Numerical methods in chemistry. Solutions to exercises 3

Problem 1

The equivalence $f * g = g * f$ can be proven by writing out the definition of convolution and changing the integration variable from τ to $u = t - \tau$

$$f * g = \int_0^t f(\tau)g(t-\tau)d\tau = -\int_t^0 f(t-u)g(u)du = \int_0^t g(u)f(t-u)du = g * f.$$

Problem 2

Since $\mathcal{L}[1] = 1/s$ and $\mathcal{L}[f(t)] = F(s)$ we have, by virtue of the convolution theorem,

$$\frac{F(s)}{s} = F(s) \cdot \frac{1}{s} = \mathcal{L}[f(t)] \cdot \mathcal{L}[1] = \mathcal{L}[f(t) * 1].$$

After applying inverse Laplace transform to both sides of the equation and using the definition of convolution one obtains

$$\mathcal{L}^{-1}\left[\frac{F(s)}{s}\right] = f(t) * 1 = \int_0^t f(\tau)d\tau.$$

Problem 3

The integrals can be found straightforwardly using the definition of convolution

(a)

$$\begin{aligned} t * \cos t &= \int_0^t (t-\tau)\cos\tau d\tau = t\sin\tau|_0^t - \int_0^t \tau\cos\tau d\tau = t\sin t - \int_0^t \tau\, d(\sin\tau) \\ &= t\sin t - \tau\sin\tau|_0^t + \int_0^t \sin\tau d\tau = -\cos\tau|_0^t = 1 - \cos t, \end{aligned}$$

(b)

$$t * t = \int_0^t (t-\tau)\tau d\tau = \left(t\frac{\tau^2}{2} - \frac{\tau^3}{3}\right)\Bigg|_0^t = t\frac{t^2}{2} - \frac{t^3}{3} = \frac{t^3}{6},$$

(c) the last one uses the trigonometric identity $\sin a \sin b = [\cos(a-b) - \cos(a+b)]/2$

$$\begin{aligned} \sin t * \sin t &= \int_0^t \sin(t-\tau)\sin\tau d\tau = \frac{1}{2}\int_0^t [\cos(2\tau - t) - \cos t]d\tau \\ &= \frac{1}{2}\left[\frac{1}{2}\sin(2\tau - t)\Bigg|_0^t - \tau\cos t|_0^t\right] = \frac{1}{2}(\sin t - t\cos t). \end{aligned}$$

Alternative solution:

Using the Laplace transform and the convolution theorem leads to the following expressions:

(a)

$$\begin{aligned} \mathcal{L}[t * \cos t] &= \mathcal{L}[t]\mathcal{L}[\cos t] = \frac{1}{s^2}\frac{s}{s^2+1} = \frac{1}{s(s^2+1)} = \frac{s^2+1-s^2}{s(s^2+1)} \\ &= \frac{1}{s} - \frac{s}{s^2+1}, \end{aligned}$$

hence

$$t * \cos t = \mathcal{L}^{-1}\left[\frac{1}{s}\right] - \mathcal{L}^{-1}\left[\frac{s}{s^2+1}\right] = 1 - \cos t;$$

(b)

$$\mathcal{L}[t * t] = \mathcal{L}[t]\mathcal{L}[t] = \frac{1}{s^2}\frac{1}{s^2} = \frac{1}{s^4},$$

hence

$$t * t = \mathcal{L}^{-1}\left[\frac{1}{s^4}\right] = \frac{t^3}{6};$$

(c)

$$\mathcal{L}[\sin t * \sin t] = \mathcal{L}[\sin t]\mathcal{L}[\sin t] = \frac{1}{s^2+1}\frac{1}{s^2+1} = \frac{1}{(s^2+1)^2}.$$

Finding inverse Laplace transforms for expressions appearing in (a) and (b) was straightforward, while for (c) the problem can be solved, for example, in the following two ways. **The first approach** uses the partial fraction decomposition in *complex space*

$$\frac{1}{(s^2+1)^2} = \frac{1}{(s+i)^2(s-i)^2} = \frac{\alpha}{s+i} + \frac{\beta}{(s+i)^2} + \frac{\gamma}{s-i} + \frac{\delta}{(s-i)^2},$$

where

$$\begin{cases} \alpha = i/4 \\ \beta = -1/4 \\ \gamma = -i/4 \\ \delta = -1/4 \end{cases}.$$

Applying the inverse Laplace transform yields

$$\begin{aligned} \sin t \sin t = \mathcal{L}^{-1}\left[\frac{1}{(s^2+1)^2}\right] &= \mathcal{L}^{-1}\left[\frac{i}{4}\left(\frac{1}{s+i} - \frac{1}{s-i}\right) - \frac{1}{4}\left\{\frac{1}{(s+i)^2} + \frac{1}{(s-i)^2}\right\}\right] \\ &= \left[\frac{i}{4}\left(e^{-it} - e^{it}\right) - \frac{1}{4}\left(te^{-it} + te^{it}\right)\right] = \frac{1}{2}\left(\sin t - t\cos t\right). \end{aligned}$$

The second approach uses the identity

$$\frac{\mathrm{d}}{\mathrm{d}s}\frac{s}{s^2+1} = \frac{1}{s^2+1} - \frac{2s^2}{(s^2+1)^2} = -\frac{1}{s^2+1} + \frac{2}{(s^2+1)^2}.$$

Therefore

$$\frac{1}{(s^2+1)^2} = \frac{1}{2}\left(\frac{1}{s^2+1} + \frac{\mathrm{d}}{\mathrm{d}s}\frac{s}{s^2+1}\right),$$

and

$$\begin{aligned} \sin t * \sin t = \mathcal{L}^{-1}\left[\frac{1}{(s^2+1)^2}\right] &= \frac{1}{2}\left(\mathcal{L}^{-1}\left[\frac{1}{s^2+1}\right] + \mathcal{L}^{-1}\left[\frac{\mathrm{d}}{\mathrm{d}s}\frac{s}{s^2+1}\right]\right) = \frac{1}{2}\left(\sin t - t\mathcal{L}^{-1}\left[\frac{s}{s^2+1}\right]\right) \\ &= \frac{1}{2}\left(\sin t - t\cos t\right). \end{aligned}$$

Problem 4

Applying Laplace transform to the differential equation leads to

$$sX(s) - x(0) + 3X(s) = \frac{1}{s-2}.$$

Since $x(0) = 1$ one can rewrite the equation as follows

$$X(s) = \frac{1}{(s-2)(s+3)} + \frac{1}{s+3}.$$

We now use partial fractions on the first summand

$$\frac{1}{(s-2)(s+3)} = \frac{\alpha}{s-2} + \frac{\beta}{s+3},$$

$$\begin{cases} \alpha + \beta = 0 \\ 3\alpha - 2\beta = 1 \end{cases},$$

$$\begin{cases} \alpha = -\beta \\ 5\alpha = 1 \end{cases},$$

$$\begin{cases} \beta = -\frac{1}{5} \\ \alpha = \frac{1}{5} \end{cases}.$$

This leads us to

$$X(s) = \frac{1}{5(s-2)} - \frac{1}{5(s+3)} + \frac{1}{s+3} = \frac{4}{5(s+3)} + \frac{1}{5(s-2)}.$$

$x(t)$ can now be found straightforwardly by inverse Laplace transform

$$x(t) = \frac{4}{5}e^{-3t} + \frac{1}{5}e^{2t}.$$

Problem 5

Solution 1

We have

$$\begin{aligned} \dot{a}(t) &= -k_1 a(t), \\ \dot{b}(t) &= k_1 a(t) - k_2 b(t), \\ \dot{c}(t) &= k_2 b(t), \end{aligned}$$

with the boundary conditions $a(0) = a_0$, $b(0) = c(0) = 0$. First we note that the first equation only contains $a(t)$, hence it can be solved separately. After accounting for the boundary conditions one obtains

$$a(t) = a_0 e^{-k_1 t}.$$

Substituing the expression for $a(t)$ into the second ODE yields

$$\dot{b}(t) + k_2 b(t) = k_1 a_0 e^{-k_1 t}.$$

Again, this equation can be solved separately to obtain $b(t)$. We apply Laplace transform to both sides of the equation, the result is

$$sB(s) - b(0) + k_2 B(s) = \frac{k_1 a_0}{s + k_1}.$$

Keeping in mind that $b(0) = 0$ the equation can be rewritten as

$$B(s) = \frac{k_1 a_0}{(s+k_1)(s+k_2)}.$$

Now we simplify $B(s)$ using partial fractions

$$B(s) = \frac{\alpha}{s+k_1} + \frac{\beta}{s+k_2},$$

$$\begin{cases} \alpha + \beta = 0 \\ \alpha k_2 + \beta k_1 = k_1 a_0 \end{cases},$$

$$\begin{cases} \alpha = \frac{k_1 a_0}{k_2 - k_1} \\ \beta = \frac{k_1 a_0}{k_1 - k_2} \end{cases}.$$

Finally we can write

$$B(s) = \frac{k_1 a_0}{k_2 - k_1}\left(\frac{1}{s+k_1} - \frac{1}{s+k_2}\right),$$

and the inverse Laplace transform is

$$b(t) = \frac{k_1 a_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right).$$

Now we can substitute $b(t)$ into the last ODE to obtain

$$\dot{c}(t) = \frac{k_1 k_2 a_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right).$$

Applying Laplace transform leads to

$$sC(s) - c(0) = \frac{k_1 k_2 a_0}{k_2 - k_1}\left(\frac{1}{s + k_1} - \frac{1}{s + k_2}\right),$$

with $c(0) = 0$ we get

$$C(s) = \frac{k_1 k_2 a_0}{k_2 - k_1}\left[\frac{1}{s(s + k_1)} - \frac{1}{s(s + k_2)}\right].$$

We now use partial fractions

$$\frac{1}{s(s + k_1)} = \frac{\alpha}{s} + \frac{\beta}{s + k_1},$$

$$\begin{cases} \alpha + \beta = 0 \\ \alpha k_1 = 1 \end{cases},$$

$$\begin{cases} \beta = -\frac{1}{k_1} \\ \alpha = \frac{1}{k_1} \end{cases}.$$

Having done the same procedure for $1/[s(s + k_2)]$ we get

$$C(s) = \frac{k_1 k_2 a_0}{k_2 - k_1}\left[\frac{1}{k_1}\left(\frac{1}{s} - \frac{1}{s + k_1}\right) - \frac{1}{k_2}\left(\frac{1}{s} - \frac{1}{s + k_2}\right)\right].$$

The final result is obtained after applying inverse Laplace transform,

$$c(t) = \frac{k_1 k_2 a_0}{k_2 - k_1}\left[\frac{1}{k_1}\left(1 - e^{-k_1 t}\right) - \frac{1}{k_2}\left(1 - e^{-k_2 t}\right)\right].$$

Just to make sure that we didn't make some stupid mistake during the derivation let's check some of the solutions' properties. First of all, the boundary conditions at $t = 0$

$$\begin{aligned} a(0) &= a_0 e^0 = a_0, \\ b(0) &= \frac{k_1 a_0}{k_1 - k_2}\left(e^0 - e^0\right) = 0, \\ c(0) &= \frac{k_1 k_2 a_0}{k_1 - k_2}\left[\frac{1}{k_2}\left(1 - e^0\right) - \frac{1}{k_1}\left(1 - e^0\right)\right] = 0. \end{aligned}$$

Secondly, the total reactant mass should always be conserved, $a(t) + b(t) + c(t) = \text{const}$

$$\begin{aligned} a(t) + b(t) + c(t) &= a_0 e^{-k_1 t} + \frac{k_1 a_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) + \frac{k_1 k_2 a_0}{k_2 - k_1}\left[\frac{1}{k_1}\left(1 - e^{-k_1 t}\right) - \frac{1}{k_2}\left(1 - e^{-k_2 t}\right)\right] \\ &= \frac{k_1 k_2 a_0}{k_2 - k_1}\left(\frac{1}{k_1} - \frac{1}{k_2}\right) = a_0. \end{aligned}$$

Lastly, in the $t \to \infty$ limit the entire reactant mass should end up being converted to C

$$\begin{aligned} \lim_{t\to\infty} a(t) &= \lim_{t\to\infty} a_0 \cdot 0 = 0, \\ \lim_{t\to\infty} b(t) &= \lim_{t\to\infty} \frac{k_1 a_0}{k_2 - k_1}(0 - 0) = 0, \\ \lim_{t\to\infty} c(t) &= \frac{k_1 k_2 a_0}{k_1 - k_2}\left[\frac{1}{k_2}(1 - 0) - \frac{1}{k_1}(1 - 0)\right] = \frac{k_1 k_2 a_0}{k_1 - k_2}\left(\frac{1}{k_2} - \frac{1}{k_1}\right) = a_0. \end{aligned}$$

The final analytical solution is plotted in Fig. 1.

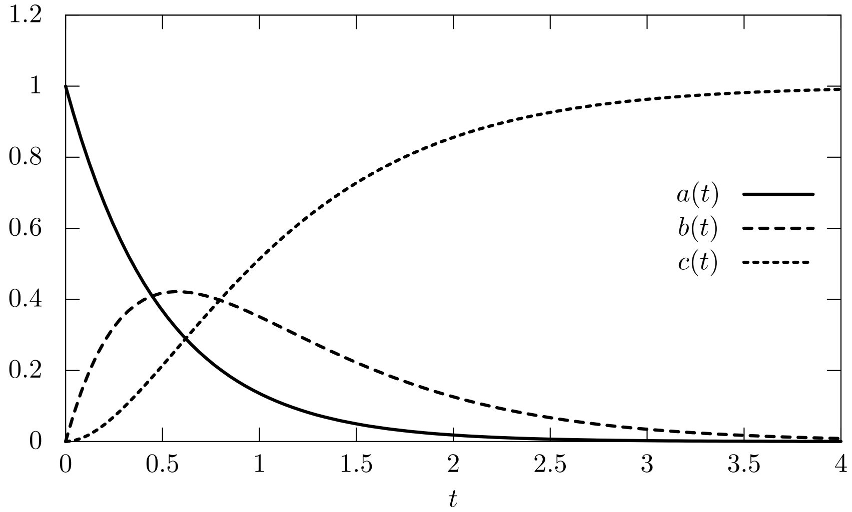

FIGURE 1: Plot of analytical solution to Problem 5, $a_0 = 1$, $k_1 = 2$, $k_2 = 1.5$.

Solution 2

In Solution 1 we kept going between time domain functions and their Laplace transforms, but it is possible to solve the problem directly in the Laplace transform space. First we apply Laplace transform to the original equation set

$$\begin{aligned} sA(s) - a(0) &= -k_1 A(s), \\ sB(s) - b(0) &= k_1 A(s) - k_2 B(s), \\ sC(s) - c(0) &= k_2 B(s). \end{aligned}$$

$A(s)$ is found straightforwardly from the first equation and the fact that $a(0) = a_0$,

$$A(s) = \frac{a_0}{s + k_1}.$$

Substituing $A(s)$ into the second one readily yields $B(s)$

$$B(s) = \frac{k_1 a_0}{(s + k_1)(s + k_2)}$$

(we already accounted for $b(0) = 0$). Lastly, introducing $B(s)$ into the third equation leads to

$$C(s) = \frac{k_1 k_2 a_0}{s(s + k_1)(s + k_2)}$$

(again, $c(0) = 0$). For $a(t)$ finding the Laplace transform is straightforward, for $b(t)$ and $c(t)$ we need to use partial fractions as discussed in Solution 1.