CHEM1034 - Week 21 Lecture – Ordinary Differential Equations, Part II

Sections 11.1-11.6 of Steiner, "The Chemistry Maths Book", 2nd edition.

Summary so far

Separable first-order ordinary differential equations should be solved in the following way:

1. Using appropriate mathematical transformations, bring the equation to the following form:

$$g(y)dy = f(x)dx \tag{1}$$

   Some equations may require a variable substitution before they can be brought into this form.

2. Integrate both sides and note that a sum or difference of two unknown constants is a *single* unknown constant. The solution that contains this constant is called the *general solution*.

3. Use the initial condition to determine the constant. The solution with all unknown constants eliminated is called the *particular solution*.

4. Check the solution by substituting it back into the differential equation and the initial condition. If both are satisfied, the solution is correct.

Some examples of the application of this procedure are given below.

Examples of separable first-order ODEs and their solutions

Problem: find the general solution of the equation

$$\frac{dy}{dx} = x + 10\sin x \tag{2}$$

and the particular solution for which $y(\pi) = 0$.

Solution:

1. Multiplying by dx brings the equation into the separated form:

$$dy = (x + 10\sin x)dx \tag{3}$$

2. Integrating both sides creates the general solution:

$$\int dy = \int (x + 10\sin x)dx \quad \Rightarrow \quad y = \frac{x^2}{2} - 10\cos x + C \tag{4}$$

3. Using the initial condition creates an algebraic equation for the constant C:

$$0 = \frac{\pi^2}{2} - 10\cos\pi + C \quad \Rightarrow \quad C = -\frac{\pi^2}{2} - 10 \tag{5}$$

   The particular solution therefore is:

$$y = \frac{x^2}{2} - 10\cos x - \frac{\pi^2}{2} - 10 \tag{6}$$

4. Substituting Equation (6) back into Equation (2) and the initial condition confirms that it is the correct solution.

Problem: a curve passing through the point with $x=1$, $y=0$ has slope $1/x-2x$. What is the equation of that curve?

Solution: the slope of the curve is the derivative of the corresponding function, therefore the differential equation that we have to solve is

$$\frac{dy}{dx}=\frac{1}{x}-2x \tag{7}$$

with the boundary condition $y(1)=0$. Solution stages:

1. Multiplying by dx brings the equation into the separated form:

$$dy=\left(\frac{1}{x}-2x\right)dx \tag{8}$$

2. Integrating both sides creates the general solution:

$$\int dy=\int\left(\frac{1}{x}-2x\right)dx \quad\Rightarrow\quad y=\ln x-x^2+C \tag{9}$$

3. Using the initial condition creates an algebraic equation for the constant C:

$$0=\ln(1)-1^2+C \quad\Rightarrow\quad C=1 \tag{10}$$

   The particular solution therefore is:

$$y=\ln x-x^2+1 \tag{11}$$

4. Substituting Equation (11) back into Equation (7) and the initial condition confirms that it is the correct solution.

Not all first-order ODEs are instantly separable – considerable effort and skill may be required to separate some of them and there are equations (not considered here) that cannot be separated at all.

Problem: use $u=y/x$ substitution to bring the following equation

$$\frac{dy}{dx}=\frac{x+y}{x} \tag{12}$$

to a separable form and find its general solution.

Solution:

1. The substitution function has the following differential:

$$y=ux \quad\Rightarrow\quad dy=xdu+udx \tag{13}$$

2. After making the substitution, we obtain an equation where variables can be separated:

$$\frac{xdu+udx}{dx}=1+u \quad\Rightarrow\quad x\frac{du}{dx}+u=1+u \quad\Rightarrow\quad du=\frac{1}{x}dx \tag{14}$$

3. We can now solve that equation and perform the inverse substitution:

$$u=\ln|x|+C \quad\Rightarrow\quad \frac{y}{x}=\ln|x|+C \quad\Rightarrow\quad y=x\ln|x|+Cx \tag{15}$$

   The result is the general solution of the original equation.

N.B. There are *much faster* ways of solving linear ODEs and their systems than the method described above, but they require fairly deep mathematical background on the user's part – look up *matrix exponential* and *Laplace transform* if you are interested.

Steady state solutions

Many time-dependent processes in chemistry eventually reach an *equilibrium state*: the situation when concentrations, masses and pressures stop changing because the quantities *arriving into* a particular chemical form and the quantities *departing from* that chemical form become equal. The reaction still proceeds in both directions, but without changes in concentrations. In this situation, the differential equations describing system dynamics, *e.g.*:

$$\begin{cases} \dfrac{d[A]}{dt} = f_1([A],[B]) \\ \dfrac{d[B]}{dt} = f_2([A],[B]) \end{cases} \tag{16}$$

become algebraic equations because the time derivatives of constant concentrations are zero:

$$\begin{cases} f_1\left([A]_{\text{eq}},[B]_{\text{eq}}\right) = 0 \\ f_2\left([A]_{\text{eq}},[B]_{\text{eq}}\right) = 0 \end{cases} \tag{17}$$

Algebraic equations are usually easier to solve and therefore the problem of finding the equilibrium state of the physical system is usually simpler than the problem of calculating its time dynamics, particularly when the latter is non-linear.

Problem: determine the equilibrium concentrations of the reagents A and B in a reversible chemical reaction $A \rightleftarrows B$ that starts in a state with $[A](0) = a_0$, $[B](0) = b_0$ and obeys the following system of differential equations

$$\begin{cases} \dfrac{d[A]}{dt} = -k_+[A] + k_-[B] \\ \dfrac{d[B]}{dt} = +k_+[A] - k_-[B] \end{cases} \tag{18}$$

Solution: after equating both derivatives to zero and observing that, due to the conservation of matter, we always have $[A]+[B] = a_0 + b_0$, we obtain:

$$\begin{cases} -k_+[A]_{\text{eq}} + k_-[B]_{\text{eq}} = 0 \\ +k_+[A]_{\text{eq}} - k_-[B]_{\text{eq}} = 0 \\ [A]_{\text{eq}} + [B]_{\text{eq}} = a_0 + b_0 \end{cases} \tag{19}$$

The first and the second equations are the same. Solving the system of two linear algebraic equations with two unknowns yields:

$$[A]_{\text{eq}} = \frac{(a_0 + b_0)k_-}{k_- + k_+}, \qquad [B]_{\text{eq}} = \frac{(a_0 + b_0)k_+}{k_- + k_+} \tag{20}$$

Numerical ODE solvers

A typical modern CPU is capable of over *50 billion floating-point multiplications per second*. It is therefore advantageous to reformulate the ODE solution problem in a way that would make use of that formidable power. The methods that use computer arithmetic to solve ODEs are called *finite-difference methods* because they use the approximate definition of the derivative:

$$\frac{dy}{dt}=f(y,t) \quad \Rightarrow \quad \left[\begin{array}{ll} \dfrac{y_{k+1}-y_k}{t_{k+1}-t_k}\approx f(y_k,t_k) & \text{[explicit Euler method]} \\ \dfrac{y_{k+1}-y_k}{t_{k+1}-t_k}\approx f(y_{k+1},t_{k+1}) & \text{[implicit Euler method]} \end{array}\right.$$

At the cost of making the derivatives approximate, these relationships transform differential equations into algebraic equations that relate the future value of the function y_{k+1} to its previous value y_k, where y_0 is the initial condition. The computer can thus proceed step-by-step from that initial condition. The accuracy depends on the size of the time step – the shorter it is, the closer the finite-difference approximation is to the real derivative and the more accurate the calculation:

$$\begin{array}{ll} y_{k+1}\approx y_k+(t_{k+1}-t_k)f(y_k,t_k) & \text{[explicit Euler method]} \\ y_{k+1}\approx y_k+(t_{k+1}-t_k)f(y_{k+1},t_{k+1}) & \text{[implicit Euler method]} \end{array} \qquad (21)$$

The implicit Euler method is harder (the function $f(y,t)$ needs to be inverted), but more accurate when the time step size is large. There is a large family of more sophisticated numerical methods for ODEs – look up *Runge-Kutta methods*, *symplectic integration methods* and *exponential integrator methods* if you are interested.

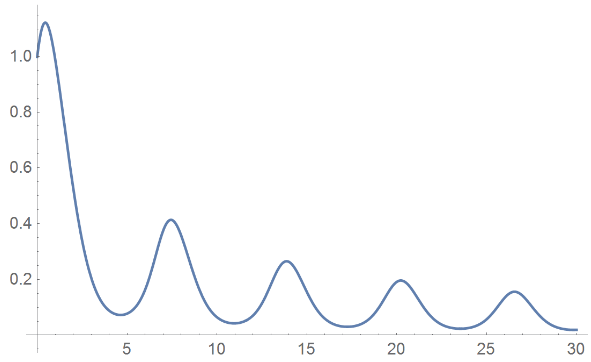
Symbolic algebra systems

Mathematica would easily solve most commonly occurring ODEs, for example:

```
In[1]:=
DSolve[y'[x] == (x + y[x])/x, y[x], x]
Out[1]=
{{y[x] → x C[1] + x Log[x]}}
```

In situations when an analytical solution does not exist in a satisfactory form, a numerical solution may be requested instead:

```
In[10]:=
S = NDSolve[{y'[t] == y[t] Cos[t + y[t]], y[0] == 1}, y, {t, 0, 30}];
Plot[Evaluate[y[t] /. S], {t, 0, 30}, PlotRange → All]
Out[11]=
```



Mathematica uses advanced versions of the numerical algorithms discussed in the previous section.

Week 22 workshop exercises

Steiner, 2nd edition: section 11.8, problems 16-18, 22-25, 41,42.

Extra difficulty exercises for the brave

Steiner, 2nd edition: section 11.8, problems 33-40.