1 Two disc ion detection problem

We consider the problem of an inlaid disc of radius a subjected to a constant flux of H+ ions, with no flux boundary conditions on the rest of the plane. The H+ ions are subject to a reversible reaction with a base A- in the bulk solution, with product B:

$$H + A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B, \tag{1}$$

so that the forward and back rate constants are given by k_f (mol^{-1}m^{3}s^{-1}) and k_b (s^{-1}) respectively. We would like to know how the concentration varies across the plane. In particular we would like to know what the concentration is on an inlaid detector disc of radius b, whose centre is a distance L away from the centre of the first disc.

Ingoring any electric effects and seeking only steady solutions, the governing equations for the concentration of the three species H, A and B, are

$$D_H \nabla^2 H = k_f HA - k_b B, \tag{2}$$
$$D_A \nabla^2 A = k_f HA - k_b B, \tag{3}$$
$$D_B \nabla^2 B = -k_f HA + k_b B. \tag{4}$$

The boundary conditions for H are given by

$$D_H \frac{\partial H}{\partial z} = -Q, \quad \text{for } r < a, \ z = 0, \tag{5}$$
$$\frac{\partial H}{\partial z} = 0, \quad \text{for } r > a, \ z = 0, \tag{6}$$
$$H(r, z) \to 0, \quad \text{as } |\, \mathbf{r} \,| \to \infty, \tag{7}$$

Here Q is the constant flux of ions from the disc, and has the dimensions mol m^{-2} s^{-1}. We shall also assume that the diffusion coefficient is constant, and we assume that the bulk concentration of H is zero.

The boundary conditions for A are:

$$\frac{\partial A}{\partial z} = 0, \quad \text{on } z = 0, \tag{8}$$
$$A(r, z) \to A_\infty, \quad \text{as } |\, \mathbf{r} \,| \to \infty, \tag{9}$$

where A_∞ is the bulk concentration of the base.

The boundary conditions for B are:

$$\begin{aligned} \frac{\partial B}{\partial z} &= 0, \quad \text{on } z = 0, & (10) \\ B(r,\, z) &\to 0, \quad \text{as } |\, \mathbf{r} \,| \to \infty. & (11) \end{aligned}$$

The first thing we note is that by adding (3) and (4), and using the boundary conditions for A and B, it follows that

$$\nabla^2 \left(D_A A + D_B B \right) = 0, \tag{12}$$

subject to the boundary conditions

$$\begin{aligned} \frac{\partial \left(D_A A + D_B B \right)}{\partial z} &= 0, \quad \text{on } z = 0, & (13) \\ D_A A + D_B B &\to D_A A_\infty, \quad \text{as } |\, \mathbf{r} \,| \to \infty. & (14) \end{aligned}$$

This means that the quantity $D_A A + D_B B$ is conserved, and

$$D_A A + D_B B = D_A A_\infty. \tag{15}$$

Solving for B and substituting in, we find that the governing equations reduce to two equations for H and A:

$$\begin{aligned} D_H \nabla^2 H &= k_f H A - \frac{k_b D_A}{D_B}(A_\infty - A), & (16) \\ D_A \nabla^2 A &= k_f H A - \frac{k_b D_A}{D_B}(A_\infty - A). & (17) \end{aligned}$$

To non-dimensionalise, we choose the following scalings:

$$r = a\hat{r}, \quad z = a\hat{z}, \quad H = \frac{Qa}{D_H}\hat{H}, \quad A = A_\infty \hat{A}. \tag{18}$$

On dropping the hats, the equations become

$$\begin{aligned} \nabla^2 H &= k_1 H A - k_2(1 - A), & (19) \\ k_3 \nabla^2 A &= k_1 H A - k_2(1 - A), & (20) \end{aligned}$$

where the non-dimensional parameters k_1, k_2 and k_3 are given by

$$k_1 = \frac{k_f a^2 A_\infty}{D_H}, \quad k_2 = \frac{k_b a A_\infty D_A}{Q D_B}, \quad k_3 = \frac{A_\infty D_A}{Qa}. \tag{21}$$

The boundary conditions for H are

$$\frac{\partial H}{\partial z} = -1, \quad \text{for } r < 1,\ z = 0, \tag{22}$$

$$\frac{\partial H}{\partial z} = 0, \quad \text{for } r > 1,\ z = 0, \tag{23}$$

$$H(r,\, z) \to 0, \quad \text{as } \mid \mathbf{r} \mid \to \infty, \tag{24}$$

and boundary conditions for A

$$\frac{\partial A}{\partial z} = 0, \quad \text{on} z = 0, \tag{25}$$

$$A(r,\, z) \to 1, \quad \text{as } \mid \mathbf{r} \mid \to \infty, \tag{26}$$

Now we note that if we subtract (20) from (19) we find that

$$\nabla^2 (H - k_3 A) = 0, \tag{27}$$

with boundary conditions

$$\frac{\partial (H - k_3 A)}{\partial z} = -1, \quad \text{for } r < 1,\ z = 0, \tag{28}$$

$$\frac{\partial (H - k_3 A)}{\partial z} = 0, \quad \text{for } r > 1,\ z = 0, \tag{29}$$

$$(H - k_3 A) \to -k_3, \quad \text{as } \mid \mathbf{r} \mid \to \infty. \tag{30}$$

Using the Hankel transform, it is easy to show that the solution to this problem is given by

$$H(r,\, z) - k_3 A(r,\, z) = -k_3 + \int_0^\infty J_0(\alpha r) J_1(\alpha) \exp(-\alpha z) \, \frac{d\alpha}{\alpha}, \tag{31}$$

where J_0 and J_1 are Bessel functions of order zero and one. The concentration of H on the plane $z = 0$ is therefore given by

$$H(r,\, 0) = \int_0^\infty J_0(\alpha r) J_1(\alpha) \, \frac{d\alpha}{\alpha} - k_3 \left(1 - A(r,\, 0)\right). \tag{32}$$

This means that the concentration of H is equal to the concentration for a disk generator with no reaction less the amount that has reacted with A, which is proportional to $(1-A)$. It is very important to note that the reaction with A only makes a noticeable difference to the concentration of H detected if k_3 is at least $O(1)$. This is vital in determining sensor design.

From (31), we may write

$$H(r,\, z) = k_3\,(A(r,\, z) - 1) + H_1(r,\, z), \tag{33}$$

where H_1 is the solution for the disc generator with no bulk reaction, which we emphasize is known. Substituting into (20), we find a governing equation for A

$$\begin{aligned} \nabla^2 A &= k_1\,(A-1)\,A + \frac{k_1}{k_3} A H_1 - \frac{k_2}{k_3}(1-A), & (34) \\ &= k_1 A^2 + A\left(\frac{k_1}{k_3} H_1 + \frac{k_2}{k_3} - k_1\right) - \frac{k_2}{k_3}, & (35) \end{aligned}$$

with boundary conditions (25) and (26). Hence we have reduced three governing equations down to one governing equation for A with simple boundary conditions. It is still a complicated equation, and is non-linear in A, but we may be able to do some asymptotics depending on the sizes of the parameters k_1, k_2 and k_3. We shall assume that Q has been chosen such that $k_3 = O(1)$.

We note that in general k_f and k_b have the following magnitudes

$$\begin{aligned} k_f &\approx 10^6 - 10^7 \text{mol}^{-1}\ \text{m}^3\ \text{s}^{-1}, & (36) \\ k_b &\approx 10^3 - 10^4 \text{s}^{-1}. & (37) \end{aligned}$$

This implies that k_1 will be large, while depending on the value of Q , k_2 will be around $O(1)$. Dividing through by k_1, the governing equation becomes:

$$\frac{1}{k_1}\nabla^2 A = A^2 + A\left(\frac{1}{k_3} H_1 + \frac{k_2}{k_1 k_3} - 1\right) - \frac{k_2}{k_1 k_3}. \tag{38}$$

Provided that we are not near the disc then the lefthand side may be neglected and the solution to the following quadratic satisifes the boundary conditions (25) and (26):

$$A^2 + A\left(\frac{1}{k_3} H_1 + \frac{k_2}{k_1 k_3} - 1\right) - \frac{k_2}{k_1 k_3} = 0. \tag{39}$$

so that

$$A = \frac{1}{2}\left(-\left(\frac{1}{k_3}H_1 + \frac{k_2}{k_1 k_3} - 1\right) + \sqrt{\left(\frac{1}{k_3}H_1 + \frac{k_2}{k_1 k_3} - 1\right)^2 + 4\frac{k_2}{k_1 k_3}} \right), \tag{40}$$

where we have taken the positive square root to ensure that $A > 0$. Inserting this into (33) we obtain

$$H(r,\, z) = \frac{1}{2}\left(H_1(r,\, z) - \frac{k_2}{k_1} - k_3 + \sqrt{\left(H_1(r,\, z) + \frac{k_2}{k_1} - k_3\right)^2 + 4\frac{k_2 k_3}{k_1}} \right). \tag{41}$$

In the limit that $k_2/k_1 \ll 1$, we have to be a bit more careful. Letting $k_2/k_1 = \epsilon$, and expanding the original quadratic in powers of ϵ, so that

$$A = A_0 + \epsilon A_1 + \epsilon^2 A_2 + \ldots. \tag{42}$$

Then the solution is given by

$$A_0 = 1 - \frac{H_1}{k_3}, \tag{43}$$

$$A_1 = \frac{H_1}{k_3(k_3 - H_1)}. \tag{44}$$

2 Concentration on disc far away

Suppose that we now would like to measure the concentration on a disc whose centre is a non-dimensional distance λ away from the centre of the generator disc, and let us assume that $\lambda \gg 1$. Then it is convenient to write the solution for $H_1(r,\, z)$ in the following form:

$$H_1(r,\, z) = \frac{2}{\pi}\int_0^1 \mathrm{K}\left(\frac{2\sqrt{rs}}{(r+s)^2 + z^2}\right)\frac{s\, ds}{\sqrt{(r+s)^2 + z^2}}, \tag{45}$$

where $\mathrm{K}(\cdot)$ denotes a complete elliptic integral of the first kind. Then the far field behaviour as $r \to \infty$ on $z = 0$ is easily shown to be

$$H_1(r,\, z) \sim \frac{1}{2r} + O\left(\frac{1}{r^3}\right), \tag{46}$$

so that the disc is a point source as expected. Subtituting this into the solution (49), we obtain:

$$H(r,\,z) \sim \frac{1}{2}\left(\frac{1}{2r} - \frac{k_2}{k_1} - k_3 + \sqrt{\left(\frac{1}{2r} + \frac{k_2}{k_1} - k_3\right)^2 + 4\frac{k_2 k_3}{k_1}}\right). \tag{47}$$

Writing r in terms of a cylindrical coordinate system $(s,\,\theta)$ centered at the centre of the detection disc, so that

$$r = \sqrt{\lambda^2 + 2\lambda s\cos\theta + s^2}, \tag{48}$$

and expanding in powers of λ, we obtain:

$$H(s,\,\theta) \sim \frac{k_2}{2(k_2 + k_1 k_3)\lambda} + \frac{k_2(k_1^2 k_3 - 2(k_2 + k_1 k_3)^2 s\cos\theta)}{4(k_2 + k_1 k_3)^3\lambda^2} + O\left(\frac{1}{\lambda^3}\right). \tag{49}$$

Hence the average concentration across the detection disc is given by (assuming that the non-dimensional radius is b):

$$\begin{aligned} H_{\text{Av}} &= \frac{1}{\pi b^2}\int_0^b\int_0^{2\pi} H(s,\,\theta) s\,ds\,d\theta, && (50)\\ &= \frac{k_2}{2(k_2 + k_1 k_3)\lambda} + O\left(\frac{1}{\lambda^2}\right). && (51) \end{aligned}$$

In dimensional terms, we have to leading order

$$H_{\text{Av, dim}} = \frac{Qa}{2\left(D_H + \frac{k_f}{k_b}A_\infty D_B\right)\lambda} \tag{52}$$