# TAKE HOME PROJECT 1

(a) The rates of change of Ce (free) and Cm (trapped) are given by the differential equations:

$$\left| \begin{aligned} \frac{dC_e}{dt} &= k_1 C_p - (k_2+k_3) C_e + k_4 C_m \\ \frac{dC_m}{dt} &= k_3 C_e - k_4 C_m \end{aligned} \right.$$

And initial concentrations are assumed to be zero:

$$C_e(0) = C_m(0) = 0$$

Rearranging the terms of the differential equations gives:

$$\left| \begin{aligned} \frac{dC_e}{dt} + (k_2+k_3) C_e - k_4 C_m &= k_1 C_p \\ -k_3 C_e + \frac{dC_m}{dt} + k_4 C_m &= 0 \end{aligned} \right.$$

Taking the Laplace transform for both equations gives:
(using the Laplace transform forms for a first derivative)

$$\left| \begin{aligned} (s+k_2+k_3)\, \bar{C_e}(s) - k_4\, \bar{C_m}(s) &= k_1\, \bar{C_p}(s) \\ -k_3\, \bar{C_e}(s) + (s+k_4)\, C_m(s) &= 0 \end{aligned} \right.$$

Since

$$\mathcal{L}\left\{\frac{dCe}{dt}\right\} = s\,\overline{Ce}(s) - Ce(0) = s\,\overline{Ce}(s) - 0 = s\,\overline{Ce}(s)$$

$$\mathcal{L}\left\{\frac{dCm}{dt}\right\} = s\,\overline{Cm}(s) - Cm(0) = s\,\overline{Cm}(s) - 0 = s\,\overline{Cm}(s)$$

Now we put the equations in matrix form:

$$\begin{bmatrix} s+k_2+k_3 & -k_4 \\ -k_3 & s+k_4 \end{bmatrix} \begin{bmatrix} \overline{C}_e(s) \\ \overline{C}_m(s) \end{bmatrix} = \begin{bmatrix} k_1 \overline{C}_p(s) \\ 0 \end{bmatrix}$$

Solving for $\overline{Ce}(s)$ and $\overline{Cm}(s)$, Cramer's rule gives:

$$\overline{Ce}(s) = \frac{\begin{vmatrix} k_1 \overline{C}_p(s) & -k_4 \\ 0 & s+k_4 \end{vmatrix}}{D} \qquad \overline{Cm}(s) = \frac{\begin{vmatrix} s+k_2+k_3 & k_1 \overline{C}_p(s) \\ -k_3 & 0 \end{vmatrix}}{D}$$

where $D = \begin{vmatrix} s+k_2+k_3 & -k_4 \\ -k_3 & s+k_4 \end{vmatrix} = (s+k_2+k_3)(s+k_4) - k_3 k_4$

$$= s^2 + (k_2+k_3+k_4)s + (k_2+k_3)k_4 - k_3 k_4$$

$$= s^2 + (k_2+k_3+k_4)s + k_2 k_4$$

The roots of this quadratic expression are:

$$r_1 = \frac{1}{2}\left[-(k_2+k_3+k_4) - \sqrt{(k_2+k_3+k_4)^2 - 4k_2k_4}\right]$$

$$r_2 = \frac{1}{2}\left[-(k_2+k_3+k_4) + \sqrt{(k_2+k_3+k_4)^2 - 4k_2k_4}\right]$$

Thus $D = (s - r_1)(s - r_2)$

We have a solution for $C_e$ and $C_m$ in sspace and we need an expression for $C_i = C_e + C_m$ in tspace; so we have to take the inverse laplace transform.

But first we need a nice form for $\bar{C}_e(s)$ and $\bar{C}_m(s)$ so we can look it up in a laplace transform table.

$$\bar{C}_e(s) = k_1 \bar{C}_p(s) \frac{s + k_4}{(s - r_1)(s - r_2)}$$

We then use a partial fraction expansion:

$$\frac{s + k_4}{(s - r_1)(s - r_2)} = \frac{A}{s - r_1} + \frac{B}{s - r_2}$$

$$= \frac{A(s - r_2) + B(s - r_1)}{(s - r_1)(s - r_2)}$$

$$= \frac{(A + B)s - Ar_2 - Br_1}{(s - r_1)(s - r_2)}$$

By equating powers of s in the numerator

$s^1$: $A + B = 1$

$s^0$: $-Ar_2 - Br_1 = k_4$

$\Rightarrow B = 1 - A$ and $-Ar_2 - (1 - A)r_1 = k_4$

$$\Rightarrow \quad A(r_1 - r_2) - r_1 = k_4$$

$$\Rightarrow \quad A = \frac{k_4 + r_1}{r_1 - r_2}$$

$$B = 1 - A = 1 - \frac{k_4 + r_1}{r_1 - r_2}$$

$$= -\frac{k_4 + r_2}{r_1 - r_2}$$

Thus we have $\bar{C}_e(s) = \frac{k_1 \bar{C}_p(s)}{r_1 - r_2} \left[ \frac{k_4 + r_1}{s - r_1} - \frac{k_4 + r_2}{s - r_2} \right]$

$$= \frac{k_1 (k_4 + r_1)}{r_1 - r_2} \times \frac{1}{(s - r_1)} \times \bar{C}_p(s)$$

$$- \frac{k_1 (k_4 + r_2)}{r_1 - r_2} \times \frac{1}{(s - r_2)} \times \bar{C}_p(s)$$

The Laplace transform of the convolution is:

$$\mathcal{L}\left[ \int_0^t f(t') \, g(t - t') \, dt' \right] = \bar{f}(s) \, \bar{g}(s)$$

We set $\bar{f}(s) = \bar{C}_p(s)$ and $\bar{g}(s) = \frac{1}{s - r_1}$

$$\mathcal{L}^{-1}(\bar{f}(s)) = \mathcal{L}^{-1}(\bar{C}_p(s)) = C_p(t)$$

$$\mathcal{L}^{-1}(\bar{g}(s)) = \mathcal{L}^{-1}\left(\frac{1}{s - r_1}\right) = e^{r_1 t}$$

we get then

$$\mathcal{L}\left[ \int_0^t C_p(t') \, e^{r_1 (t - t')} dt' \right] = \frac{C_p(s)}{s - r_1}$$

Taking the inverse laplace transform on both sides of the previous equation, we have:

$$\int_0^t c_p(t')\, e^{r_1(t-t')}\, dt' = \mathcal{L}^{-1}\left\{ \frac{\bar{c}_p(s)}{s-r_1} \right\}$$

Similarly $$\int_0^t c_p(t')\, e^{r_2(t-t')}\, dt' = \mathcal{L}^{-1}\left\{ \frac{\bar{c}_p(s)}{s-r_2} \right\}$$

Now we take the inverse laplace transform of $\bar{c}_e(s)$ using the previous two results:

$$\mathcal{L}^{-1}\{\bar{c}_e(s)\} = c_e(t) = \frac{k_1(k_4+r_1)}{r_1-r_2}\, \mathcal{L}^{-1}\left\{ \frac{\bar{c}_p(s)}{s-r_1} \right\} - \frac{k_1(k_4+r_2)}{r_1-r_2}\, \mathcal{L}^{-1}\left\{ \frac{\bar{c}_p(s)}{s-r_2} \right\}$$

$$\Rightarrow c_e(t) = \frac{k_1(k_4+r_1)}{r_1-r_2} \int_0^t c_p(t')\, e^{r_1(t-t')}\, dt' - \frac{k_1(k_4+r_2)}{r_1-r_2} \int_0^t c_p(t')\, e^{r_2(t-t')}\, dt'$$

Next we follow the same steps for $c_m(t)$:

$$\bar{c}_m(s) = k_1 k_3 \frac{\bar{c}_p(s)}{(s-r_1)(s-r_2)}$$

The partial fraction expansion is $\bar{c}_m(s) = \frac{k_1 k_3 \bar{c}_p(s)}{r_1-r_2}\left[ \frac{1}{s-r_1} - \frac{1}{s-r_2} \right]$

Taking the inverse Laplace transform on both sides

$$\mathcal{L}^{-1}\{\bar{C}_m(s)\} = C_m(t) = \frac{k_1 k_3}{r_1-r_2}\left[\mathcal{L}^{-1}\left\{\frac{\bar{C}_p(s)}{s-r_1}\right\} - \mathcal{L}^{-1}\left\{\frac{\bar{C}_p(s)}{s-r_2}\right\}\right]$$

$$\Rightarrow C_m(t) = \frac{k_1 k_3}{r_1-r_2}\int_0^t C_p(t')\, e^{r_1(t-t')}\,dt' - \frac{k_1 k_3}{r_1-r_2}\int_0^t C_p(t')\, e^{r_2(t-t')}\,dt'$$

$$C_i(t) = C_e(t) + C_m(t)$$

$$= \left(-\frac{k_1(k_4+r_2)}{r_1-r_2} - \frac{k_1 k_3}{r_1-r_2}\right)\int_0^t C_p(t')\, e^{r_2(t-t')}\,dt'$$

$$+\left(\frac{k_1(k_4+r_1)}{r_1-r_2} + \frac{k_1 k_3}{r_1-r_2}\right)\int_0^t C_p(t')\, e^{r_1(t-t')}\,dt'$$

$$= \left(-\frac{k_1}{r_1-r_2}\right)(k_3+k_4+r_2)\int_0^t C_p(t')\, e^{r_2(t-t')}\,dt'$$

$$+ \frac{k_1}{r_1-r_2}(k_3+k_4+r_1)\int_0^t C_p(t')\, e^{r_1(t-t')}\,dt'$$

In the associated paper by Brooks

$$\alpha_{1,2} = \frac{1}{2}\left[k_2+k_3+k_4 \mp \sqrt{(k_2+k_3+k_4)^2 - 4k_2k_4}\right]$$

we see that: $\alpha_1 = -r_2$

$\alpha_2 = -r_1$

Substitute the alphas back into $C_i(t)$ gives:

$$C_i(t) = \frac{k_1(k_3+k_4-\alpha_1)}{\alpha_2-\alpha_1}\int_0^t e^{-\alpha_1(t-t')}C_p(t')\,dt'$$

$$+ \frac{k_1(\alpha_2-k_3-k_4)}{\alpha_2-\alpha_1}\int_0^t e^{-\alpha_2(t-t')}C_p(t')\,dt'$$

$$= A\int_0^t e^{-\alpha_1(t-t')}C_p(t')\,dt' + B\int_0^t e^{-\alpha_2(t-t')}C_p(t')\,dt'$$

where $A = k_1(k_3+k_4-\alpha_1)/(\alpha_2-\alpha_1)$

$B = k_1(\alpha_2-k_3-k_4)/(\alpha_2-\alpha_1)$

When $k_4 \ll k_2+k_3$ the two terms above simplify to:

$A \simeq k_1 k_3/(k_2+k_3)$

$B \simeq k_1 k_2/(k_2+k_3)$