

Connections between Mathematics and Chemical Kinetics - Experimental and Theoretical

0 Introduction - Connections between chemical kinetics and mathematics

Kinetics is the branch of physical chemistry concerned with the rates and mechanisms of chemical reactions, and mathematics has proven to be a useful tool in helping to advance our knowledge of chemical kinetics. The aim of this essay is to try to describe, and link together, several concepts in mathematics and kinetics - these are numerical approximations of solutions to ODEs, random walks and probability, the rate equation of a chemical reaction and Brownian Motion.

1 Runge-Kutta and Rates of Reaction

1.0 Outline of Section

In this section, we give a short introduction to the key principles in the theory of kinetics in chemistry, including the important concept of the rate equation of a reaction. Then, we go through the main mathematics of the section - the use of numerical analysis to estimate solutions to first order ODEs, including a discussion about the Runge-Kutta methods. Finally, we give a brief explanation of how such approximation methods are used, in tandem with chemical experiments, to develop models for the mechanism of a reaction.

1.1 Basic Ideas in Kinetics

In the study of kinetics of chemical reactions, chemists look at the rate at which reactions progress. One of the key factors when looking at rate of a reaction is the concentration of the reactants. The reader may be familiar with experiments, such as the reaction between marble chips and hydrochloric acid, that demonstrate how increasing the concentration of one of the

reactants speeds up the reaction. With simple cases as the one above, the notion of the reaction rate was limited to OVERALL rate - that is, you noted the time for the WHOLE reaction to go to completion. In more advanced chemistry, establishing rates of reaction involves looking at the INSTANTANEOUS speed of the reaction. The "speed" is measured as the rate of change of the concentration of a particular reactant. This means that we can track the progress of a reaction by monitoring just one chemical. Furthermore, it has been shown that the speed of a reaction at a particular instant in time is determined by the concentration of certain reactants in the reaction mixture (or "system") at that point in time. We can then define an equation which illustrates this relationship.[1, pp243-244]

Definition. *The rate equation and overall order of a chemical reaction*

*For a reaction involving reactants (which ALSO includes chemicals involved in the reaction that are left unmodified), A_1, A_2, \dots, A_n , where $n \in \mathbb{N}$ and is small, **the rate equation for the reaction with respect to chemical A_i** , where $1 \leq i \leq n$, is:*

$$r_{A_i} = -\frac{d[A_i]}{dt} = k[A_1]^{a_1}[A_2]^{a_2} \dots [A_n]^{a_n}$$

where:

- r_{A_k} is the rate of reaction with respect to chemical A_1
- k is a constant of proportionality called **the rate constant**
- $[A_j] \in \mathbb{R}_{>0}$ is the concentration of chemical A_j in the system, where $1 \leq j \leq n$
- $a_i \in \mathbb{R}$, $i = 1, 2, \dots, n$, are **the orders of the reaction with respect to reactant A_i**

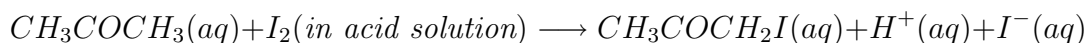
The overall order of the reaction is $\sum_{i=1}^n a_i$.

There are a few things to note at this point. First, we have restricted n to being "small". Although the number of reactants involved does not usually matter [6], there are cases where, with the presence of many chemicals, an intermediate chemical is formed, which is then converted into the final product. This results in the rate equation taking a more complicated

form [4, §1]. Second, the orders need not be integers, and some can be zero (i.e. the concentration of a particular reactant may not affect the rate of the reaction). Third, we have defined "reactants" to include chemicals left unaffected by the reaction - catalysts. This will be explained later when we discuss the notion of the mechanism of a reaction. Finally, and somewhat more importantly than the previous points, the orders of the reaction with respect to each chemical CANNOT be determined from the chemical equation of a reaction. Two examples are given below to illustrate the importance of these three points.

Example. *The reaction of Propanone CH_3COCH_3 and Iodine I_2 in acid [1, p251]*

This reaction is given by the chemical equation



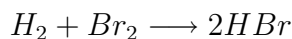
but has the following rate equation

$$r_{\text{iodine}} = k[\text{Propanone}][\text{Hydrogen ion } H^+ \text{ from acid solution}]$$

Bizarrely, the iodine concentration has no effect on the rate of the reaction (i.e. the reaction has order zero with respect to iodine)! Even more strange is the presence of the acid solution (in which the iodine is dissolved) in the rate equation, even though it does not appear explicitly in the reaction equation. This example should explain why the set of reactant chemicals in the definition of the rate equation had to include chemicals which are not altered by the reaction.

Example. *The reaction of Hydrogen and Bromine [4, p8]*

The equation for this reaction is very simple.



However the rate equation for the reaction is somewhat surprising!

$$\text{rate} = k[H_2][Br_2]^{\frac{1}{2}}$$

It is not clear as to where the half order with respect to bromine could have come from!

It should be clear by now that there is no obvious way of determining the orders of the reaction with respect to these reactants, and that *the only way to determine the rate equation for a reaction is by experiment*. In the next part of this essay, we will look at ways of trying to find the orders of chemicals in rate equations using experimental data and numerical analysis. For now, we close this subsection with a discussion of the importance of the rate equation.

A key property of the rate equation for a reaction is that it is very closely linked to the mechanism of that reaction - the sequence of steps a reaction takes for reactants to be turned into products. More specifically, it is related to the *rate determining step* of a mechanism - the SLOWEST step of a reaction. So the link is that the form of the rate equation reflects the chemicals involved in the rate determining step, since this step regulates the speed of the reaction. Furthermore, the orders of a reaction with respect to individual chemicals in a rate equation, give an indication of how involved these chemicals are in the rate determining step of the reaction mechanism [4, pp6-8]. Referring back to the example of the iodination of propanone, it has been shown that the rate determining step of the reaction involves a slow attack of the propanone molecules by hydrogen ions - no iodine molecules are involved [1, p251]. This explains the zero order of the reaction with respect to iodine. Note however that the orders are only *empirical values* derived from experiment. They don't give a full indication of what the mechanism, let alone the rate determining step, of a reaction is [4, p7] - for example, in the case of the reaction between hydrogen and bromine, it does not specifically say that half a molecule of bromine and one molecule of hydrogen are involved in the rate determining step. The only hint given is that of the half order of the reaction w.r.t. bromine, indicating that the mechanism could consist of several steps.

In conclusion, although determining the orders of a reaction with respect to individual reactants does not provide a clear idea as to the nature of a reaction mechanism, it certainly helps chemists go some way to finding the mechanism.

1.2 Numerical Analysis and Taylor's Theorem

The definition of a rate equation indicates that it takes the form of a first order ordinary differential equation. This may give the impression that, if

we had the values for the orders in the rate equation, we should be able to find a solution quite easily, using standard calculus methods. However this is not always the case, principally because the rate equation is an autonomous ODE and involves many dependent variables - the concentrations of each of the reactants, making obtaining a solution very tricky, if not impossible. So where else can we start? The only feasible way we can progress any further is to find numerical approximations to solutions of the rate equation. This part of the essay will outline the key ideas involved in the formulation of various techniques of numerical approximation of solutions to ODEs.

Our first point of call is Taylor's Theorem, which we state here without proof (The reader can find a proof in [5, pp116-117])

Theorem. *Taylor's Theorem for a function $x(t)$ expanded around t_0*

For $-\infty < t_0 < t < \infty$, suppose that $x : [t_0, t] \rightarrow \mathbb{R}$ is, for some $n \in \mathbb{N}$, C^n on $[t_0, t]$ and $n + 1$ times differentiable on (t_0, t) . Then

$$R_{n+1}(t)_{t_0} = x(t) - P_n(t)_{t_0}$$

where

$$P_n(t)_{t_0} = x(t_0) + x'(t_0)(t - t_0) + x''(t_0)\frac{(t - t_0)^2}{2!} + \dots + x^{(n)}(t_0)\frac{(t - t_0)^n}{n!}$$

and

$$R_{n+1}(t)_{t_0} = x^{(n+1)}(\theta)\frac{(t - t_0)^{n+1}}{(n + 1)!}$$

for some $\theta \in (t_0, t)$.

We also define $P_n(t)_{t_0}$ to be **the n th degree Taylor expansion of $x(t)$ around t_0**

This is a useful starting point for us, as it illustrates one of the key ideas of numerical analysis - the compromise between accuracy and ease of calculation.

Say that we know that $\frac{dx}{dt} = f(x, t)$ for some function $f : \mathbb{R} \rightarrow \mathbb{R}$, and we also know that $x = x_0$ when $t = t_0$, for some value $t_0 \in \mathbb{R}$. Assume also that f was C^{n-1} and n times differentiable on \mathbb{R} , for some $n \in \mathbb{N}$, so

that we can calculate $x''(t)(= \frac{df}{dt}), \dots, x^{(n+1)}(t)(= \frac{d^n f}{dt^n})$. Then we can Taylor-expand the function $x(t)$ around $t = t_0$ using the above theorem. Then, if the error term $R_{n+1}(t)_{t_0}$ is sufficiently small, we would then be able to use $P_n(t)_{t_0}$ to find approximate values of $x(t)$, for values of t which are close to t_0 .

However, things aren't always that easy. Sometimes the nature of the function f adds complications:

- f may not always satisfy the conditions (such as that of "n + 1 times differentiable") of the assumption above making it difficult to Taylor-expand $x(t)$ in the first place.
- Even if f did satisfy the conditions, we may still end up with an error term $R_{n+1}(t)_{t_0}$ that isn't small enough to certify that we can use $P_n(t)_{t_0}$ as a suitable approximation for $x(t)$. This may simply be due to the value chosen for n not being large enough.
- There may also be problems associated with the amount of calculations involved. Ideally, we would want a simple way to approximate $x(t)$ - so we would prefer not to evaluate many derivatives or calculate many complicated expressions. Thus lower values of n may be more suitable.

1.3 Taylor's Theorem and the rate equation

Having discussed some of the details of Taylor's Theorem, the reader may wonder how it is relevant to our study of the rate equation. It corresponds to a rate equation of the form:

$$r_{A_1} = -\frac{d[A_1]}{dt} = k[A_1]^{a_1}$$

So

$$x(t) = [A_1](t) \text{ and } f(x, t) = -k[A_1]^{a_1}$$

with $(t_0, x_0) = (0, [A_1]_0)$, where $[A_1]_0$ is the initial concentration of chemical A_1 before the reaction. In the case where $a_1 = 1$, i.e. the overall order is one, the rate equation has a simple solution which we can obtain with normal calculus.

$$[A_1](t) = ([A_1]_0)e^{-kt}$$

But when $a_1 \neq 1$, standard methods of calculus are not enough, and so Taylor's Theorem still has a part to play. However, a key question must be answered before proceeding further - Is the use of Taylor's Theorem with the rate equation valid? The answer is that, in most cases and up to a certain extent, we can use Taylor's Theorem. The first thing to realise is that the concentration of a reactant in a chemical reaction is a continuous function of time. The next thing to note is that the rate equation expresses the rate of change of concentration of reactants as a function of the reactant concentrations. Since these are continuous, then, *provided that none of the orders are negative (which is the case almost always)*, by product and chain rules of continuity and differentiation, the rate of change of the concentration of the reactant is also continuous and differentiable. We can repeat this argument for successive derivatives too, since we will always end up with a function of the concentrations of the individual reactants. However, the argument will fall down if any one of the concentrations is raised to a negative power, since this will result in a discontinuity at zero.

Recall that our aim was to try to find a numerical approximation to a solution of the rate equation. Equipped with our knowledge of Taylor's Theorem given above, we can now start to think about how to use it to obtain such an approximation. We will use $x(t) = [A_1](t)$ and $f(x, t) = x'(t) = -k[A_1]^{a_1} = -kx^{a_1}$, with initial conditions $t_0 = 0$ and $x_0 = [A_1]_0$, as well as the notation used in Taylor's Theorem given above. There are a couple of points which need to be made clear before we can go further:

- We need to have numerical values for $[A_1]_0$ (the initial concentration of A_1) which will be set as x_0 , a_1 (the order of the reaction with respect to A_1) and the rate constant k (this can also be found by experiment, but by direct calculations, rather than the approximation methods used to obtain the orders of a rate equation - for further details, the reader may refer to [1, pp256-258]) in order to numerically approximate x .
- We want to approximate values of $x(t)$ at various times, $t_0 (= 0), t_1, t_2, t_3, \dots$, each separated by a constant time step, h (so $t_i - t_{i-1} = h$). Sometimes, we only want to consider points in a specified interval (usually $[0, T]$, where T is the time for the whole reaction to go to completion). We must decide how many time points we wish to calculate approximations for $x(t)$ - too many points will lead to the process taking a very long time, but too few points will lead to the whole approximation being less

accurate. Alternatively, if we don't have a fixed interval to consider, then the value of h needs to be decided upon. A similar compromise needs to be sought - if h is too large, the Taylor approximation is not as accurate; if h is too small, then the process will take a long time.

- We shall denote the approximation of $x(t)$ at time t_0, t_1, t_2, \dots as x_0, x_1, x_2, \dots , and actual values of $x(t)$ as $x(t_0), x(t_1), x(t_2), \dots$ (notation used here is similar to that used in [2, §7]).
- To use Taylor's Theorem, we need to evaluate $x''(t), x'''(t), \dots, x^{(n)}(t_1)$ (for some $n \in \mathbb{N}$ - see the next point for further discussion.). We can use the rate equation to get expressions for the derivatives of x which themselves do not contain derivatives. For example:

$$x''(t) = \frac{d}{dt}x'(t) = -k \frac{d}{dt}x^{a_1} = -ka_1x^{a_1-1} \frac{dx}{dt} = k^2a_1x^{2a_1-1}$$

- We need to pick a value of n to truncate the Taylor Expansion. From discussions in the previous section, we realise that several factors need to be taken into consideration. First, we need to be sure that the conditions of Taylor's Theorem are upheld - recall that this meant that we would not want $x = [A_1]$ to be raised to a negative power in any of the expressions for the derivatives (since this would give a discontinuity at $t_0 = 0$). Second, the amount of computation - if n is large, the results will be more accurate by the theorem, but the process will involve a large amount of time computing all the derivatives and values; if n is small, the process will be much faster, but the approximations will be less accurate.

With all this in mind, we can now finally describe a method of calculating an approximate solution to the rate equation $f(x, t) = x'(t) = -kx^{a_1}$, given values for a_1 and x_0 at $t_0 = 0$ (As explained above).

1. Set $t_1 = t_0 + h = 0 + h = h$. Calculate $P_n(t_1)_{t_0}$. Set this value as x_1 .
2. Move on to the next time point, $t_2 = t_1 + h = h + h = 2h$. Calculate $P_n(t_2)_{t_1}$ but this time using x_1 as an approximate value for $x(t_1)$.
3. Move on to $t_3 = 3h$. Calculate $P_n(t_3)_{t_2}$ using x_2 as an approximate value for $x(t_2)$.

- Continue this process iteratively, until the desired number of points have been obtained. Plot the x_i on the vertical axis against the t_i on the horizontal axis, and you should obtain an approximate solution curve for the rate equation.

In summary, the $i + 1$ 'th step of the process gives the approximation x_{i+1} for $x(t_{i+1}) (= x((i + 1)h))$, with:

$$x_{i+1} = x_i + hx'_i + \frac{h^2 x''_i}{2!} + \dots + \frac{h^n x_i^{(n)}}{n!}$$

where $x_i^{(j)}$, for $0 \leq j \leq n$, is an approximate value of $x^{(j)}(t_i)$ generated by using x_i in place of $x(t_i)$. Notice that this method will incur an error of

$$R_{n+1}(t_{i+1})_{t_i} = \frac{h^{n+1} x^{(n+1)}(\theta)}{(n + 1)!}$$

for some $\theta \in (t_i, t_{i+1}) (= (ih, (i + 1)h))$ at the $i + 1$ 'th step [2, p215]. This is the clearest illustration so far of how the values of n and h affect the error of the approximation - a small h and a large n help to minimize the error. The reader should also be aware that we have to keep shifting the point which we expand $x(t)$ around from t_0 to t_1 to t_2 and so on, since we want to restrict the width of the interval in which θ lies to h . This again helps to minimise the error, by restricting the range of values θ can take, and, therefore, the values that $x^{(n+1)}(\theta)$ can take.

1.4 More complicated rate equations and Euler's Method

We've seen so far how to use Taylor's Theorem to find a numerical approximation to a solution of the rate equation involving only one chemical. Most of the time, however, the rate equation involves more than one chemical, and so we need to develop our existing method to cope with this situation. For example, take the two coupled rate equations:

$$x'(t) = -k_1 x^{a_1} y^{a_2} \text{ and } y'(t) = -k_2 x^{b_1} y^{b_2}$$

where $x, y : \mathbb{R}_{\geq 0} \rightarrow \mathbb{R}_{\geq 0}$, $a_1, a_2, b_1, b_2 \in \mathbb{R}$ but not all zero and $k_1, k_2 \in \mathbb{R} \setminus \{0\}$. Let us assume that x and y are both differentiable at least up to the second

order (so a_1, a_2, b_1, b_2 are greater than zero), and are C^1 . Now we shall try to find the second derivative of x :

$$\begin{aligned} x''(t) &= \frac{d}{dt}(-k_1 x^{a_1} y^{a_2}) = -k_1 a_1 x^{a_1-1} y^{a_2} \frac{dx}{dt} - k_1 a_2 y^{a_2-1} x^{a_1} \frac{dy}{dt} \\ &= k_1^2 a_1 x^{2a_1-1} y^{2a_2} + k_1 k_2 a_2 y^{a_2+b_2-1} x^{a_1+b_1} \end{aligned}$$

The expression is already much more complicated than in the one chemical case, and we can expect things to be more complicated for higher derivatives of x (and y). Such expressions mean that using the Taylor expansion method developed in the one chemical case may give rise to a procedure which is very cumbersome. Furthermore, the reader can imagine the trouble if we had three or more chemicals to consider! It is therefore useful to consider restricting ourselves to going as far as the *first derivative*. That is, we can apply the Taylor method as before, but using just the rate equation and initial conditions to get an approximation, rather than using these AND derivatives too. The procedure obtained by doing this is the **basic Euler method**.

We can summarise the Euler method applied to the two chemical case described above, keeping in mind the following:

- Similar to notation used previously in the one chemical case (part 1.4), we shall use time points t_0, t_1, t_2, \dots , separated by time step h . Since we are also taking $t_0 = 0$, we can conclude that, as before, $t_i = ih$.
- We will need to have a value for $x(t_0)$ ($= x(0)$), and $y(t_0)$ ($= y(0)$), setting each of these to equal x_0 and y_0 respectively. We will also need numerical values for the orders a_1, a_2, b_1, b_2 , and the rate constants k_1, k_2 of the rate equations.
- This method will calculate numerical approximations x_1, x_2, x_3, \dots and y_1, y_2, y_3, \dots for $x(t_1), x(t_2), x(t_3), \dots$ and $y(t_1), y(t_2), y(t_3), \dots$

Taking the above into account, we can now summarise the formulae of the Euler method applied to this two chemical situation. At the $i + 1$ 'th step of the process, the approximate values for $x((i + 1)h)$ and $y((i + 1)h)$ are:

$$x_{i+1} = x_i + hx'_i = x_i - hk_1 x_i^{a_1} y_i^{a_2} \quad \text{and} \quad y_{i+1} = y_i + hy'_i = y_i - hk_2 x_i^{b_1} y_i^{b_2}$$

and the errors at this step are:

$$\frac{h^2 x''(\alpha)}{2} \text{ and } \frac{h^2 y''(\theta)}{2}$$

for some $ih < \alpha, \theta < (i+1)h$. Although the local step-wise error is of the order h^2 , it can be shown [2, p216] that the total error of the whole approximation is of the order h (i.e. as $h \rightarrow 0$, the whole error tends to zero). Thus a small value of h needs to be picked, which usually means that we have to carry out more steps than if we were to use the standard Taylor method with the higher derivatives. However, it is not just the number of steps which is a problem with the Euler method.

Consider figure 1, modified from the figure given in [2, p217]. Here, the graph illustrates what happens at the $i+1$ 'th step. The lower line is that of the curve formed by joining up the approximation points. The upper line is that of the original function $x(t)$. The dashed line between these is a line tangent to the curve $x = x(t)$ at t_i , with gradient $x'_i = x'(t_i)$ (so it is parallel to the lower line). E_i is the cumulative error of the previous i steps. e_{i+1} is the error of the $i+1$ 'th step. The problem is that the curve follows the slope dictated by x'_i throughout the interval (t_i, t_{i+1}) , and only changes gradient at t_{i+1} . We want the approximation to have some way of being aware of the change in the gradient of the $x(t)$ curve that occurs within this interval. This way, we can reduce the size of e_{i+1} and, therefore, the overall error. However, we also want to keep the calculations as simple as possible, which means not going further than the first derivative. We need an alternative to the Euler method. Enter the Runge-Kutta methods...

1.5 Formulation of the Runge-Kutta Methods

The Runge-Kutta methods are single-step procedures (i.e. they only rely on the approximation obtained at the previous point, to calculate the approximation at the next point), as are the Taylor expansion and basic Euler methods. They also use make use of derivatives of no higher degree than the first, just like the basic Euler method again. However, these methods may also generate errors which are much smaller than those incurred in the basic Euler process. To demonstrate the principle, we shall examine the way in which these methods can be applied to a function of the form $x(t)$ where

$x'(t) = f(t, x)$ for some function f . The idea of the Runge-Kutta (or R-K) methods is to detect a change in the gradient of $x(t)$ within an interval, (t_i, t_{i+1}) say, by evaluating the function at some point (or points) within the interval, and then using this information to produce an approximation that agrees with an approximation obtained via the Taylor expansion method. The methods can be summarised in the following form [3, p420]:

$$x_{i+1} = x_i + hF(t_i, x_i, h; f)$$

where $h = t_{i+1} - t_i$ is the time-step (as before) and F is a function specific to the R-K method used. We shall look at one example of the form that F may take, and derive the method.

Example. *Derivation of some second order R-K methods*

The following is modified (mainly in notation) from the method used in [2, pp218-219], but the reader can find a more detailed description in [3, §6.10]. We shall look at the situation when F takes the form

$$F(t_i, x_i, h; f) = ak_1 + bk_2$$

with

$$k_1 = f(t_i, x_i) \text{ and } k_2 = f(t_i + h\alpha, x_i + h\beta k_1)$$

where a, b, α and β are constants to be determined so that $x_{i+1} = x_i + hF(t_i, x_i, h; f)$ agrees with the prediction given by a second-order (or second-degree) Taylor expansion.

(Warning - these expressions for k_1 and k_2 do not correspond to any "rate constant", and this example does not consider a rate equation.)

The first thing we do is expand the R-K function, $f(t_i + h\alpha, x_i + h\beta k_1)$, as a first-degree Taylor expansion in two variables around (t_i, x_i) . We get

$$k_2 = f(t_i + h\alpha, x_i + h\beta k_1) = f + h\alpha f_t + h\beta f_x k_1 + O(h^2)$$

where $O(h^2)$ is the Taylor error term of order h^2 , the terms f_t and f_x are the partial derivatives of f with respect to t and x , evaluated at (t_i, x_i) , and f denotes $f(t_i, x_i)$. (It is enough to get a first-degree Taylor expansion here, since any quadratic terms required to match terms in the second-degree Taylor prediction of $x(t_{i+1})$ can be generated by multiplying k_2 by h in the R-K

equation $x_{i+1} = x_i + hF(t_i, x_i, h; f)$).

Now, realising that $k_1 = f$, we can substitute this into the Taylor expansion of k_2 to get

$$k_2 = f + h\alpha f_t + h\beta f_x f + O(h^2)$$

Then, substituting this into the expression for F , and then substituting F into the R-K equation gives

$$x_{i+1} = x_i + h(a + b)f + h^2(b\alpha f_t + b\beta f_x f) + O(h^3)$$

Next, we need to generate the second-degree Taylor expansion of $x(t_{i+1})$ around t_i . This gives us

$$\begin{aligned} x(t_{i+1}) &= x(t_i) + hx'(t_i) + \frac{1}{2}h^2x''(t_i) + O(h^3) \\ &= x(t_i) + hf + \frac{1}{2}h^2(f_t + f_x f) + O(h^3) \end{aligned}$$

We want our expression for x_{i+1} to match the Taylor prediction for $x(t_{i+1})$. So, our last step is to equate the coefficients of h and h^2 . This gives us the following formulae to calculate the constants.

$$a + b = 1$$

$$b\alpha = \frac{1}{2}$$

$$b\beta = \frac{1}{2}$$

The choice of a, b, α and β is restricted by these three equations - otherwise, we have freedom in what values we choose! We can list two special cases here:

- When we pick $a = 1$ and $b = 0$, the quadratic (h^2) term vanishes, leaving us with the basic Euler method of

$$x_{i+1} = x_i + hf(t_i, x_i)$$

- To improve on the Euler method, we want to retain the quadratic term. One choice of constants that will do this is $a = 0$, $b = 1$ and $\alpha = \beta = \frac{1}{2}$, which gives us the R-K equation as:

$$x_{i+1} = x_i + hf\left(t_i + \frac{1}{2}h, x_i + \frac{1}{2}hf(t_i, x_i)\right)$$

On closer inspection, we can see how the formula works in accounting for the change in gradient of $x(t)$. Starting at (t_i, x_i) , we calculate the slope of $x(t)$ at this point, and find that it is equal to $f(t_i, x_i)$. So we draw a line with slope $f(t_i, x_i)$ from (t_i, x_i) , and extend it to a point in the middle of the time interval, at $t = t_i + \frac{1}{2}h$ (rather than to $t = t_{i+1}$, as we did in the basic Euler method). We then evaluate the gradient of $x(t)$ at this point, and get that it is equal to $f(t_i + \frac{1}{2}h, x_i + \frac{1}{2}hf(t_i, x_i))$. We then draw a new line from (t_i, x_i) with this gradient, and extrapolate to the point $t = t_{i+1}$, to obtain an approximation x_{i+1} for $x(t_{i+1})$. Figure 2 gives a pictorial description of the above account.

This method is known as the **modified Euler method**, as it follows the basic form of formulae as the Euler method, but the gradient used is modified to ensure that the line which generates the next approximation follows more closely to the true curve of the function $x(t)$. The result is that the error e_{i+1} generated by the $i+1$ 'th is much smaller than with the basic Euler method, as can be seen in figure 2.

In the example above, the values of k_1 and k_2 were the original gradient at (t_i, x_i) and the modified gradient calculated at a point in the middle of the time interval. The Runge-Kutta method generate approximations in a similar fashion to the basic Euler method, but the gradient of the line from (t_i, x_i) is calculated by a "weighted" mean of the gradient of $x(t)$ calculated at different points (so in the example above, the basic Euler method relied on k_1 alone, whereas the modified Euler method relied on just k_2). The "weights" are partially controlled by the restrictions imposed upon the constants in the R-K methods by ensuring that it matches a Taylor approximation. But otherwise, the values of the constants can be set as pleased, leading to a wide family of numerical methods. The main advantage of these methods is that we achieve approximations which concur with those achieved with Taylor methods, but we need not calculate derivatives of order higher than one. However, one big drawback is that, to maintain a sufficient level of accuracy in our approximations, we need to use a small h , which generally means more steps at which we need to make approximations, lengthening the process. The requirement for small h arises from our use of Taylor's Theorem in the deriving the R-K methods.

1.6 Using Runge-Kutta with experimental data and the rate equation

The reader may wonder, after our discussion of Runge-Kutta methods above, why this has anything to do with our goal of determining the orders of a rate equation. The R-K methods are useful in their ability to generate approximate numerical solutions to ODEs. We can utilise this to find an approximate solution to rate equations with values for the orders, as with the previous methods discussed. But we can also use the R-K methods to help us find numerical values for the orders in a rate equation, with the help of data obtained by running the reaction in laboratory experiments. This is possible, mainly with the use of computers, which can have R-K procedures programmed into them (one common example is that of the "ODE45" command in the programme Matlab[®], which uses a sophisticated R-K method.[7]). With this in mind, we can now outline an approach that will generate numerical approximations to the orders of a rate equation for a particular reaction.

1. First, run the experiment and obtain a plot of the concentration of a particular reactant, say A_1 against time.
2. Calculate the rate constant, using further experiments (given the theory of rate constants described in [1, pp257-258]).
3. Derive the rate equation for the reaction with respect to chemical A_1 (using the general form of rate equation described in §1.1), , but use the value obtained in step 2 for the rate constant.
4. Plug in first estimates of the orders of the reaction into the rate equation. These estimates should be sensible. For example, if the experimental data obtained from step 1 suggests that the reaction has an overall order of one, then the estimate orders should sum to one to give an overall order of one!
5. Run the R-K method for the rate equation. Obtain a graph of the approximate numerical solution obtained by the method.
6. Compare the graph obtained from the experiments of step 1 with the graph of step 5. Determine whether or not the graphs are "close fitting" (The definition of this term varies with the level of accuracy required). If they are, then the rate equation generated with the order values used

is sufficient. If not, redo step 4 with a new estimate. Then repeat steps 5 and 6. Keep going until the graphs are determined to be close fitting. The values of the orders used in the final repeat are the numerical approximations of the orders in the rate equation of the reaction.

The reader may wonder why we didn't use neither the basic Euler method nor the Taylor expansion method to do this in the first place. The main reason for not using the basic Euler method was that, although relatively easy to apply, the error generated is substantially larger than related R-K methods. The method based on Taylor's Theorem was not used for the opposite reason - using higher derivatives would lead to a low level of accumulated error, but the level of calculation involved to obtain all the derivatives required would mean the process taking much longer. The R-K methods seem to strike a balance between relative ease of computation (which also links to the fact that it is possible to program computers to run R-K methods), combined with means to minimise errors in approximating solutions, making them useful in finding solutions for ODEs, and finding orders of a reaction with respect to individual reactants!

*NB - Although no example is given here of using the R-K methods on rate equations, the reader is advised to consult [8] to see an example. However, it must be noted that the rate equation in this example is not of the standard form outlined in §1.1, as the reaction is an **equilibrium** reaction. If the reader is interested however, he or she may consult [1] and [4] for further theory.*

2 An introduction to Brownian Motion

2.0 Outline of Section

In this section, we discuss the concept of random walks, and see how it links to describing the random motion of particles in liquids through the concept of Brownian Motion. We will also outline the equations that underpin this concept.

2.1 Random Walks

Before we discuss the notion of a random walk, we shall deviate to briefly discuss the history behind the study of random walks. One key idea is that of

the so-called "Drunkard's Walk", mentioned in a letter to the journal *Nature* sent by English statistician Karl Pearson in 1905, on *The problem of the random walk* [9, p53]:

"A man starts from a point O and walks l yards in a straight line; he then turns through any angle whatever and walks another l yards in a second straight line. He repeats this process n times. I require the probability that after n of these stretches he is at a distance between r and r + δr from his starting point O."

This anecdote illustrates the notion of a random walk as being the path consisting of short straight segments (of constant equal length in this case) joined together, but with the angles between each pair of segments picked in a random way (i.e. the directions of each of the segments are independently chosen).

In mathematical notation, we describe a random walk as follows [10]. We say that a particle, starting from the origin O , experiences a sequence of displacements \mathbf{r}_i with $i = 1, 2, \dots$, where the magnitude and direction of each of the \mathbf{r}_i is determined by a probability distribution. Then, after N displacements, the position of the particle is given by

$$\mathbf{R} = \sum_{i=1}^N \mathbf{r}_i$$

We wish to know the probability distribution of \mathbf{R} .

Although we won't go into the details of formal solutions (which would require knowledge of Fourier Transforms [9, §2]), we can look at a simple example of a random walk that leads to a surprising result.

Example. *"Forwards and backwards"*

Let us restrict the directions in which our particle can travel to one dimension, and fix the displacements that the particle can undergo to +1(forwards), -1(backward). We shall also say that it is equally likely that a displacement is either +1 or -1. So

$$\forall i = 1, 2, \dots P(\mathbf{r}_i = +1) = P(\mathbf{r}_i = -1) = \frac{1}{2}$$

Now, after N displacements, we can work out the expected position of the particle, $E(\mathbf{R})$. Calculating this, we get:

$$E(\mathbf{R}) = E\left(\sum_{i=1}^N \mathbf{r}_i\right) = \sum_{i=1}^N E(\mathbf{r}_i) \text{ as each of the displacements are independent}$$

$$= \sum_{i=1}^N \left[\left(\frac{1}{2} \times -1\right) + \left(\frac{1}{2} \times +1\right)\right] = 0$$

So we expect the particle to be back at the origin after N steps! However, if we consider $E(\mathbf{R}^2)$, we get an interesting result.

$$E(\mathbf{R}^2) = E\left(\left(\sum_{i=1}^N \mathbf{r}_i\right)^2\right) = E(\mathbf{r}_1^2) + E(\mathbf{r}_2^2) + \dots + E(\mathbf{r}_N^2) + 2E(\mathbf{r}_1\mathbf{r}_2) + 2E(\mathbf{r}_1\mathbf{r}_3) + \dots$$

$$= E(\mathbf{r}_1^2) + E(\mathbf{r}_2^2) + \dots + E(\mathbf{r}_N^2) \text{ since, by independence, for } i \neq j, E(\mathbf{r}_i\mathbf{r}_j) = E(\mathbf{r}_i) \times E(\mathbf{r}_j) = 0$$

$$\text{but } \forall i = 1, 2, \dots, E(\mathbf{r}_i^2) = 1, \text{ so } E(\mathbf{R}^2) = N$$

The above result gives us the idea that the particle has covered a distance \sqrt{N} after the N displacements!

Such a bizarre result indicates that, although cases of random walks may seem simple enough, these cases must be treated with caution, as we may get results that are unexpected! The reader will therefore be pleased to hear (!) that we shall move on to describing the key equations of Brownian Motion.

2.2 Brownian Motion and it's relevance to the kinetics of chemical reactions

In 1827, Robert Brown, a botanist, was investigating the action of pollen in plants. During these investigations, he noted the random motion of pollen granules in still water. He later wrote, in 1828, that [11]:

”These motions were such as to satisfy me, after frequently repeated observation, that they arose neither from currents in the Fluid, nor from its gradual evaporation, but belonged to the particle itself”

And thus the theory of Brownian Motion was born. It was not until the early 20th Century when significant progress was achieved when Albert Einstein published several papers on the subject. In this part of the essay, we shall describe the details of Einstein’s description of Brownian Motion. Further details on what follows below can be found in [10].

We start with the assumption that a free particle (so called because of the lack of restrictions in the directions in which it can travel) has its motion governed by the following equation:

$$\frac{d\mathbf{u}}{dt} = -\eta\mathbf{u} + \mathbf{A}(t)$$

where:

- \mathbf{u} denotes the instantaneous velocity of the particle.
- $-\eta\mathbf{u}$ is the ”dynamical friction term”, where η is dependent on the viscosity of the fluid and the mass and radius of the particle.
- $\mathbf{A}(t)$ is the ”fluctuating part”. There are further assumptions for the nature of this part. First, it is *independent* of \mathbf{u} . Second $\mathbf{A}(t)$ is said to vary extremely rapidly compared with \mathbf{u} . This means that for any small time interval Δt , $\mathbf{u}(t + \Delta t) - \mathbf{u}(t)$ is negligible, compared to the difference between $\mathbf{A}(t + \Delta t)$ and $\mathbf{A}(t)$, and these differences have no correlation to each other.

Furthermore, if we are to consider the net change in the velocity of the particle in a time interval Δt

$$\mathbf{B}(\Delta t) = \int_t^{t+\Delta t} \mathbf{A}(\alpha) d\alpha$$

then:

- The values of \mathbf{B} over any two successive time intervals $(t, t + \Delta t_1)$ and $(t + \Delta t_1, t + \Delta t_1 + \Delta t_2)$ have no correlation to each other.

- The probability distribution of the net changes in velocity over any given time interval is given by the following distribution

$$\omega[\mathbf{B}(\Delta t)] = \frac{1}{(4\pi q \Delta t)^{\frac{3}{2}}} \exp\left[-\frac{|\mathbf{B}(\Delta t)|^2}{4q \Delta t}\right]$$

where q is a "diffusion constant" related in some way to the η of the "dynamical friction term"

The details of the assumptions above give a sense of the vast amount of theory behind this model of Brownian Motion. However, what does this have to do with random walks? It turns out that the model is related to the case of a random walk where the number of displacements N is large, the displacements themselves \mathbf{r}_i are small and are governed by the following spherically symmetrical (i.e. the probability that an \mathbf{r}_i has a certain length and points in one direction is equal to the probability that it has the same length in a different direction) probability distribution $\tau(\mathbf{r})$. Then, the distribution of \mathbf{R} can be shown to be

$$\omega[\mathbf{R}] = \frac{1}{\left(\frac{2\pi N \langle r^2 \rangle_{Av}}{3}\right)^{\frac{3}{2}}} \exp\left[-\frac{3|\mathbf{R}|^2}{2N \langle r^2 \rangle_{Av}}\right]$$

where

$$\langle r^2 \rangle_{Av} = \int_{-\infty}^{+\infty} \tau(\mathbf{r}) r^2 d\mathbf{r}$$

is the mean square displacement of the particle to be expected for any occasion. Then, take the number of displacements which take place over a unit of time, and call this n . Then, after a small time interval Δt , in which many displacements have taken place, \mathbf{R} has the following distribution.

$$\omega[\mathbf{R}] = \frac{1}{(4\pi q \Delta t)^{\frac{3}{2}}} \exp\left[-\frac{|\mathbf{R}|^2}{4q \Delta t}\right]$$

where $q = \frac{1}{6} n \langle r^2 \rangle_{Av}$. This is how we derive the distribution of $B(\Delta t)$.

Finally, the reader may ask what the relevance of all this is to the kinetics of chemical reactions. Quite simply, these equations and assumptions are the tools that we can use to describe the random motion of particles or molecules in a fluid. This random movement is an essential part of the kinetics of chemical reactions, and can help us to develop models that replicate particle behaviour in fluids, and so help chemists model chemical reactions, including effects regarding the diffusion of substances into one another.

3 Conclusion

In this essay, I have shown you two areas of mathematics, numerical analysis and statistics, and have described to you some ways in which they have relevance to the study of chemical kinetics - numerical analysis has tools in helping chemists to study rate equations of reactions, mainly in the form of the Runge-Kutta methods; and probability theory has helped us to understand the concept of Brownian Motion, a concept central to the study of the interaction of chemicals in a reaction, by the random movement of molecules.

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