of decrease of the reactant A. It is conventional to have the rate of a reaction be a positive quantity so the rate of the reaction is expressed as

$$r = -[A]'(t) = \frac{d[A]}{dt} = [X]'(t) \tag{1.4}$$

More generally, the rate of any *elementary* reaction, that is a reaction which actually occurs in the way described by the chemical equation

$$aA + bB + cC... \to xX + yY + zZ... \tag{1.5}$$
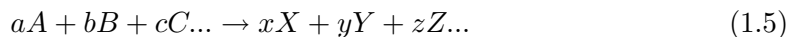
can be obtained from the rate of change of concentration of any one of the reactants or products, as

$$r = -\frac{1}{a}\,[A]' = -\frac{1}{b}\,[B]' = -\frac{1}{c}\,[C]' = \;...\; = \frac{1}{x}\,[X]' = \frac{1}{y}\,[Y]' = \frac{1}{z}\,[Z]' = \;... \tag{1.6}$$

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1.2 The rate law

The rate of a reaction at any instant in time is determined by the concentration of the chemicals in the system. In general this can be written as the rate law, where the functional form is

$$r = k \ [A]^{\alpha} \ [B]^{\beta} \ [C]^{\gamma} \ ... \ [X]^{\chi} \ [Y]^{\epsilon} \ [Z]^{\zeta} \ ... \ [L]^{\lambda}. \tag{1.7}$$

In addition to reactants and products, catalysts and inhibitors (denoted here as L) can also enter the rate law. The symbol k denotes the rate constant. The powers on the concentrations $\alpha, \beta, ...$, need to be obtained by comparison with experimental data. There is for a general reaction no relationship to the stoichiometric coefficients $a, b, ...$, (Only if the reaction is an *elementary* reaction are the stoichiometric coefficients equal to the powers on the reactant concentrations, $\alpha = a, \beta = b, \gamma = c$). Since r involves the derivative of one of the unknown functions (for example $[A]'/a$), the rate law is a *differential equation.* After formulating a rate law for a given chemical reaction, the task is to solve the differential equation and obtain the value of the concentration of the various chemicals as a function of time. By comparison with experimentally measured concentration as a function of time, the rate constant and the powers $\alpha, \beta, ...$, can, in principle, be determined.

1.3 Integrated rate laws for simple systems

1.3.1 First order reactions

The simplest case is a reaction with only one reactant

$$A \rightarrow X \tag{1.8}$$

and one where the reaction rate depends on the first power of $[A]$ (i.e. $\alpha = 1$). If we focus on the initial rate only, i.e. when the reaction has just started and only insignificant amounts of products are present, then the rate law is

$$r = -[A]' = k[A]. \tag{1.9}$$

This differential equation can be solved easily to give the concentration of $[A]$ as a function of time

$$[A](t) = [A]_0 \ e^{-kt}. \tag{1.10}$$

Here $[A]_0$ denotes the initial concentration of A. This is called a first order reaction and the solution shows that the concentration decreases exponentially with time.

1.3.2 Second order reactions

For some reactions the square of the reactant concentration appears in the rate law

$$\frac{-d[A]}{dt} = k[A]^2 \tag{1.11}$$

This indicates that the mechanism of the elementary reaction involves a collision of an A molecule with another A molecule. In this case the solution is

$$[A](t) = \frac{[A]_0}{1 + kt[A]_0}. \tag{1.12}$$

Another second order reaction is when two reactants are involved

$$A + B \rightarrow X \tag{1.13}$$

each appearing with the first power in the rate law

$$r = -\frac{d[A]}{dt} = k\ [A]\ [B] \tag{1.14}$$

in which case the solution is

$$\frac{1}{[B]_0 - [A]_0} \ln \frac{[B]/[B]_0}{[A]/[A]_0} = kt \tag{1.15}$$

It is clear that the solution rapidly becomes quite complicated as the rate law includes more chemicals. You will see how Mathematica can be used to obtain these as well as more complicated solutions to rate laws in your problem set.

1.3.3   Back reactions

The solutions above will only be valid for a short time after the reaction starts, because the back reaction was neglected in the rate law. Including the back reaction complicates the mathematics and is therefore often neglected in the treatment of reaction rates in chemistry textbooks. Returning to the first order reaction, but now including the reappearance of A from the products

$$A \rightleftharpoons X \tag{1.16}$$

with forward and backward rate constants k_f and k_b. Assuming the back reaction is also first order gives the rate law

$$\frac{d[A]}{dt} = -k_f[A] + k_b[X]. \tag{1.17}$$

The second term on the right takes into account the reapperance of A due to back reaction. The solution is

$$[A](t) - [A]_{eq} = ([A]_0 - [A]_{eq}) \, e^{-(k_f + k_b)t}. \tag{1.18}$$

The concentration still falls exponentially, but now approaches a finite value $[A]_{eq}$ rather than zero.

1.3.4 Integrated rate law for a more complex mechanism

More generally, an overall chemical reaction is the net change in the system after a sequence of chemical reactions. A simple example is

$$A \rightarrow B \rightarrow C \tag{1.19}$$

This kind of sequence can be verified directly by observing the presence of the intermediate B in the chemical mixture. The complexity of the solution quickly increases as more steps are introduced into the sequence.

A frequently used approximation in such a situation is to assume that one of the steps is much slower than the others, in which case it becomes the bottleneck in the sequence of reactions. This one step then determines the overall rate and is thus called the 'rate limiting step'. The approximation is called the *rate limiting step approximation*. Another approximation is the *steady state approximation* which assumes that the concentration of one or more intermediate does not change with time (after the reaction 'gets started').

Sometimes these approximations work well. More generally, however, they fail and a numerical solution of the rate law is necessary to make quantitative comparison with experiment. The steady state approximation is often better than the rate limiting step approximation but is often not good (in extreme cases the concentration of intermediates can actually oscillate with time!).

In addition to the complication of consecutive reactions, there can be many competing reactions going on in parallel. As an example, in modeling the photochemical smog, a model of 81 chemical equations has been used (L. A. Farrow and D. Edelson, International Journal of Chemical Kinetics, Vol VI, 787, 1974) and it was found that the use of steady state approximation led to significant errors in the time variation of the concentrations, in particular the NO concentration peak.

1.4 Numerical solutions

1.4.1 Euler method

A very simple method for solving rate laws numerically is the Euler method. It is the simplest example of so called 'finite difference' approximations, which will, for example, also be useful in solving for wavefunctions and classical trajectories. The finite difference approximation provides a method for turning a differential equation (or a set of coupled differential equations) into an algorithm that can be programmed on a computer. The basic idea is very simple.

The definition of a derivative of a function

$$u'(x) = \lim_{h \to 0} \frac{u(x+h) - u(x)}{h} \tag{1.20}$$

cannot be implemented directly in a digital computer where real numbers are represented with finite precision. Eventually, as h becomes small enough, the difference

calculation $[u(x + h) - u(x)]$ becomes meaningless. The simplest way of dealing with this is to make h small but keep it finite

$$u' \approx \frac{u(x + h) - u(x)}{h} \tag{1.21}$$

with h being 'small enough' and yet 'not too small'. This estimate of the derivative is actually most appropriate at the midpoint $(x + h/2)$. When used in that way it is called a central difference approximation. It can also be used as a (less accurate) estimate of the derivative at $x + h$ in which case it is called a forward difference approximation. Any differential equation involving one or more derivative of a function $u(x)$ can be turned into a relationship among values of $u(x)$ (not differentiated) at two or more points: $u(x)$, $u(x \pm h)$, $u(x \pm 2h)$, etc.

Taking as an initial example the simple first order rate law

$$A'(t) = -k\, A(t) \tag{1.22}$$

(now dropping the square brackets when denoting concentrations, just to reduce the writing), the numerical algorithm can be derived by applying a forward finite difference approximation to $A'(t)$

$$A'(t) \approx \frac{A(t + h) - A(t)}{h} \tag{1.23}$$

Inserting this into the rate law gives

$$A(t + h) = A(t) - h\, k\, A(t) \tag{1.24}$$

This is a relation that can be used to obtain the value of the function at a later point in time $t + h$ if the function is known at the point, t. This kind of relation is often called a recursion relation. By iterating, the function can be found at any point $t + nh$, where n is an integer. This gives a representation of the function on a grid of points where the grid spacing is h. Effectively, time has been discretized, it evolves in jumps of size h. The fact that we need to know the concentration at one point in time to start the calculation is directly related to the fact that the rate law is a first order differential equation and it takes one initial condition to specify a unique solution (a second order differential equation requires two boundary/initial conditions to specify a unique solution).

Turning now to a more challenging sequential reaction

$$A \to B \to C \to D \to E \tag{1.25}$$

the Euler method can be used to calculate the concentrations as a function of time in the following way: Assume that initially $t = 0$ and only A is present, i.e. $B_0 = C_0 = D_0 = E_0 = 0$ and assume the rate law is first order with respect to each of the

chemicals, the rate equations are

$$
\begin{aligned}
A' &= -k_1 A \\
B' &= k_1 A - k_2 B \\
C' &= k_2 B - k_3 C \\
D' &= k_3 C - k_4 D \\
E' &= k_4 D.
\end{aligned}
\tag{1.26}
$$

Introducing the notation $A_n = A(nh)$, $B_n = B(nh)$, etc, the Euler scheme then gives the following recursion relations

$$
\begin{aligned}
A_{n+1} &= A_n - h\, k_1 A_n \\
B_{n+1} &= B_n + h(k_1 A_n - k_2 B_n) \\
C_{n+1} &= C_n + h(k_2 B_n - k_3 C_n) \\
D_{n+1} &= D_n + h(k_3 C_n - k_4 D_n) \\
E_{n+1} &= E_n + h\, k_4 D_n.
\end{aligned}
\tag{1.27}
$$

By using a looping procedure in a computer program with n starting at $n = 1$, then $n = 2$, etc., the concentration of all species is generated as a function of time. This kind of algorithm can work well for a large number of simultaneous reactions and can be written without too much effort.

1.4.2   Runge-Kutta method

Effectively the Euler method assumes that each segment on the curve $A(t)$ can be taken as a straight line with the slope obtained from the tangent at the initial point in the segment. The fourth order Runge-Kutta method is much more effcient in that the time steps can be much larger, because it takes into account possible curvature or deviation from straight line behavior. The slope of the curve is evaluated at three intermediate points in the time interval h and a weighted average is used in calculating the new point $A(t + h)$. (See 'Numerical Recipes', ch. 16.1).