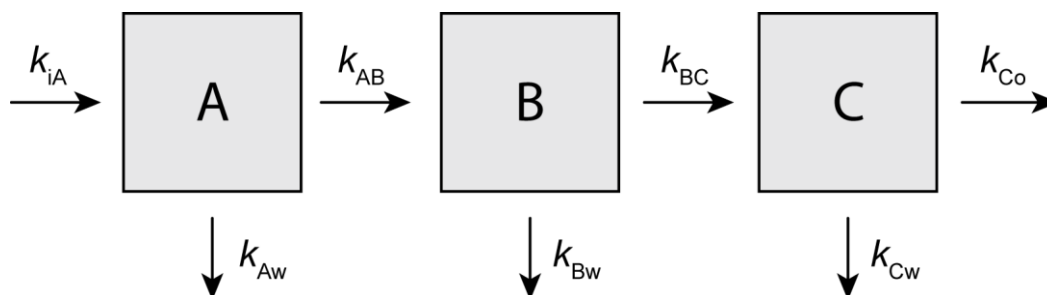


## CHEM1047 – Week 6 Lecture 1 – Reaction rate equations

- Sections 11.1-11.6 of Steiner, "The Chemistry Maths Book", 2<sup>nd</sup> edition.
- Sections 7.1-7.3 of Cockett and Doggett, "Maths for Chemists", Vol 1.

Chemical systems often feature sequential reactions or sequential industrial processes, each with its own rate of substance inflow, product outflow, and reagent waste – for example:



In such systems, the unknowns are functions – in the above case, time dependences of the various concentrations. Equations that involve unknown functions and their derivatives are called *differential equations*. They are ubiquitous in science and engineering – the most powerful models of reality (*general relativity theory*, *quantum field theory*, theories of *fluid dynamics*, etc.) are formulated in terms of differential equations. In chemistry, their primary applications are in *chemical kinetics*.

A good example of differential equations being used in mathematical modelling is given by *population dynamics*. Consider a lawn covered with grass, with a population of rabbits and a population of foxes. We shall make the following assumptions:

1. Grass growth rate is constant. Grass death rate has two contributions: one is proportional to the quantity of grass and the other is a second order reaction between rabbits and grass. Therefore:

$$\frac{d}{dt}G(t) = k_{gg} - k_{gd}G(t) - k_{ge}R(t)G(t) \quad (1)$$

2. Rabbit population growth rate is proportional to the number of rabbits and the amount of grass. Rabbit death rate has two contributions: one is proportional to the number of rabbits and the other is a second-order reaction between rabbits and foxes. Therefore:

$$\frac{d}{dt}R(t) = k_{rb}R(t)G(t) - k_{rd}R(t) - k_{re}R(t)F(t) \quad (2)$$

3. Fox population growth rate is proportional to the number of foxes and the number of rabbits. Fox death rate is proportional to the size of the fox population. Therefore:

$$\frac{d}{dt}F(t) = k_{fb}R(t)F(t) - k_{fd}F(t) \quad (3)$$

The result is one of the many possible population dynamics models in this system. It is clear that solutions are unlikely to be simple here. Assuming the following initial conditions and settings:

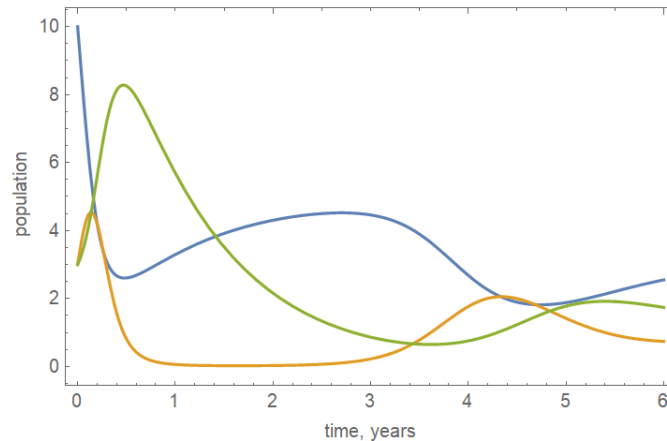
$$\begin{aligned} k_{gg} &= 5 \text{ yr}^{-1}; k_{gd} = 1 \text{ yr}^{-1}; k_{ge} = 1 \text{ yr}^{-1}; \\ k_{rb} &= 1 \text{ yr}^{-1}; k_{rd} = 1 \text{ yr}^{-1}; k_{re} = 1 \text{ yr}^{-1}; \\ k_{fb} &= 1 \text{ yr}^{-1}; k_{fd} = 1 \text{ yr}^{-1}; \end{aligned}$$

$$G(0) = 10; R(0) = 1; F(0) = 1;$$

we can fire up *Mathematica* and instruct it to solve the system numerically:

```
S = NDSolve[{G'[t] == 5 - G[t] - R[t] G[t],
  R'[t] == R[t] G[t] - R[t] - R[t] F[t],
  F'[t] == R[t] F[t] - F[t], G[0] == 10, R[0] == 3, F[0] == 3},
  {G, R, F}, {t, 0, 6}];

Plot[{Evaluate[G[t] /. S], Evaluate[R[t] /. S],
  Evaluate[F[t] /. S]}, {t, 0, 6}, PlotRange -> All,
  Frame -> True, FrameLabel -> {"time, years", "population"}]
```



The solution shows complicated oscillatory behaviour; at some point the rabbits (yellow curve) nearly die out. When the equations are solved for an extended period of time, this system settles into the classical oscillating *predator-prey dynamics*.

### 1. Differential equations, initial conditions, boundary conditions

Differential equations are classified into *ordinary differential equations* (ODEs) that involve derivatives with respect to one variable only, for example time:

$$\frac{dA(t)}{dt} = -kA(t) \quad \text{[radioactive decay, first order kinetics]} \quad (4)$$

and *partial differential equations* (PDEs) that involve derivatives with respect to multiple variables, e.g.:

$$\frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} \quad \text{[Schrödinger's equation for a free particle in 1D]} \quad (5)$$

The task of solving a differential equation consists in finding a function that satisfies it.

**Example 1:** demonstrate that  $f(t) = \sin(\omega t)$  satisfies the *wave equation*  $f''(t) = -\omega^2 f(t)$ .

A differential equation does not usually define the function uniquely. For example, the equation describing radioactive decay:

$$\frac{dA(t)}{dt} = -kA(t) \quad (6)$$

is satisfied by the following class of functions:

$$A(t) = C \exp(-kt) \quad (7)$$

where  $C$  is an arbitrary constant. To pin down the value of this constant, additional information must be provided. In the case of radioactive decay it is usually the amount of substance at time zero:

$$A(0) = A_0 \quad \Rightarrow \quad A(t) = A_0 \exp(-kt) \quad (8)$$

Additional information of this kind is called the *initial condition*. If the information is provided at some other point, or in some other way, it is called the *boundary condition*.

**Example 2:** demonstrate that the function describing the  $2p_z$  orbital of the hydrogen atom

$$\psi(r, \theta, \varphi) = \frac{r \cos \theta}{4\sqrt{2\pi}a_0^{5/2}} e^{-\frac{r}{2a_0}}, \quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \quad (9)$$

satisfies the following boundary condition:  $\lim_{r \rightarrow \infty} [\psi(r, \theta, \varphi)] = 0$ .

## 2. Solving linear first order ODEs

Solving a differential equation requires bringing it into a form that allows integration, taking the indefinite integral, and using initial and / or boundary conditions to eliminate arbitrary coefficients. The recipe for first-order ODEs is roughly as follows:

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

$$g(y)dy = f(x)dx \quad (10)$$

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.

**Example 3:** find the general solution of the equation

$$\frac{dy}{dx} = x + 10 \sin x \quad (11)$$

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

Solution:

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

$$dy = (x + 10 \sin x) dx \quad (12)$$

2. Integrating both sides creates the general solution:

$$\int dy = \int (x + 10 \sin x) dx \quad \Rightarrow \quad y = \frac{x^2}{2} - 10 \cos x + C \quad (13)$$

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

$$0 = -10 \cos(0) + C \quad \Rightarrow \quad C = 10 \quad (14)$$

The particular solution therefore is:

$$y = \frac{x^2}{2} - 10 \cos x + 10 \quad (15)$$

4. Substituting Equation (15) back into Equation (11) 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 bring an ODE into the form prescribed by Equation (10). Variable substitution is a common strategy.

**Example 4:** use  $u = y/x$  substitution to bring the following equation

$$\frac{dy}{dx} = \frac{x+y}{x} \quad (16)$$

into a separable form and find its general solution.

Solution:

1. The substitution function has the following differential:

$$y = ux \Rightarrow dy = xdu + udx \quad (17)$$

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

$$\frac{xdu + udx}{dx} = 1 + u \Rightarrow x \frac{du}{dx} + u = 1 + u \Rightarrow du = \frac{1}{x} dx \quad (18)$$

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

$$u = \ln x + C \Rightarrow \frac{y}{x} = \ln x + C \Rightarrow y = x \ln x + Cx \quad (19)$$

The result is the general solution of the original equation.

### 3. Steady state solutions to ODEs

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.*:

$$\begin{cases} \frac{d[A]}{dt} = f_1([A],[B]) \\ \frac{d[B]}{dt} = f_2([A],[B]) \end{cases} \quad (20)$$

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

$$\begin{cases} f_1([A]_{\text{eq}}, [B]_{\text{eq}}) = 0 \\ f_2([A]_{\text{eq}}, [B]_{\text{eq}}) = 0 \end{cases} \quad (21)$$

Algebraic equations are easier to solve, and therefore the problem of finding the equilibrium state of the physical system is simpler than the problem of calculating its time dynamics.

**Example 5:** determine the equilibrium concentrations of the reagents A and B in a reversible chemical reaction  $A \rightleftharpoons B$  that starts in a state with  $[A](0) = a_0$ ,  $[B](0) = b_0$  and obeys the following system of differential equations

$$\begin{cases} \frac{d[A]}{dt} = -k_+ [A] + k_- [B] \\ \frac{d[B]}{dt} = +k_+ [A] - k_- [B] \end{cases} \quad (22)$$

**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:

$$\begin{cases} -k_+ [A]_{\text{eq}} + k_- [B]_{\text{eq}} = 0 \\ +k_+ [A]_{\text{eq}} - k_- [B]_{\text{eq}} = 0 \\ [A]_{\text{eq}} + [B]_{\text{eq}} = a_0 + b_0 \end{cases} \quad (23)$$

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

$$[A]_{\text{eq}} = \frac{(a_0 + b_0)k_-}{k_- + k_+}, \quad [B]_{\text{eq}} = \frac{(a_0 + b_0)k_+}{k_- + k_+} \quad (24)$$