Ordinary Differential Equations
Linear First Order

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To The Reader

These slides cannot replace a math course. They can hopefully remind you or provide you with the tools necessary to support you on your chemical physics journey. Most examples are inspired from Mary L. Boas' book ISBN-13 9780471198260. I have in some cases expanded on the examples

Introduction

- We will look at the general method of solving linear first-order ordinary differential equations.
- We will illustrate the procedure with two examples, one mathematical and other more related to physical chemistry
- We will use python-generated graphs to aid in the interpretation of the results.

Linear First Order Differential Equations

- A differential equation is an equation that relates a function and its derivative.
- When partial derivatives are involved, we say that we have a *partial differential equation*. Otherwise, we say we have an ordinary differential equation (diff.eqs) or simply differential equation.
- the order of a differential equation is given by the order of the highest derivative in the equation. Hence first order diff.eqs are ones where only the first derivative is present.

Linear First Order Differential Equations

- A first order diff.eq is linear if the coefficients multiplying y solely depend on x
- Hence they do not admit terms with y^n where $n > 1$
- Although in some cases it is possible to recast an equation with y^n term in into a first order equation (e.g. Bernoulli equation)

Separable equations

The simplest form of 1st order linear diff.eq we can solve are the separable kind. They are of the form:

$$y' = f(x)dx \text{ or} \tag{1}$$
$$dy = f(x)dx$$

We see here that we are able to write y terms on one side and x terms on one side. For such a case, it is trivial to simply integrate each side to solve for y

$$\int dy = \int f(x)dx \tag{2}$$

$$y = \int f(x)dx + c \tag{3}$$

Example of Separable Equation

Let us look at an example. Suppose we have a unimolecular reaction where a substance A decomposes into another substance B. If we write [A] as the concentration of A. The diff.eq which describes this process is:

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -k_1[A] \tag{4}$$

Recognizing this is an equation of the separable kind, we can write:

$$\frac{d[A]}{[A]} = -k_1\,dt \tag{5}$$

$$\ln[A] = -k_1 t + C \tag{6}$$

$$[A] = N e^{-k_1 t} \tag{7}$$

Equation (5) is a family of solutions for the differential equation, because N is not specified here. Suppose we are given the initial condition that at $t = 0$, $[A] = [A]_0$. We can use this condition to find the one equation, among the family, that fits our problem specifically. In so doing we find:

$$[A] = [A]_0 e^{-k_1 t} \tag{8}$$

Linear First Order

Linear first order equations are of the form:

$$y' + Py = Q \tag{9}$$

Where P and Q are functions of x or are constants. Let us look at the case where $Q = 0$. In this case, we obtain the *separable* equation because we can have all the terms in y on one side, and P on the other side. In fact we obtain the same equation as in the previous example. Let us carry the same procedure as above:

$$\frac{dy}{y} = -P \tag{10}$$

$$\ln y = -\int P dx + C \tag{11}$$

$$y = Ae^{-\int P dx} \tag{12}$$

Where we used $e^C = A$.

Solutions of Linear First Order Equations

We can write

$$I = \int P \, dx \tag{13}$$

In this case equation (12) can be rewritten as $y = Ae^{-I}$ or $ye^{I} = A$.

Notice from our definition of I, its derivative with respect to x is just P.

Now let us take the derivative of $ye^{I} = A$

$$\frac{\mathrm{d}(ye^{I})}{\mathrm{d}x} = y\frac{\mathrm{d}I}{\mathrm{d}x}e^{I} + y'e^{I} \tag{14}$$

$$= yPe^{I} + y'e^{I} \tag{15}$$

$$= e^{I}(y' + Py) \tag{16}$$

We see in that we have obtained the left-hand side of our first order equation, multiplied by a factor e^{I}. In light of that, let us then multiply our first order equation by e^{I}

$$e^{I}(y' + Py) = Qe^{I} \tag{17}$$

Solutions of Linear First Order Equations

We know integrating the left-hand side yields ye^I. Hence, integrating both sides, we obtain:

$$ye^I = \int Qe^I dx + C \tag{18}$$

$$y = e^{-I} \int Qe^I dx + Ce^{-I} \tag{19}$$

Solutions of Linear First Order Equations

We have done it! Equation (19) is the general solution to a linear first order differential equation. Since multiplying by e^I allowed us to easily integrate the equation, we call it an *integrating factor*. In the remaining slides, we will look at an example of physical relevance.

Consecutive Reaction

Suppose we have a consecutive radioactive decay $A \rightarrow B \rightarrow C$. We define N_1, N_2 and N_3 as the amounts of A, B and C respectively at time t. In addition, N_{A_0} is the amount of A at $t = 0$. We can write a differential equation for each species as a function of time:

$$\frac{dN_1}{dt} = -k_1 N_1 \quad \frac{dN_2}{dt} = k_1 N_1 - k_2 N_2 \quad \frac{dN_3}{dt} = k_2 N_2 \qquad (20)$$

The first equation is simply the *separable* kind. Its solution is obtained by separating and integrating. The solution is $N_1 = N_{A_0} e^{-k_1 t}$ (make sure you convince yourself of that.)

Let us solve the second equation:

$$\frac{dN_2}{dt} = k_1 N_1 - k_2 N_2 \quad \Rightarrow \boxed{\frac{dN_2}{dt} = k_1 (N_{A_0} e^{-k_1 t}) - k_2 N_2} \qquad (21)$$

Solving for N_2

The fact that we solved for N_1 allowed us to rewrite the equation for N_2 in terms of one dependent-variable N_2 instead of two (N_1 and N_2), thereby making our equation linear. Putting all terms with N_2 on one side, we obtain:

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} + k_2 N_2 = k_1(N_{A_0}e^{-k_1 t}) \tag{22}$$

Here we see that $P = k_2$ and $Q = k_1(N_{A_0}e^{-k_1 t})$. Recall $I = \int P dt$ So we can multiply this equation by our integrating factor ($e^{k_2 t}$) and integrate.

$$e^{k_2 t}(\frac{\mathrm{d}N_2}{\mathrm{d}t} + k_2 N_2) = (k_1 N_{A_0}e^{k_2 - k_1 t}) \tag{23}$$

$$e^{k_2 t}N_2 = \int k_1 N_{A_0}e^{k_2 - k_1 t}dt + C \Rightarrow \boxed{N_2(t) = \frac{e^{-k_2 t}k_1 N_{A_0}}{k_2 - k_1}e^{(k_2 - k_1)t} + Ce^{k_2 t}} \tag{24}$$

Complete Solution of N_2

Using the suitable initial condition, namely that at $t = 0$, $N_2 = 0$, we can solve for C. We see that $C = \dfrac{-k_1 N_{A_0}}{k_2 - k_1}$. So the complete solution for N_2 is:

$$N_2(t) = \frac{k_1 N_{A_0}}{k_2 - k_1} \left(e^{-k_1 t} - e^{k_2 t} \right) \tag{25}$$

Solution for N_3

Recall that N_3 obeyed the differential equation:

$$\frac{\mathrm{d}N_3}{\mathrm{d}t} = k_2 N_2 \Rightarrow \frac{\mathrm{d}N_3}{\mathrm{d}t} = k_2 \left(\frac{k_1 N_{A_0}}{k_2 - k_1} \left(e^{-k_1 t} - e^{k_2 t} \right) \right) \qquad (26)$$

We will simply give the solution here, but realize we have the factor $\left(\frac{k_2 k_1 N_{A_0}}{k_2 - k_1} \right)$ in front, we will have two integrals (one on $e^{-k_1 t}$ minus the one on $e^{-k_2 t}$). Performing the integral and solving for C using the initial condition $N_3 = 0$, we get:

$$N_3(t) = \frac{k_1 N_{A_0} e^{-k_2 t}}{k_2 - k_1} - \frac{k_2 N_{A_0} e^{-k_1 t}}{k_2 - k_1} + \frac{k_2 - k_1}{k_2 k_1} \qquad (27)$$

Visualizing the Solutions

Below is a python-generated graph where we have the condition that $N_{A_0} = 1$ and $k_1 = 2$, $k_2 = 1$. These conditions tell us, as N_1 decays, we should expect some build up of species N_2 because the rate constant related to its formation is twice as much as that related to its decay. We should also observe the growth of N_3
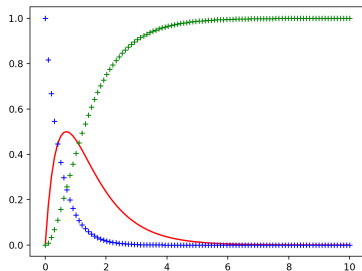

Figure: Amount of species N_1, N_2, N_3 as a function of time

Steady-State

- In the consecutive decay of radium to radon to polonium, the half life of radium decay is on the order of 10^5 longer than that of radon decay.
- This fact suggests as radium takes a very long time to decay, and radon decays relatively fast, we would not expect a significant build up of radon (corresponding to an unchanging amount of radon $\frac{\mathrm{d}N_2}{\mathrm{d}t} = 0$)
- It would be as if radium decayed directly to polonium (this is NOT the case.)

We would obtain new expressions for the rates:

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = k_1 N_1 - k_2 N_2 = 0 \Rightarrow k_1 N_1 = k_2 N_2 \tag{28}$$

$$\boxed{N_2(t) = \frac{k_1 N_{A_0}}{k_2} e^{-k_1 t}} \tag{29}$$

Steady-State

For N_3 we would have:

$$\frac{\mathrm{d}N_3}{\mathrm{d}t} = k_2 N_2 \tag{30}$$

$$\frac{\mathrm{d}N_3}{\mathrm{d}t} = k_2 \left(\frac{k_1 N_{A_0}}{k_2} e^{-k_1 t} \right) \tag{31}$$

Simplifying and integrating gives:

$$\boxed{N_3(t) = N_{A_0}(1 - e^{-k_1 t})} \tag{32}$$

- As we can see, the expressions for N_2 and N_3 changed when we invoke this approximation.
- It is important to note that the mathematical results in this case are only valid, that is, they approach the same numerical values as the equations obtained without the approximation, only in the limit of $k_1 << k_2$

Visualizing Steady State

On the graph on the left, we show the case where $N_{A_0} = 1$ and $k_1 = 2$, $k_2 = 1$. Notice how the steay-state approximation (in yellow) leads to a bad prediction in this case for the amount of $N_3(t)$, since k_1 and k_2 are of the same order of magnitude. On the graph on the right, however, $k_1 = 2$ and $k_2 = 2 \times 10^5$. Notice how the steady-state approximation reproduces the correct values for $N_3(t)$.
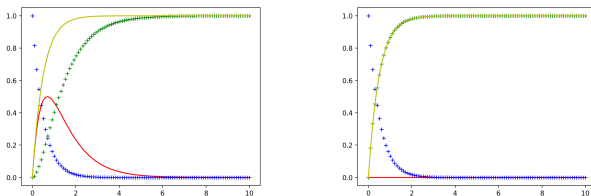

Figure: Left: Overlay of amount of species N_1, N_2, N_3 and N_{3_s} as a function of time, steady-state fails; Right: Steady-state reproduces exact solutions.

Concluding Remarks

Lastly, we could have also obtained the equations for the steady-state approximation by inspecting the exact equations in the limit that $k_2 >> k_1$ (try it!)