Appendix A

SOLUTION OF FICK'S SECOND LAW

The general diffusion equation for one-dimensional analysis under non-steady state condition is defined by Fick's second law, eq. (4.19). Hence,

$$\frac{\partial C}{dt} = D\frac{\partial^2 C}{\partial x^2} \tag{A1}$$

Let D be a constant and use the function $y = f(x,t)$ be defined by

$$y = \frac{x}{2\sqrt{Dt}} \tag{A2}$$

Thus, the partial derivatives of eq. A2 are

$$\frac{\partial y}{\partial x} = \frac{1}{2\sqrt{Dt}} \text{ and } \frac{\partial y}{\partial t} = -\frac{x}{4\sqrt{Dt^3}} \tag{a}$$

By definition,

$$\begin{aligned} \frac{\partial C}{\partial t} &= \frac{dC}{dy}\frac{\partial y}{\partial t} = -\frac{x}{4\sqrt{Dt^3}}\frac{dC}{dy} && \text{(b)} \\ \frac{\partial^2 C}{\partial x^2} &= \frac{\partial}{\partial x}\left[\frac{dC}{dy}\left(\frac{\partial y}{\partial x}\right)\right] = \frac{1}{4Dt}\frac{d^2C}{dy^2} && \text{(c)} \end{aligned}$$

Substituting eqs. (b) and (c) into A1 yields

$$\frac{dC}{dy} = -\frac{\sqrt{Dt}}{x}\frac{d^2C}{dy^2} \tag{A.3}$$

Combining eq. (A2) and (A3) gives

$$\frac{dC}{dy} = -\frac{1}{2y}\frac{d^2C}{dy^2} \tag{A4}$$

Now, let $z = dC/dy$ so that eq. (A4) becomes

$$\begin{aligned} z &= -\frac{1}{2y}\frac{dz}{dy} && \text{(a)} \\ -2\int y dy &= \int \frac{dz}{z} && \text{(b)} \end{aligned}$$

Then,

$$-y^2 = \ln z - \ln B \tag{c}$$

where B is an integration constant. Rearranging eq. (c) yields

$$z = B \exp(-y^2) \tag{A5}$$

and

$$\int dC = B \int \exp(-y^2) dy \tag{A6}$$

The function $f = \exp(-y^2)$ represents the so-called "Bell-Shaped Curves". The solution of the integrals are based on a set of boundary conditions.

A.1 FIRST BOUNDARY CONDITIONS

In order to solve integrals given by eq. (A6) a set of boundary conditions the concentration and the parameter y are necessary. This boundary conditions are just the integral limits. Thus,

$$\begin{aligned} C &= \begin{cases} C_x = C_o & \text{for } y = 0 \text{ at } t > 0 \text{ and } x = 0 \\ C_x = C_b & \text{for } y = \infty \text{ at } t = 0 \text{ and } x > 0 \end{cases} && \text{(a)} \\ \int_{C_o}^{C_b} dC &= B \int_o^\infty \exp(-y^2) dy && \text{(c)} \\ C_b - C_o &= B \int_o^\infty \exp(-y^2) dy && \text{(A7)} \end{aligned}$$

Use the following integral definitions and properties of the error function $\text{erf}(y)$

$$\begin{aligned}
\int_o^\infty \exp(-y^2)dy &= \frac{\sqrt{\pi}}{2} && \text{(a)} \\
\int_{-\infty}^\infty \exp(-y^2)dy &= \sqrt{\pi} && \text{(b)} \\
erf(y) &= \frac{2}{\sqrt{\pi}}\int_o^y \exp(-y^2)dy && \text{(c)} \\
\operatorname{erf} c(y) &= \frac{2}{\sqrt{\pi}}\int_y^\infty \exp(-y^2)dy && \text{(d)} \\
\operatorname{erf}(y) + \operatorname{erf} c(y) &= 1 \quad \text{and} \quad \operatorname{erf}(-y) = -\operatorname{erf}(y) && \text{(e)} \\
\operatorname{erf}(0) &= 0 \quad \text{and} \quad \operatorname{erf}(\infty) = 1 && \text{(f)}
\end{aligned}$$

By definition, the function erf $c(y)$ is the complement of $\operatorname{erf}(y)$. Inserting eq. (a) into (A7) yields the constant B defined by

$$B = \frac{2}{\sqrt{\pi}}(C_b - C_o) \tag{A8}$$

A.2 SECOND BOUNDARY CONDITIONS

The second set of boundary conditions are given below

$$C = \begin{cases} C_x = C_x \text{ at } y < \infty \\ C_x = C_b \text{ at } y = \infty \end{cases} \qquad \text{(a)}$$

Setting the limits of the integral given by eq. (A6) and using eq. (A8) yields the solution of Fick's second law of diffusion when the bulk concentration ($C_b = C_x$ **at** $x = \infty$) is greater than the surface concentration ($C_o = C_x$ at $x = 0$). Hence, the solution of eq. (A1) for **concentration polarization** ($C_b > C_o$) becomes

$$\begin{aligned}
\int_{C_b}^{C_x} dC &= B\int_\infty^y \exp(-y^2)\,dy = -B\int_y^\infty \exp(-y^2)\,dy && \text{(b)} \\
C_x - C_o &= -\frac{2}{\sqrt{\pi}}(C_b - C_o)\frac{\sqrt{\pi}}{2}\operatorname{erf} c(y) && \text{(c)} \\
\frac{C_x - C_b}{C_o - C_b} &= 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad \text{for } C_b > C_o && \text{(A9)}
\end{aligned}$$

A.3 THIRD BOUNDARY CONDITIONS

Similarly, the solution of eq. (A1) for **activation polarization** ($C_o < C_b$) upon using the boundary conditions given below as well as eqs. (A6) and (A8) yields the normalized concentration expression

$$
\begin{aligned}
C &= \begin{cases} C_x = C_x \text{ at } & y > 0 \\ C_x = C_o \text{ at } & y = 0 \end{cases} && \text{(a)} \\
\int_{C_o}^{C_x} dC &= B \int_0^y \exp\left(-y^2\right) dy && \text{(b)} \\
C_x - C_o &= \frac{2}{\sqrt{\pi}} \left(C_b - C_o\right) \frac{\sqrt{\pi}}{2} \operatorname{erf}(y) && \text{(c)} \\
\frac{C_x - C_o}{C_b - C_o} &= \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad \text{For } C_o < C_b && \text{(A10)}
\end{aligned}
$$

This concludes the analytical procedure for solving Fick's second law of diffusion for concentration and activation polarization cases.