

Hydrodynamic methods

A true steady-state can be achieved only by stirring the solution. Because at steady-state the rate of an electrode reaction equals to the rate of mass transfer onto the electrode, we also have to solve the transport equation along the rate equation. We restrict to a trace-ion case, i.e. when the concentration of the electroactive species under study, c_k , is much lower than that of the **supporting electrolyte** that does not react at the electrode. This has the consequence that the transport of the trace-ion takes place only by diffusion and convection. Furthermore, at the electrode surface the velocity of the solvent is usually zero (**non-slip condition**) which means that

$$\frac{I}{nF} = \pm D_k (\nabla c_k)_{\text{surface}} \quad (6.1)$$

In 1-D studies the gradient operator ∇ is replaced by $\partial/\partial x$. The equation to be solved at steady-state hence is

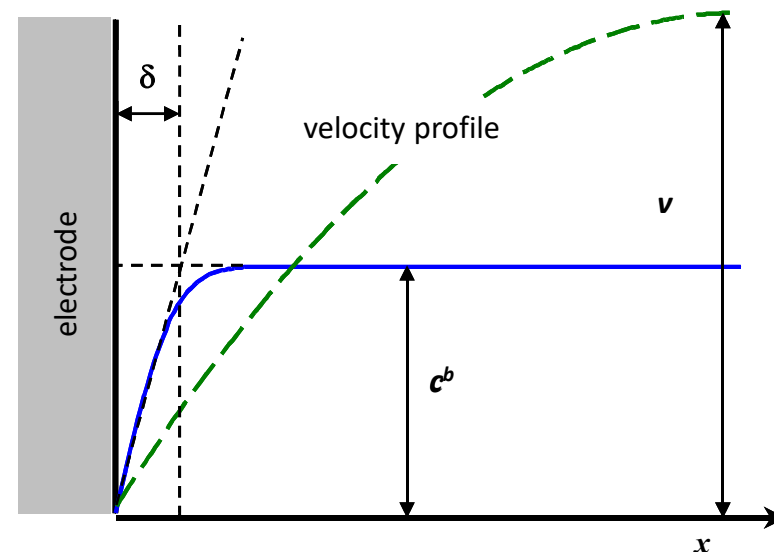
$$D_k \nabla^2 c_k - \vec{v} \nabla c_k = 0 \quad (6.2)$$

using the boundary condition given above it; \vec{v} is the linear velocity of the solvent (m/s). In a 1-D case, $\nabla^2 = \partial^2/\partial x^2$ and in the absence of convection ($\vec{v} = 0$) we get a linear concentration profile $c_k(x) = Ax + B$ as its solution. Hence, it is clear that $c_k(x \rightarrow \infty)$ would increase without limits if we do not stir the solution. An exception is spherical symmetry where

$$\nabla^2 c_k = \frac{\partial^2 c_k}{\partial r^2} + \frac{2}{r} \frac{\partial c_k}{\partial r}, \quad (6.3)$$

giving a steady-state solution $c_k = A + B/r$ that is limited when $r \rightarrow \infty$ (r is the radial distance from the electrode centre).

When the solution is stirred the situation is something like what is depicted in the picture aside. At the electrode the solution velocity is zero but increases towards the bulk of the solution (green line) with a manner that depends on the stirring method. The concentration profile (blue line) may develop much faster to its bulk value, c^b . The thickness of the boundary layer is defined as depicted but it is only a thought, virtual definition, because we cannot measure it. Therefore, it is eliminated from the solution as described in the first lecture, using the measurable limiting current, and assuming that that in the region $0 < x < \delta$ there is no convection.



In order to fully utilize stirring we have to resort to methods where the velocity profile can be explicitly known; a stirrer bar or a paddle does not create a well-defined velocity profile.

In this course, three methods will be introduced: a rotating disk electrode (RDE), a channel flow electrode and a wall-jet electrode. The velocity profile is (in principle) obtained from the solution of the Navier-Stokes equation which reads for a non-compressible fluid

$$\rho \left(\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} \right) = -\nabla p + \eta \nabla^2 \vec{v}, \quad (6.4)$$

(ρ = density, η = viscosity, p = pressure) together with the continuity equation $\frac{\partial \vec{v}}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0$. The solution is rather demanding and we take it from the literature for these two cases.

Rotating Disk Electrode, RDE

When an electrode is rotated a velocity field is formed in its vicinity in a manner illustrated in the picture aside. Navier-Stokes equation has been solved for this case in the form of a power series; we need only the first term of the series:

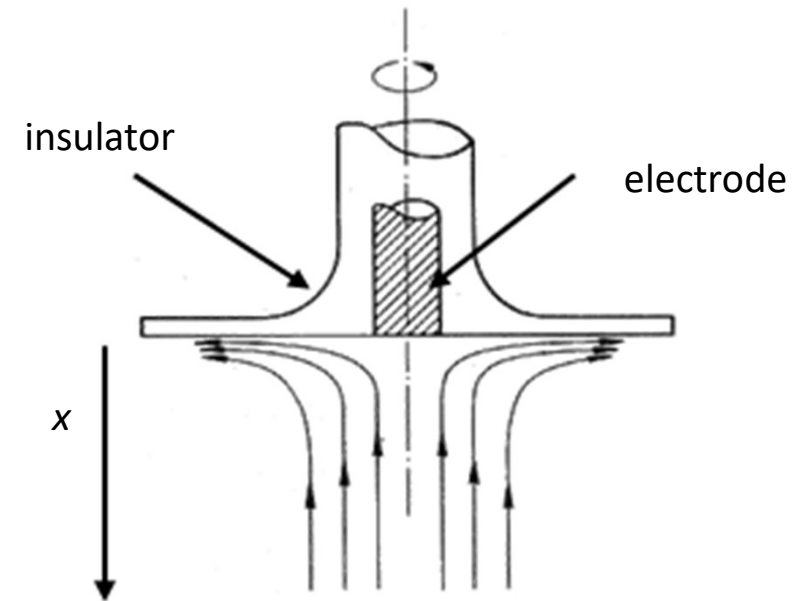
$$\vec{v}(x) = -\left(\frac{\omega^3}{\nu}\right)^{1/2} 0.510x^2 = -Ax^2 \quad (6.5)$$

where ω is the rotation speed ($\omega = 2\pi f$, rad/s) and ν is the kinematic viscosity of the solution (η/ρ , for water ~ 0.01 cm²/s at 25 °C). This equation seems to give an absurd result that $\vec{v}(x)$ increases without any limit as x increases. The full series would, naturally, die to zero as $x \rightarrow \infty$ but we do not need that.

As seen in the picture, the solution is flowing along the electrode in the radial direction, but the radial velocity component has no effect on electric current because only the flux perpendicular to the surface is counted in the current. The problem thus is:

$$\frac{d^2c}{dx^2} - \frac{\vec{v}(x)}{D} \frac{dc}{dx} = 0 \quad ; \quad c(x \rightarrow \infty) = c^b \quad ; \quad \frac{I}{nF} = \pm D \left(\frac{dc}{dx} \right)_{x=0} \quad (6.6)$$

In the current boundary condition, plus sign applies to oxidation and minus sign to reduction of the trace-ion. The velocity profile given in eq. (6.5) will be used now in eq. (6.6).



Defining $p = dc/dx$, eq. (2) can be converted in the form from which its integration is straightforward:

$$\frac{dp}{dx} = \frac{\vec{v}(x)}{D} p \Leftrightarrow \frac{dp}{p} = -\frac{A}{D} x^2 dx \Rightarrow \ln \frac{p(x)}{p(0)} = -\frac{A}{3D} x^3 \Rightarrow \frac{dc}{dx} = \pm \frac{I}{nFD} e^{-Ax^3/3D} \quad (6.7)$$

Integrating eq. (3) from $x = 0$ to $x = \infty$ gives:

$$c^b - c(0) = \pm \frac{I}{nFD} \int_0^{\infty} e^{-Ax^3/3D} dx \quad (6.8)$$

In order to calculate the last integral, a change of variables is needed: $u = \frac{Ax^3}{3D} \Rightarrow dx = \left(\frac{D}{9A}\right)^{1/3} u^{-2/3} du$

$$\int_0^{\infty} e^{-Ax^3/3D} dx = \left(\frac{D}{9A}\right)^{1/3} \int_0^{\infty} e^{-u} u^{-2/3} du = \left(\frac{D}{9A}\right)^{1/3} \Gamma(1/3) \approx 2.679 \left(\frac{D}{9A}\right)^{1/3} \quad (6.9)$$

where Gamma function $\Gamma(n) = \int_0^{\infty} e^{-u} u^{n-1} du$ is used; its values are tabulated. It has the property $n\Gamma(n) = \Gamma(n+1)$.

Limiting current density is obtained by setting $c(0) = 0$, as usual:

$$I_L = \pm 0.620 nFD^{2/3} c^b \omega^{1/2} \nu^{-1/6} \quad (6.10)$$

Equation (6.10) is known as the **Levich equation** and it tells the important fact that $i_L \sim \omega^{1/2}$. Comparing eq. (6.10) with the expression $I_L = nFDc^b/\delta$, we see that the thickness of the diffusion boundary layer can explicitly be defined as

$$\delta = 1.61D^{1/3} \omega^{-1/2} \nu^{1/6}. \quad (6.11)$$

A commentary is needed: In the evaluation of the integral, infinity is used as the upper limit while the approximation via eq. (6.5) is valid only very close to the electrode. The function $\exp(-Ax^3/3D)$ decays, however, so rapidly to zero that it makes no difference whether the upper limit is δ or ∞ .

If current density $I < I_L$ we can write as usual $I = nFD[c^b - c(0)]/\delta$ and $c(0) = c^b(1 - I/I_L)$. Let's consider an oxidation reaction when "O" is initially absent. Then current is $I = nF[k_{ox}c_R(0) - k_{red}c_O(0)]$ and at sufficiently positive potentials the latter term can be omitted. Therefore,

$$I = nFk_{ox}c_R^b \left(1 - I/I_L^{ox}\right) \Leftrightarrow I = \frac{nFk_{ox}c_R^b}{1 + nFk_{ox}c_R^b/I_L^{ox}} \Leftrightarrow \frac{1}{I} = \frac{1}{nFk_{ox}c_R^b} + \frac{1}{0.620 nF c_R^b D^{2/3} \nu^{-1/6} \omega^{1/2}} = \frac{1}{I_{kin}} + \frac{1}{I_L^{ox}} \quad (6.12)$$

where the expression of the limiting current density, eq. (6.10) has been applied; I_{kin} would be current density if no concentration polarization i.e. mass transfer occurred.

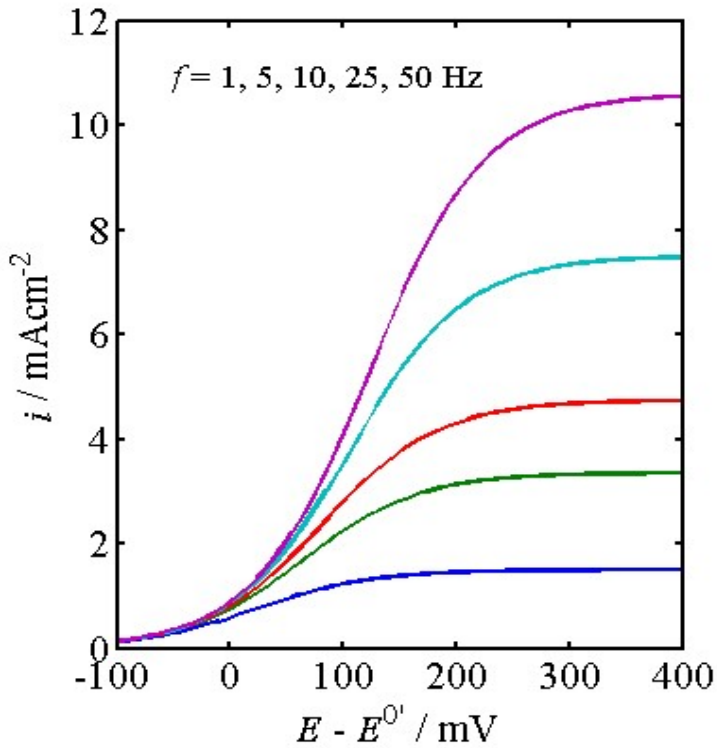
Eq. (6.12) is the corner stone of the RDE analysis. Plotting $1/I$ at constant potential as the function of $1/\sqrt{\omega}$ and extrapolating to zero, gives kinetic current at that potential and hence the value of k_{ox} . Alternatively, I_{kin} can be solved from eq. (6.12) as

$$I_{kin} = \frac{I_L \cdot I}{I_L - I} \quad (\text{both "ox" and "red"}) \quad (6.13)$$

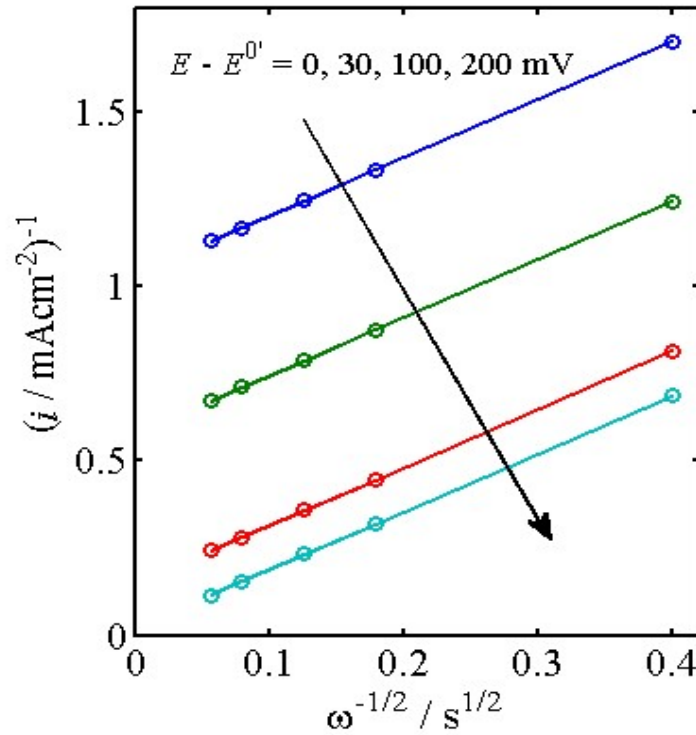
along the current-voltage curve. This has an advantage that current, corrected for mass transfer, is then readily available for the Tafel slope analysis because I_{kin} should be independent of ω .

The plots on the next page illustrate the former type of analysis.

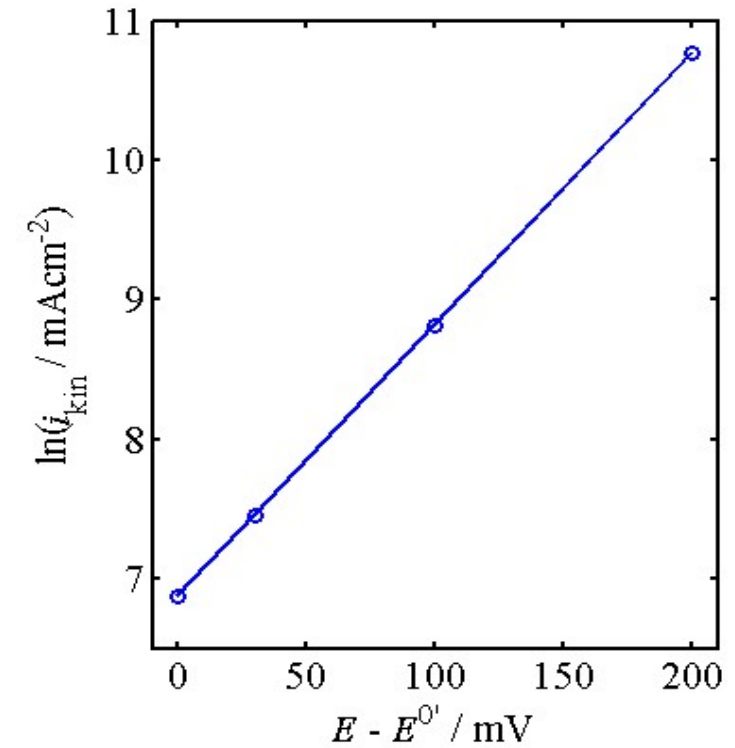
Analysis of current-voltage curves measured with an RDE



i - E curves at varying rotation speeds as indicated. Check that $i_L \sim \sqrt{\omega}$.

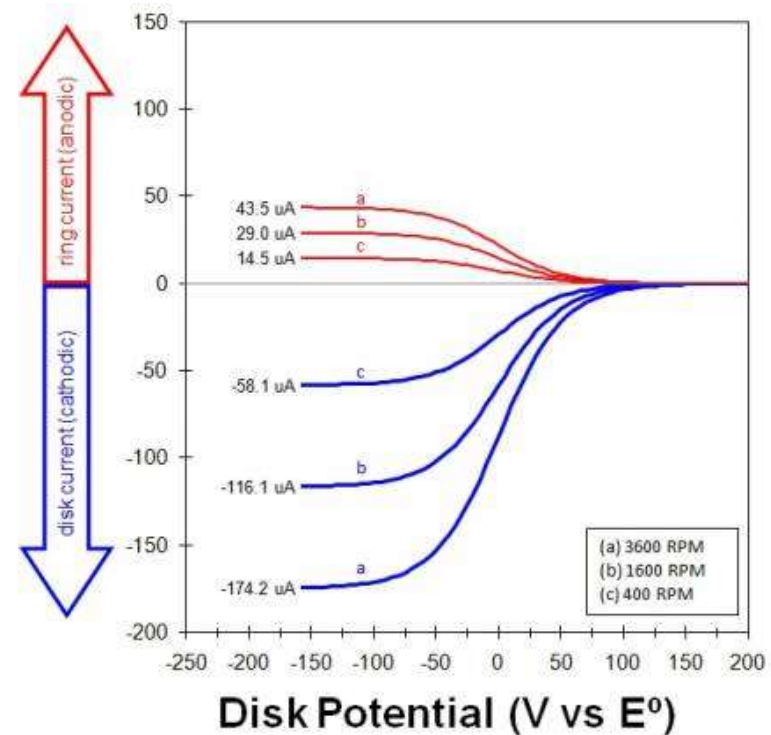
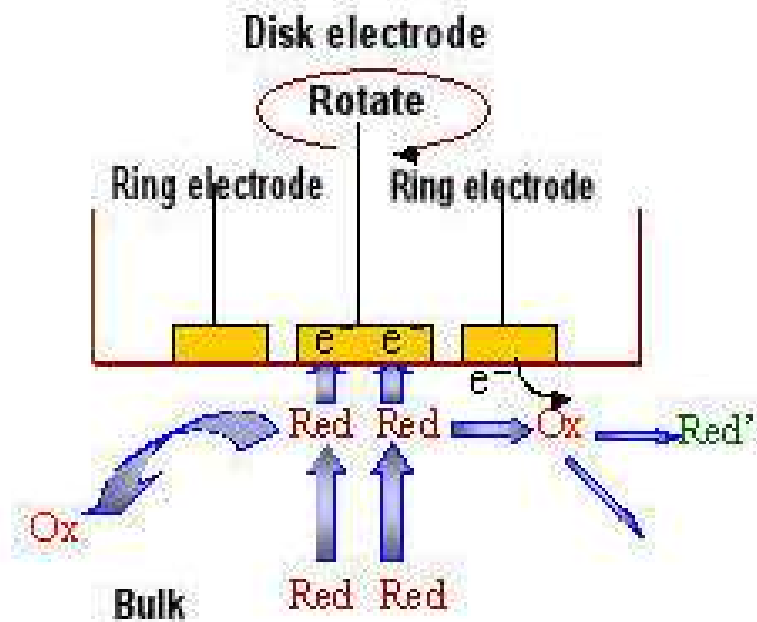


Koutecký-Levich plots from the curves on the left at fixed potentials as indicated. Extrapolation to infinite rotation speed, i.e. to zero gives kinetic current at each potential.



Plotting $\ln(i_{\text{kin}})$ as the function of potential gives exchange current density i_0 at $E = E^{0'}$.

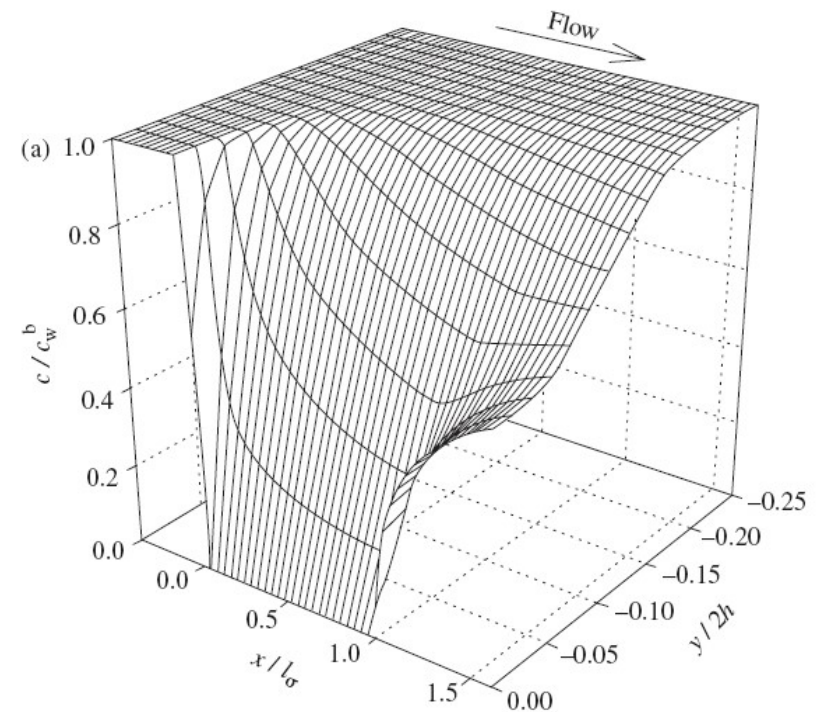
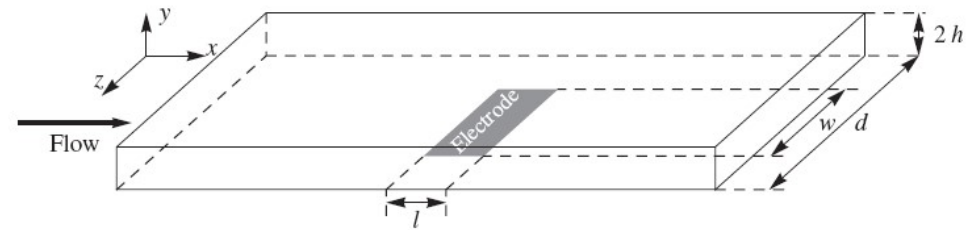
An RDE has an important modification, a rotating ring-disk electrode (RRDE) where a concentric ring is placed around the disk at the distance of the order of 1 mm. Its purpose is to detect species on the ring that are formed on the disk. This can help in the determination of the reaction mechanisms where reaction intermediates are short-lived. Calculus of the transport problem is rather demanding. An RRDE is calibrated by defining a **collector efficiency** with some known redox couple, i.e. what fraction of the species detected on the ring is, basically the ratio of the ring and disk currents.



Channel flow electrode

The channel flow electrode (CFE) is frequently used as a detector in liquid chromatography, capillary electrophoresis and flow injection analysis. In a typical experimental set-up aside, a channel electrode is located downstream after the separation unit and is biased at a sufficiently positive (or negative) potential such that the analyte is readily oxidized (reduced) at the electrode. Thus, a CFE is operated under limiting current conditions. The reference electrode is usually situated upstream of the working electrode, preferably via a liquid junction, while the counter electrode is placed downstream to prevent contamination of the working electrode due to the electrolysis products formed at the counter electrode.

Another large application area of CFEs is in the study of homogeneous chemical reactions (C) coupled to electrochemical reactions (E). Since hydrodynamics has a strong effect on the concentration profiles of the species reacting in the bulk of the solution, while the electrochemical step takes place at the electrode only, it is possible to distinguish between, say, CE and EC or ECE reaction mechanisms.



The mass transfer problem at a CFE can be solved in closed form, because the convection velocity can be determined from the solution of the Navier-Stokes equation. In the fully developed **Poiseuille flow** the flow profile is parabolic and the flow velocity is zero on the channel walls (**non-slip condition**). In a channel with a rectangular cross-section limiting current is obtained from the following equation that is also known as the Levich equation.

$$I_L = -0.9244 z_1 F D_1^{2/3} c_1^b w \left(\frac{\ell^2 \dot{V}}{h^2 d} \right)^{1/3} \quad (6.14)$$

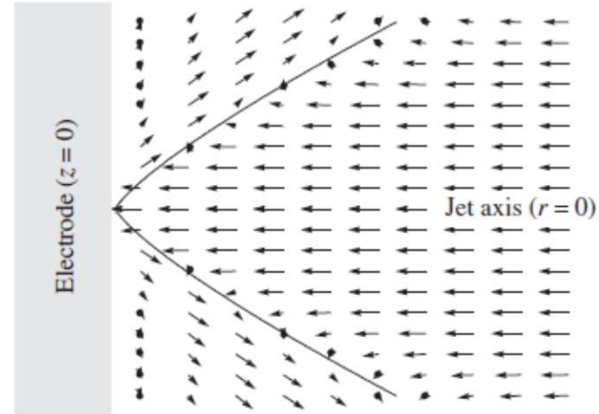
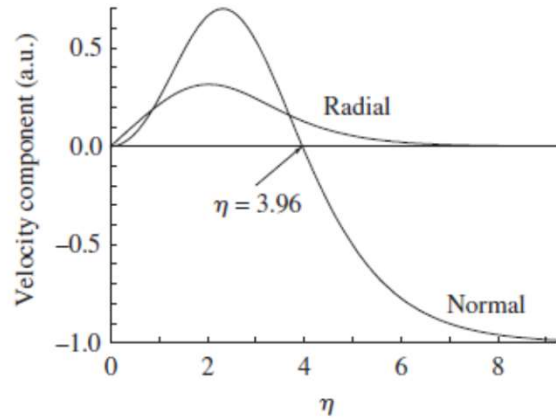
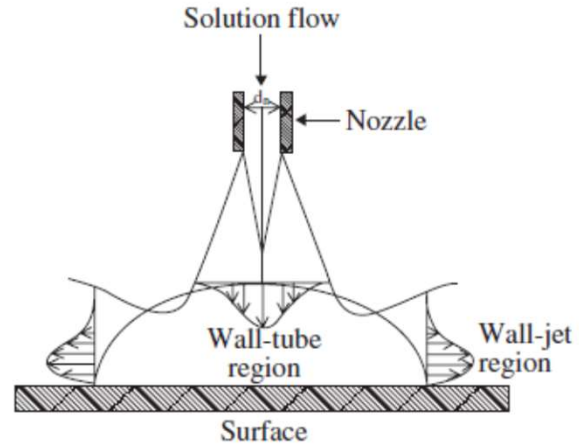
Sometimes the numerical coefficient is replaced by 0.835 depending on the simplifying assumptions made in the derivation of the velocity profile. The essential finding is, however, that the limiting current is proportional to the cubic root of the volume flow rate. In any case, a detector is always calibrated with known solutions prior to use.

Today the flow problem can be numerically solved in an arbitrary channel geometry (like in the picture on the previous page) but an analytical solution has the advantage that the dependence of current on the various parameters is explicitly known, while a number of numerical simulations must be carried out to see those correlations. In a numerical solution, the Navier-Stokes equation must be solved first and the obtained flow profile is then inserted in the convective diffusion equation. The numerical solution of fluid dynamics is, however, a very difficult task and large errors can easily be made if no cross-checking with experimental data is possible. Therefore, specific software packages have been developed for Computational Fluid Dynamics (CFD) purposes.

Wall-jet electrode:

Fig. 3.11.

Schematic picture of a wall-jet electrode. At the wall-tube region the axial and at the wall-jet region the radial velocity is governing. The lengths of the arrows indicate their relative magnitude. (Reproduced from Ref. [19] with permission.)



$$I_L = -1.3735z_1FD_1^{2/3}c_1^b \frac{(\dot{v}a)^{3/4}}{d_n^{1/2}v^{5/12}} \quad (6.15)$$

Some properties of Laplace transformation

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

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

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

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

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

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

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):

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

An initial condition is needed which is

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

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 :

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

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

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

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:

$$\frac{c_O^s}{c_R^s} = \theta = \exp\left[\frac{nF}{RT}(E - E^{0'})\right] \quad \text{reversible} \quad (7.5) \qquad \frac{i(t)}{nF} = k_{ox}c_R^s - k_{red}c_O^s \quad \text{quasi-reversible} \quad (7.6)$$

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

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

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 $x \rightarrow \infty$ (boundary condition, eq. (7.3)), it is required that $B(s) = 0$. $A(s)$ is found using the current boundary condition (7.4):

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

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

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

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

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

$$c_o^s = \theta c_R^s \Rightarrow \bar{c}_o^s = \theta \bar{c}_R^s$$

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

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

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,

$$I(t) = \frac{nF\sqrt{D_o}\theta c_R^b}{1 + \xi\theta} \frac{1}{\sqrt{\pi t}} \quad (7.12)$$

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

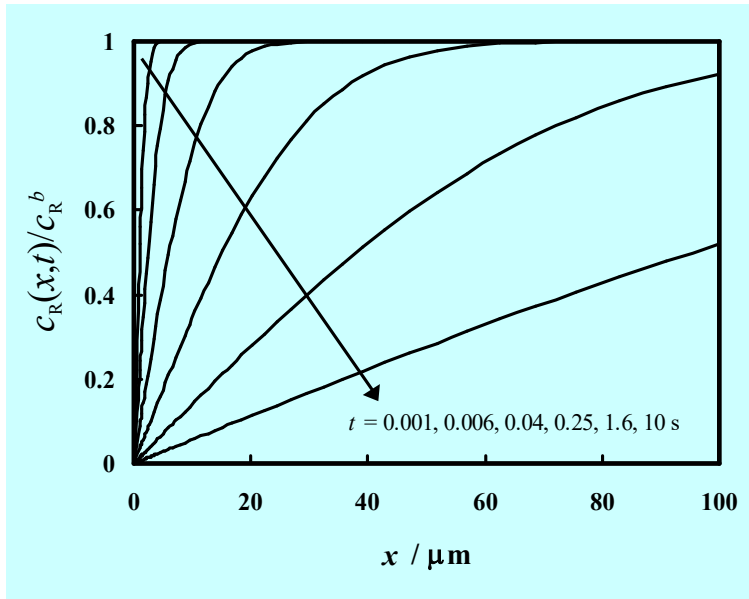
$$\bar{I}_d(s) = \frac{nF\sqrt{D_R} c_R^b}{\sqrt{s}} \Rightarrow I_d(t) = \frac{nF\sqrt{D_R} c_R^b}{\sqrt{\pi t}} \quad \text{Cottrell equation} \quad (7.13)$$

Inserting eq. (7.11) into eq. (7.9), the concentration profile is obtained in Laplace domain as

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

The inverse transform is found in the table as

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



$\operatorname{erf}(x)$ is the error function and $\operatorname{erfc}(x)$ its complement.

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

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

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 given by the **Sand equation**:

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

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:

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

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

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

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

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.

