13 Ordinary differential equations

(1) In a simple sequential reaction scheme, $A \rightarrow B \rightarrow C$, compound A is converted to B which then turns into C. If the concentrations of A, B and C at time t are a, b and c, respectively, solve the associated first-order simultaneous differential equations

$$-\frac{da}{dt} = k_1 a\,, \qquad -\frac{db}{dt} = -k_1 a + k_2 b \qquad \text{and} \qquad \frac{dc}{dt} = k_2 b$$

where k_1 and k_2 are the rate constants for the consecutive steps, and the initial ($t=0$) concentrations are $a = a_o$, $b=0$ and $c=0$.

The first equation is separable, so that

$$\int \frac{da}{a} = -k_1 \int dt \qquad \Rightarrow \qquad \ln a = \alpha - k_1 t$$

where the boundary condition, $a(0) = a_o$, gives the constant of integration as $\alpha = \ln a_o$. Taking exponentials,

$$\underline{a = a_o e^{-k_1 t}}$$

Substituting this into the second equation,

$$\frac{db}{dt} + k_2 b = k_1 a_o e^{-k_1 t}$$

which can be solved by multiplying through by the integrating factor $e^{k_2 t}$

$$\frac{d}{dt}\left[b\, e^{k_2 t}\right] = a_o k_1 e^{(k_2 - k_1)t}$$

Integrating both sides with respect to t,

$$b\, e^{k_2 t} = \frac{a_o k_1}{k_2 - k_1} e^{(k_2 - k_1)t} + \beta$$

where $b(0) = 0$ requires that $\beta = -a_o k_1/(k_2 - k_1)$. Hence,

$$\underline{b = \frac{a_o k_1}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right]}$$

This could be substituted into the third equation to ascertain $c(t)$, but a simpler way of solving the final part of the problem is to realize that the sum of the three concentrations is fixed and equal to a_o:

$$\frac{da}{dt}+\frac{db}{dt}+\frac{dc}{dt} = \frac{d}{dt}(a+b+c)=0 \quad \Rightarrow \quad a+b+c=\gamma$$

where the constant $\gamma = a(0)+b(0)+c(0) = a_o$. This leads to

$$c = a_o - \frac{a_o}{k_2-k_1}\left[k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right]$$

While the behaviour of $b(t)$ and $c(t)$ is not immediately obvious when $k_1 = k_2$, it follows from a careful consideration of the limit $k_1 \to k_2$. Alternatively, setting $k_1 = k_2 = k$ explicitly from the outset gives $a = a_o e^{-kt}$ and

$$\frac{d}{dt}\left[b\, e^{kt}\right] = a_o k \quad \Rightarrow \quad b = a_o k\, t\, e^{-kt}$$

and leads to

$$c = a_o\left[1-(1+kt)e^{-kt}\right]$$

The solution for the three concentrations are illustrated graphically below for the cases $k_2 = 2k_1$ and $k_1 = 2k_2$.