Some properties of Laplace transformation

Definition: $\mathcal{L}\{f(t)\} = \bar{F}(s) = \int_0^\infty f(t)e^{-st}dt$

Linearity: $\mathcal{L}\{af(t) + bg(t)\} = a\bar{F}(s) + b\bar{G}(s)$

$\mathcal{L}\{f(t)g(t)\} \neq \bar{F}(s)\bar{G}(s)$

Derivative: $\mathcal{L}\{f'(t)\} = s\bar{F}(s) - f(0)$

Integral: $\mathcal{L}\left\{\int_0^t f(u)du\right\} = \frac{1}{s}\bar{F}(s)$

Convolution: $\mathcal{L}^{-1}\{\bar{F}(s)\bar{G}(s)\} = \int_0^t f(u)g(t-u)du$

Translation: $\mathcal{L}\{e^{at}f(t)\} = \bar{F}(s-a)$

Time-dependent aka Transient methods

Time-dependent methods are particularly suitable for the determination of the reaction kinetics, and they provide often a clear qualitative picture of what is going on in an electrochemical cell. We concentrate, again, on the trace-ion case in the absence of migration and convection, leaving diffusion as the only mechanism of mass transport.

Since we are considering time-dependent behavior, we have to solve Fick's 2nd law (in 1-D):

$$\frac{\partial c_k}{\partial t} = D_k \frac{\partial^2 c_k}{\partial x^2} \qquad (7.1)$$

An initial condition is needed which is

$$c_k(x, t = 0) = c_k^b \qquad (7.2)$$

The bulk concentration c_k^b can naturally be also zero if the species 'k' is initially absent. "Far from the electrode" (a few μm) concentration naturally is c_k^b:

$$c_k(x \rightarrow \infty, t) = c_k^b \qquad (7.3)$$

The current boundary condition completes the problem set-up, as usual:

$$\frac{i(t)}{nF} = \pm D_k \left(\frac{\partial c_k}{\partial x} \right)_{x=0} \qquad (7.4)$$

In an electrochemical problem, in order to obtain the dependence of current on potential, we need, in addition, the values of the surface concentrations of the electroactive species. We have two choices: for a very fast (reversible) reaction we use Nernst equation and for a slow (quasi-reversible) reaction Butler-Volmer equation:

$$\frac{c_O^s}{c_R^s} = \theta = \exp\left[\frac{nF}{RT}\left(E - E^{0'}\right)\right] \quad \text{reversible} \quad (7.5)$$

$$\frac{i(t)}{nF} = k_{ox}c_R^s - k_{red}c_O^s \quad \text{quasi-reversible} \quad (7.6)$$

Note that E can be time dependent, making also k_{ox} and k_{red} potential dependent; they assume the forms of Butler-Volmer kinetics.

How these boundary conditions are used depends on the transient methods used, but the general solution of the Fick's law proceeds applying **Laplace transform**. Eq. (7.1) is transformed using the derivative property of Laplace transform

$$s\bar{c}_k - c_k^b = D_k\frac{d^2\bar{c}_k}{dx^2} \quad \Leftrightarrow \quad \frac{d^2\bar{c}_k}{dx^2} - \frac{s}{D_k}\bar{c}_k = -\frac{c_k^b}{D_k} \quad (7.7)$$

where the upper bar denotes a variable in the Laplace domain and s is the Laplace variable (do not confuse it with the superscript 's' denoting for surface). The general solution of this differential equation is

$$\bar{c}_k(x,s) = \frac{c_k^b}{s} + A(s)e^{-\lambda_k x} + B(s)e^{\lambda_k x}, \quad \lambda_k = \sqrt{\frac{s}{D_k}} \quad (7.8)$$

$A(s)$ and $B(s)$ are coefficients to be determined from the boundary conditions. In order to have $\bar{c}_k$ limited when $x \to \infty$ (boundary condition, eq. (7.3)), it is required that $B(s) = 0$. $A(s)$ is found using the current boundary condition (7.4):

$$\frac{\bar{i}(s)}{nF} = \pm D_k \left(\frac{d\bar{c}_k}{dx}\right)_{x=0} = \mp\sqrt{sD_k}\,A(s) \quad \Rightarrow \quad A(s) = \mp\frac{\bar{i}(s)}{nF\sqrt{sD_k}}$$

$$\bar{c}_k^s = \frac{c_k^b}{s} \mp \frac{\bar{i}(s)}{nF\sqrt{sD_k}} \qquad\qquad (7.9)$$

where the upper minus sign corresponds to an oxidation and the lower plus sign to a reduction reaction. It has to be emphasized that eq. (7.9) is completely general, it applies to any time-dependent electrochemical method (for a trace-ion), as well as to the impedance method where a periodical perturbation signal is applied. The concentration profile in Laplace domain is

$$\bar{c}_k^s(x,s) = \frac{c_k^b}{s} \mp \frac{\bar{i}(s)}{nF\sqrt{sD_k}}e^{-\sqrt{s/D_k}\,x} \qquad\qquad (7.10)$$

In order to proceed, a particular time-dependent method must be defined. We start with the simplest possible method, a potential step.

Potential step

In the potential step experiment, electrode potential is stepped from the region where practically no current is flowing to a value where oxidation/reduction reaction occurs. Because potential remains constant, θ in eq. (7.5) is constant and we have

$$c_O^s = \theta c_R^s \quad \Rightarrow \quad \bar{c}_O^s = \theta \bar{c}_R^s$$

Let's consider the case where 'O' is initially absent. Now: $\bar{c}_R^s = \dfrac{c_R^b}{s} - \dfrac{\bar{i}(s)}{nF\sqrt{sD_R}}$ and $\bar{c}_O^s = \dfrac{\bar{i}(s)}{nF\sqrt{sD_O}}$. Applying the above equation,

$$\bar{i}(s) = \frac{nF\sqrt{D_O}\,\theta c_R^b}{1+\xi\theta}\frac{1}{\sqrt{s}} \quad , \quad \xi = \sqrt{\frac{D_O}{D_R}} \qquad\qquad (7.11)$$

Current in the time domain is obtained from an inverse transformation which can be found tabulated. The inverse transformation of $s^{-1/2}$ is $(\pi t)^{-1/2}$. Thus,

$$i(t) = \frac{nF\sqrt{D_O}\,\theta c_R^b}{1+\xi\theta}\frac{1}{\sqrt{\pi t}} \qquad\qquad (7.12)$$

If the step is done in so anodic potential that c_R^s goes to zero ($\xi\theta \gg 1$), current is immediately obtained from eq. (7.9) as
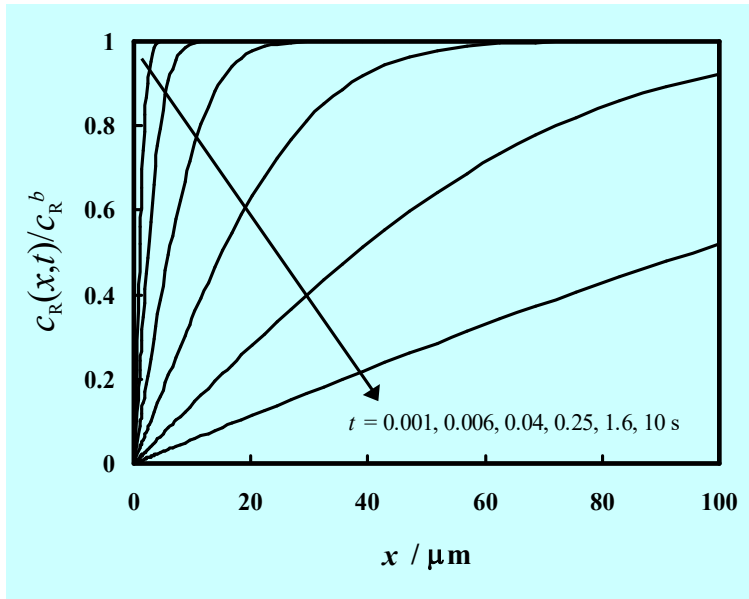
$$\bar{i}_d(s) = \frac{nF\sqrt{D_R}\,c_R^b}{\sqrt{s}} \quad \Rightarrow \quad i_d(t) = \frac{nF\sqrt{D_R}\,c_R^b}{\sqrt{\pi t}} \qquad\qquad \text{Cottrell equation} \qquad\qquad (7.13)$$

Inserting eq. (7.11) into eq. (7.10), the concentration profile is obtained in Laplace domain as

$$\overline{c}_R(x,s) = \frac{c_R^b}{s} - \frac{\xi\theta c_R^b}{(1+\xi\theta)} \cdot \frac{e^{-\sqrt{s/D_R}\,x}}{s}$$

The inverse transform is found in the table as

$$\frac{c_R(x,t)}{c_R^b} = 1 - \frac{\xi\theta}{(1+\xi\theta)}\operatorname{erfc}\left[\frac{x}{2\sqrt{D_R t}}\right] = \operatorname{erf}\left[\frac{x}{2\sqrt{D_R t}}\right] \quad ; \quad \xi\theta \gg 1$$

t = 0.001, 0.006, 0.04, 0.25, 1.6, 10 s

x / μm

erf(x) is the error function and erfc(x) its complement.

Aside: Concentration profile after a potential step to a value where surface concentration goes to zero; D = 10^{-5} cm^2/s. In a general case, surface concentrations jump at the value where eq. (7.5) is valid.

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-u^2}\,du \quad ; \quad \operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$$

Current step

Another easy technique to analyze is to apply constant current density i in the cell; Laplace transform of 1 is 1/s. Hence,

$$\bar{c}_k^s = \frac{c_k^b}{s} \mp \frac{i}{nF\sqrt{D_k}} \frac{1}{s^{3/2}}$$

Assuming again that "O" is initially absent, the inverse transforms are found easily as

$$c_R^s(t) = c_R^b - \frac{2i\sqrt{t}}{nF\sqrt{\pi D_R}} \quad \text{and} \quad c_O^s(t) = \frac{2i\sqrt{t}}{nF\sqrt{\pi D_O}}$$

The moment when c_R^s goes to zero is known as the **transition time, τ.** It is give by **Sand equation:**

$$\sqrt{\tau} = \frac{nFc_R^b\sqrt{\pi D_R}}{2i} \qquad\qquad (7.14)$$

Using the transition time, the surface concentrations can be written in a compact form as

$$c_R^s = c_R^b\left(1 - \sqrt{t/\tau}\right) \quad \text{and} \quad c_O^s = c_R^b \xi^{-1}\sqrt{t/\tau}$$

where ξ is defined by eq. (7.11).

Inserting these surface concentrations in Nernst equation,

$$E = E^{0'} - \frac{RT}{nF} \ln\left[\xi\left(\sqrt{\frac{\tau}{t}} - 1 \right) \right]$$

Plot aside shows how potential changes as the function of time. At $t = \tau$ potential jumps abruptly which gives the experimental means of determining τ.

The concentration profile is calculated as follows:

$$\overline{c}_R^S = \frac{c_R^b}{s} - \frac{i}{nF\sqrt{D_R}} \frac{1}{s^{3/2}} \exp\left(-\sqrt{\frac{s}{D_R}} x \right)$$

$$c_R(x,t) = c_R^b - \frac{i}{nF\sqrt{D_R}} \left[2\sqrt{\frac{t}{\pi}} \exp\left(-\frac{x^2}{4D_R t} \right) - \frac{x}{\sqrt{D_R}} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_R t}} \right) \right]$$

$$\frac{c_R(x,t)}{c_R^b} = 1 - \sqrt{\frac{t}{\tau}} \exp\left(-\frac{x^2}{4D_R t} \right) + \frac{\sqrt{\pi}x}{2\sqrt{D_R \tau}} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_R t}} \right)$$

Aside simulated concentration profiles with $D = 10^{-5}$ cm^2/s and $\tau = 4$ s.

Note the difference between potential and current steps: in the former surface concentration and in the latter the concentration gradient at the surface is constant.

$t = 0.5, 1.0, 2.0, 3.0, 4.0$ s