Exercise Set 4

Exercise 1 - (a)

Let's consider a test volum V in the pellet. The substract enters the pellet by diffusion and some is created and disappears due to the chemical reaction. The two contribute to the variation of mass of substract inside V. We have

$$\frac{d}{dt^*}\int_V s^*\,dV = -\int_{\partial V} D^*\nabla s^*\cdot\mathbf{n}\,dS + +\int_V k_{-1}c^*\,dV - \int_V k_1 s^* e^*\,dV.$$

After using Stokes' theorem, the surface integral becomes

$$-D^*\int_V \Delta s^*\,dV.$$

The time derivative can be moved under the integral sign as a partial derivative because the volume V does not depend on time. The equality is true for any test volume V. It must then be true pointwise and we have

$$\frac{\partial s^*}{\partial t^*} = -D^*\Delta s^* + k_{-1}c^* - k_1 s^* e^*.$$

We use the dimensionless variables and rescale the space variable as $\mathbf{x}^* = a\mathbf{x}$.

$$\frac{\partial s}{\partial t} = -\frac{D^*}{a^2 k_1 \bar{e}}\Delta s - s + (s+\kappa-\lambda)c$$

Hence,

$$D = \frac{D^*}{a^2 k_1 \bar{e}}.$$

The concentration of substract outside the pellet is uniform and we set it to 1.

(b)

When the problem is stationary, the partial derivatives with respect to time vanish and we have

$$D\Delta s - s + (s+\kappa-\lambda)c = 0 \tag{1}$$
$$s - (s+\kappa) \tag{2}$$

We use (2) to simplify equation (1) and get

$$D\Delta s - \lambda c = 0$$

From (2), we also have $c = \frac{s}{s+\kappa}$. Hence,

$$D\Delta s - \lambda\frac{s}{s+\kappa}.$$

The substract's concentration s depends only on the radius r. The Laplacian is

$$\Delta s = \frac{1}{r^2}(r^2 s')'$$

and we get

$$D(r^2 s')' - \lambda r^2 \frac{s}{s+\kappa} = 0. \tag{3}$$

The boundary conditions are $s(1) = 1$ and, for symmetry reasons, $s'(0) = 0$.

We denote by R the reaction rate within a pellet. The amount of substract transformed into the end product in the pellet is, by definition of the concentration p^*,

$$M = \int_{\mathcal{B}(a)} p^* \, dV$$

where $\mathcal{B}(a)$ denotes the pellet or a ball of radius a. Hence,

$$\begin{aligned} R &= \frac{dM}{dt^*} \\ &= \int_{\mathcal{B}(a)} \frac{dp^*}{dt^*} \, dV. \end{aligned}$$

From the chemical reaction, we have

$$\frac{dp^*}{dt^*} = k_2 c^*$$

which gives

$$R = k_2 \int_{\mathcal{B}(a)} c^* \, dV$$

We introduce the dimensionless quantities and get

$$R = k_2 \bar{e} \int_{\mathcal{B}(1)} c a^3 \, dV. \tag{4}$$

The gouverning equations (1) and (2) give us that $c = \frac{D}{\lambda}\Delta s$. Plugging that into (4), we get

$$R = \frac{k_2 D a^3 \bar{e}}{\lambda} \int_{\mathcal{B}(1)} \Delta s \, dV$$

We introduce spherical coordinates:

$$R = \frac{k_2 D a^3 \bar{e}}{\lambda} \int_0^1 \frac{1}{r^2}(r^2 s')' 4\pi r^2 \, dr.$$

Hence,

$$R = \frac{4\pi k_2 D a^3 \bar{e}}{\lambda} s'(1).$$

(c)

We assume that $\varepsilon = \frac{\lambda}{D}$ is a small parameter. We expand s as

$$s = s_0 + \varepsilon s_1 + \varepsilon^2 s_2 + o(\varepsilon^2).$$

Equation (3) becomes

$$\left[r^2(s_0' + \varepsilon s_1' + \varepsilon s_2' + o(\varepsilon^2))\right]' - \varepsilon r^2 \frac{s_0 + \varepsilon s_1 + o(\varepsilon)}{s_0 + \kappa + \varepsilon s_1 + o(\varepsilon)} = 0$$

which, after using the identity

$$\frac{1}{s_0 + \kappa + \varepsilon s_1 + o(\varepsilon)} = \frac{1}{s_0 + \kappa} - \varepsilon \frac{s_1}{(s_0 + \kappa)^2} + o(\varepsilon),$$

gives

$$(r^2 s_0')' + \varepsilon \left[(r^2 s_1')' - \frac{r^2 s_0}{s_0 + \kappa}\right] + \varepsilon^2 \left[(r^2 s_2')' - \frac{r^2 s_1}{s_0 + \kappa} + \frac{r^2 s_1 s_0}{(s + \kappa)^2}\right] + o(\varepsilon^2) = 0 \quad (5)$$

At order zero, we have

$$(r^2 s_0')' = 0.$$

It follows that $r^2 s_0'$ is a constant which must be equal to zero since, otherwise, s_0' would blow up as r tends to zero. Since $s_0' = 0$, s_0 is a constant and, because of the boundary condition $s(1) = 1$, we have

$$s_0 = 1$$

At the first order, we have from (5),

$$(r^2 s_1')' - \frac{r^2}{1 + \kappa} = 0$$

which, after integration, yields

$$r^2 s_1' - \frac{r^3}{1 + \kappa} = \textit{constant}. \quad (6)$$

The constant above must be zero since s_1' is bounded. We integrate (6) one more time and get

$$s_1 = \frac{r^2}{2(1 + \kappa)} + \textit{constant}. \quad (7)$$

The boundary condition $s(1) = 1$ implies $s_1(1) = 0$ and we get

$$s_1 = \frac{r^2 - 1}{2(1 + \kappa)}.$$

At the second order, we have

$$(r^2 s_2')' = r^2 \left[\frac{s_1}{1+\kappa} - \frac{s_1}{(1+\kappa)^2} \right]$$

which gives, after replacing s_1 by the expression given in (7),

$$(r^2 s_2')' = \frac{\kappa r^2 (r^2 - 1)}{2(1+\kappa)^3}.$$

We integrate this expression:

$$r^2 s_2' = \frac{\kappa}{10(1+\kappa)^3} r^5 - \frac{\kappa}{6(1+\kappa)^3} r^3.$$

Again, the integration constant is zero because otherwise s_2' would not be bounded. Finally, after another integration,

$$s_2 = \frac{\kappa}{(1+\kappa)^3} \left(\frac{r^4}{40} - \frac{r^2}{12} - \frac{7}{120} \right).$$

The integration constant has been set so that the boundary condition $s_2(1) = 0$ is satisfied. In conclusion, we have

$$s = 1 + \varepsilon \frac{r^2 - 1}{2(1+\kappa)} + \varepsilon^2 \frac{\kappa}{(1+\kappa)^3} \left(\frac{r^4}{40} - \frac{r^2}{12} - \frac{7}{120} \right) + o(\varepsilon^2).$$

(d)

We now assume that $\eta = \frac{D}{\lambda}$ is small. The gouverning equation is

$$\eta (r^2 s')' \frac{r^2 s}{s+\kappa} = 0. \tag{8}$$

We consider only the order 0 in the expansion of s:

$$s = s_0 + o(1).$$

Taking only the terms of order 0 in (8) leads to

$$\frac{r^2 s_0}{s_0 + \kappa} = 0.$$

Hence,

$$s_0 = 0.$$

The boundary condition $s(1) = 1$ cannot be fulfilled. The solution exhibits a boundary layer at $r = 1$. We introduce the scaling $r = 1 - \delta\rho$ around $r = 1$. The outer solution is expanded as

$$s(r) = \tilde{s}(\rho) = \tilde{s}_0(\rho) + o(1)$$

and equation (8) becomes

$$\frac{\eta}{\delta^2}\left((1-\delta\rho)^2\tilde{s}'\right)' = (1-\delta\rho)'\frac{\tilde{s}}{\tilde{s}+\kappa}.$$

To balance the two terms on both sides of the equation above, we must take

$$\delta = \eta^{\frac{1}{2}}.$$

Then, after equaling the zero-order terms, we get

$$\tilde{s}_0'' = \frac{\tilde{s}_0}{\tilde{s}_0+\kappa} \tag{9}$$

We multiply both sides of (9) by $\tilde{s}_0'$

$$\tilde{s}_0''\tilde{s}_0' = \frac{\tilde{s}_0}{\tilde{s}_0+\kappa}\tilde{s}_0'$$

and integrate:

$$\frac{1}{2}\tilde{s}_0'^2 = \tilde{s}_0 - \kappa\ln(\tilde{s}_0+\kappa) + constant. \tag{10}$$

The outer solution has to match the inner solution in an intermediate region. In practice it means that we have

$$\lim_{\rho\to\infty}\tilde{s}_0 = \lim_{r\to 1} s_0.$$

Hence, $\lim_{\rho\to}\tilde{s}_0 = 0$ and we can determine the constant in (10) by letting ρ tends to ∞. We get

$$\frac{1}{2}\tilde{s}_0'^2 = \tilde{s}_0 - \kappa\ln\left(\frac{\tilde{s}_0+\kappa}{\kappa}\right).$$

This equation leads to

$$\frac{\tilde{s}_0'}{\sqrt{2\left(\tilde{s}_0 - \kappa\ln\left(\frac{\tilde{s}_0+\kappa}{\kappa}\right)\right)}} = -1. \tag{11}$$

The minus sign on the right-hand side comes the fact that the first derivative s' is negative. Indeed, the substract is diffusing inside the pellet, the concentration of substract is therefore decreasing the further we go into the pellet. We integrate (11) and get

$$\int_0^{\tilde{s}_0}\frac{1}{\sqrt{2\left(u-\kappa\ln\left(\frac{u+\kappa}{\kappa}\right)\right)}}\,du = -\rho + constant.$$

The constant is found by using the boundary condition $\tilde{s}_0(0) = 1$. Finally, we have

$$\rho = \int_{\tilde{s}_0}^{1}\frac{1}{\sqrt{2\left(u-\kappa\ln\left(\frac{u+\kappa}{\kappa}\right)\right)}}\,du.$$