Derivation of the Butler-Volmer equation

$$\boxed{\mathrm{R(soln)} \rightleftharpoons \mathrm{e^-} + \mathrm{O(soln)}}$$

$$v_{net}(E) = v_{ox}(E) - v_{rd}(E) = \frac{i(E)}{F}$$

$$v_{ox}(E) = k_{ox}(E)a_R^s = k_{ox}(E)\gamma_R\frac{c_R^s}{c^0} = k'_{ox}(E)c_R^s$$

$$v_{rd}(E) = k'_{rd}(E)c_O^s$$

$$\boxed{\frac{i(E)}{F} = k'_{ox}(E)c_R^s - k'_{rd}(E)c_O^s}$$

Note:
k'_{ox} and k'_{rd} depend on E only, not on c_R^s or c_O^s.

At the null potential E_n the current is zero per definition:

$$\frac{i(E)}{F} = k'_{ox}(E_n)c^b_R - k'_{rd}(E_n)c^b_O = 0 \qquad (1)$$

With no current Nernst applies:

$$E_n = E^{0'} - \frac{RT}{F} \ln\left\{\frac{c^b_R}{c^b_O}\right\} \qquad (2)$$

But Eq. (1) gives

$$\frac{c^b_R}{c^b_O} = \frac{k'_{rd}(E_n)}{k'_{ox}(E_n)} \qquad (3)$$

Insertion of Eq. (3) into Eq. (2)

$$E_n = E^{0'} - \frac{RT}{F} \ln\left\{\frac{k'_{rd}(E_n)}{k'_{ox}(E_n)}\right\} \qquad (4)$$

We can change E_n arbitratily by adjusting c_R^b and c_O^b.

Since $k'_{rd} = k'_{rd}(E)$ and $k'_{ox} = k'_{ox}(E)$ (functions of potential alone):

$$E = E^{0'} - \frac{RT}{F} \ln \left\{ \frac{k'_{rd}(E)}{k'_{ox}(E)} \right\} \qquad (5)$$

From Eq. (5) at $E = E^{0'}$ we must have

$$k'_{rd}(E^{0'}) = k'_{ox}(E^{0'}) = k^{0'}$$

Eq. (5) rearranged:

$$\frac{k'_{rd}(E)}{k'_{ox}(E)} = \exp\left\{-\frac{F\left(E - E^{0'}\right)}{RT}\right\} \qquad (6)$$

For arbitrary functions $\alpha(E)$ and $\beta(E)$ we can always write $k'_{rd}(E)$ and $k'_{ox}(E)$ as

$$k'_{ox}(E) = k^{0'} \exp\left\{\frac{\beta(E) F\left(E - E^{0'}\right)}{RT}\right\} \qquad (7)$$

$$k'_{rd}(E) = k^{0'} \exp\left\{-\frac{\alpha(E) F\left(E - E^{0'}\right)}{RT}\right\} \qquad (8)$$

Inserting Eqs. (7) and (8) into Eq. (6),

$$-\alpha(E) - \beta(E) = -1 \qquad (9)$$

or

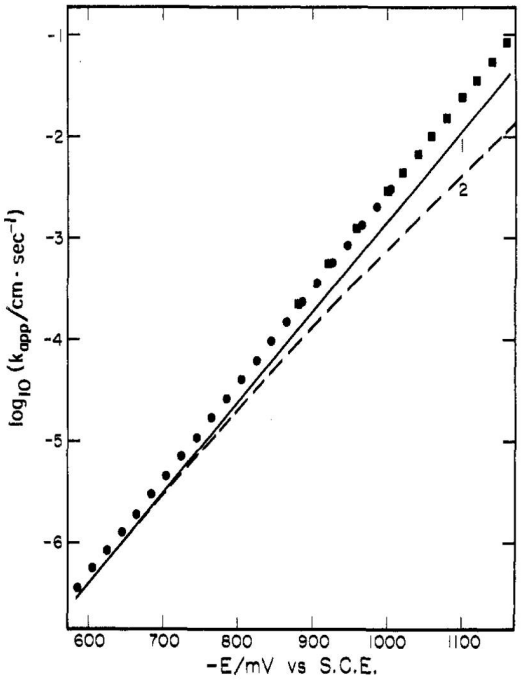
$$\beta(E) = 1 - \alpha(E) \qquad (10)$$

What is the function $\alpha\,(E)$?

The slope of $\ln k'_{rd}$ vs. the potential gives $\alpha\,(E)$:

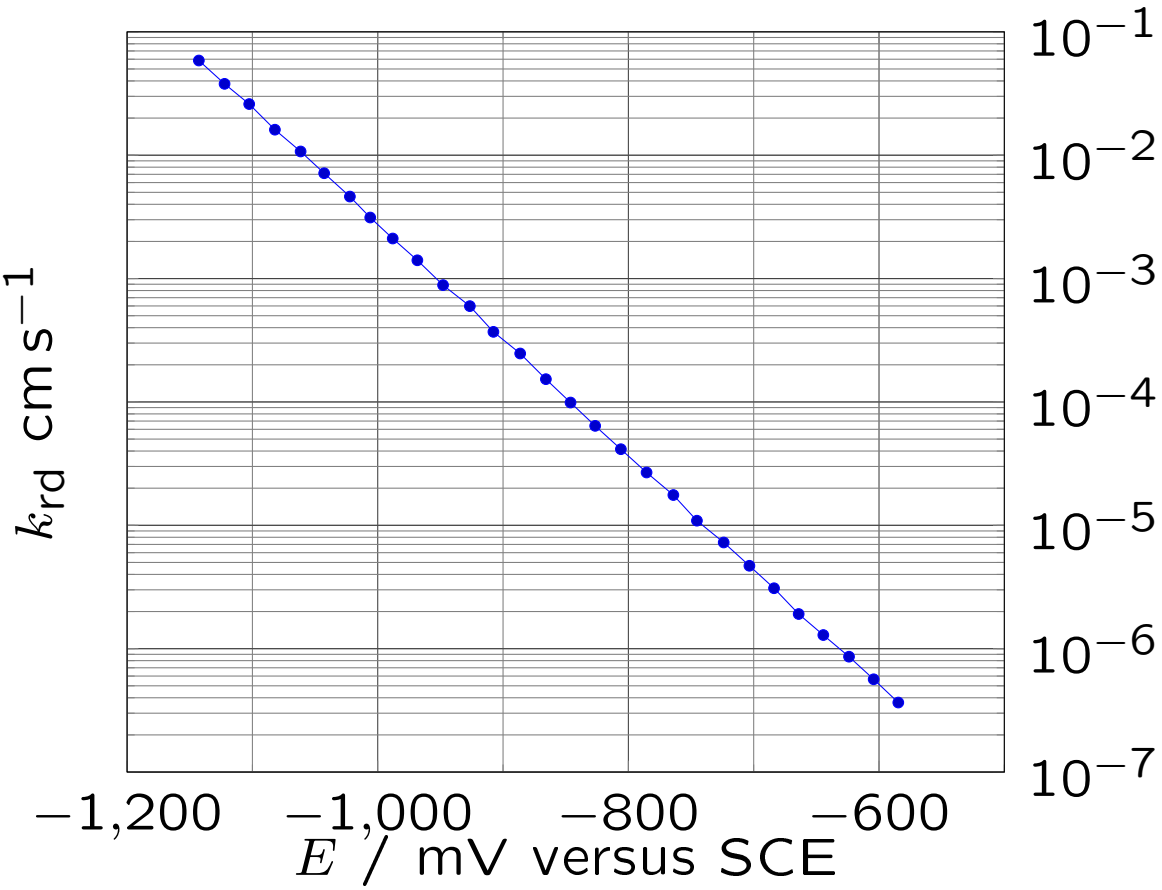
$$\ln\left\{\frac{k'_{rd}}{k^{0'}}\right\} = -\boxed{\alpha\,(E)} \times \frac{F}{RT}\left(E - E^{0'}\right)$$

Experiment: The slope is constant



Rate constant for the reduction of $[Cr(OH_2)_5OSO_3]^+$ (i.e. reduction of pentaaquasulfatochromium(III) to pentaaquasulfatochromium(II)) at single crystal gold electrodes in 1 mmol dm^{-3} $NaClO_4$ + 0.01 mmol dm^{-3} $HClO_4$. The electrode potential is measured versus a saturated calomel electrode. From Michael J. Weaver and Fred C. Anson, "Potential Dependence of the Electrochemical Transfer Coefficient. Further Studies of the Reduction of Chromium(III) at Mercury Electrodes", *J. Phys. Chem.* **80** (1976) 1861 – 1866

. . . and so is $\alpha\,(E)$!



Rate constant for the reduction of $[Cr(OH_2)_5OSO_3]^+$ at Hg electrodes in 1 mmol dm^{-3} $NaClO_4$ + 0.01 mmol dm^{-3} $HClO_4$. From Michael J. Weaver and Fred C. Anson, *J. Phys. Chem.* **80** (1976) 1861 – 1866

The symmetry factor α

$$\boxed{\beta = 1 - \alpha}$$

$$k'_{rd} = k^{0'} \exp\left\{\frac{-\alpha F}{RT}\left(E - E^{0'}\right)\right\}$$

$$k'_{ox} = k^{0'} \exp\left\{\frac{(1-\alpha)\, F}{RT}\left(E - E^{0'}\right)\right\}$$

$$\frac{I}{A} = i = F\left[-k'_{rd} c^s_O + k'_{ox} c^s_R\right]$$

The Butler-Volmer equation

$$\frac{I}{A} = i = Fk^{0'}\left[-c_O^s \exp\left\{\frac{-\alpha F}{RT}\left(E - E^{0'}\right)\right\} + c_R^s \exp\left\{\frac{(1-\alpha)\,F}{RT}\left(E - E^{0'}\right)\right\}\right] \tag{11}$$

$$\frac{I}{A} = i = i_n\left[-\frac{c_O^s}{c_O^b}\exp\left\{\frac{-\alpha F}{RT}\left(E - E_n\right)\right\} + \frac{c_R^s}{c_R^b}\exp\left\{\frac{(1-\alpha)\,F}{RT}\left(E - E_n\right)\right\}\right] \tag{12}$$

The *exchange current density*:

$$\boxed{i_n = Fk^{0'}\left(c_R^b\right)^{\alpha}\left(c_O^b\right)^{1-\alpha}}$$

Fig. 7-3

Proof that Eqs. (11) and (12) are equivalent

Eq. (11) may be written

$$i = Fk^{0'}\left[-c_O^s \quad \times \right.$$

$$\exp\left\{\frac{-\alpha F}{RT}\left(E - E^{0'} + \frac{RT}{F}\ln\left(\frac{c_R^b}{c_O^b}\right) - \frac{RT}{F}\ln\left(\frac{c_R^b}{c_O^b}\right)\right)\right\}$$

$$+ c_R^s \times$$

$$\exp\left\{\frac{(1-\alpha)\,F}{RT}\left(E - E^{0'} + \frac{RT}{F}\ln\left(\frac{c_R^b}{c_O^b}\right)\right.\right.$$

$$\left.\left.\left. - \frac{RT}{F}\ln\left(\frac{c_R^b}{c_O^b}\right)\right)\right\}\right] \quad (13)$$

But

$$-E^{0'} + \frac{RT}{F}\ln\left(\frac{c_R^b}{c_O^b}\right) = -E_\mathrm{n} \quad (14)$$

$$i = Fk^{0'} \left[-c_O^s \exp\left\{ \frac{-\alpha F}{RT} \left(E - E_\mathrm{n} \right) \right\} \exp\left\{ \alpha \ln\left(\frac{c_R^b}{c_O^b} \right) \right\} + c_R^s \exp\left\{ \frac{(1-\alpha) F}{RT} \left(E - E_\mathrm{n} \right) \right\} \exp\left\{ -(1-\alpha) \ln\left(\frac{c_R^b}{c_O^b} \right) \right\} \right] \quad (15)$$

$$i = Fk^{0'} \left[-c_O^s \left(\frac{c_R^b}{c_O^b} \right)^{\alpha} \exp\left\{ \frac{-\alpha F}{RT} \left(E - E_\mathrm{n} \right) \right\} + c_R^s \left(\frac{c_R^b}{c_O^b} \right)^{-(1-\alpha)} \exp\left\{ \frac{(1-\alpha) F}{RT} \left(E - E_\mathrm{n} \right) \right\} \right] \quad (16)$$

$$i = Fk^{0'}\left[-\frac{c_O^s c_O^b}{c_O^b}\left(\frac{c_R^b}{c_O^b}\right)^{\alpha}\exp\left\{\frac{-\alpha F}{RT}\left(E-E_{\mathsf{n}}\right)\right\}\right.$$
$$\left.+\frac{c_R^s c_R^b}{c_R^b}\left(\frac{c_R^b}{c_O^b}\right)^{-(1-\alpha)}\exp\left\{\frac{(1-\alpha)\,F}{RT}\left(E-E_{\mathsf{n}}\right)\right\}\right] \tag{17}$$

$$i = Fk^{0'}\left(c_O^b\right)^{1-\alpha}\left(c_R^b\right)^{\alpha}\left[-\frac{c_O^s}{c_O^b}\exp\left\{\frac{-\alpha F}{RT}\left(E-E_{\mathsf{n}}\right)\right\}\right.$$
$$\left.+\frac{c_R^s}{c_R^b}\exp\left\{\frac{(1-\alpha)\,F}{RT}\left(E-E_{\mathsf{n}}\right)\right\}\right] \tag{18}$$

Simplified form for stirred solutions

Assuming

$$c_R^s \approx c_R^b;\ c_O^s \approx c_O^b \tag{19}$$

then

$$i = Fk^{0'} \left(c_O^b\right)^{1-\alpha} \left(c_R^b\right)^{\alpha} \left[-\exp\left\{\frac{-\alpha F}{RT}\left(E - E_{\mathsf{n}}\right)\right\} + \exp\left\{\frac{(1-\alpha)\,F}{RT}\left(E - E_{\mathsf{n}}\right)\right\}\right] \tag{20}$$

or

$$i = i_{\mathsf{n}}\left[e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}\right]$$

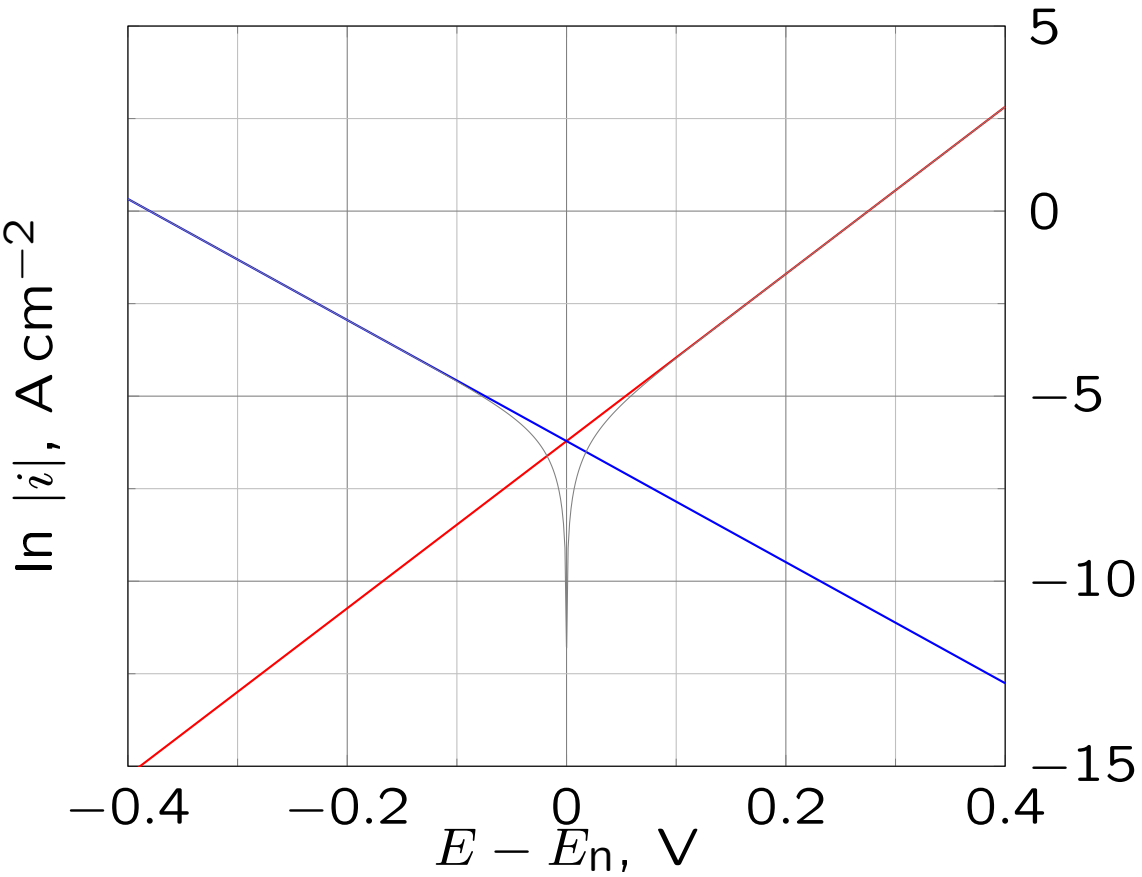
where η is the *overpotential* $\eta = E - E_{\mathsf{n}}$ and $f = F/RT$.

Approximate expressions:

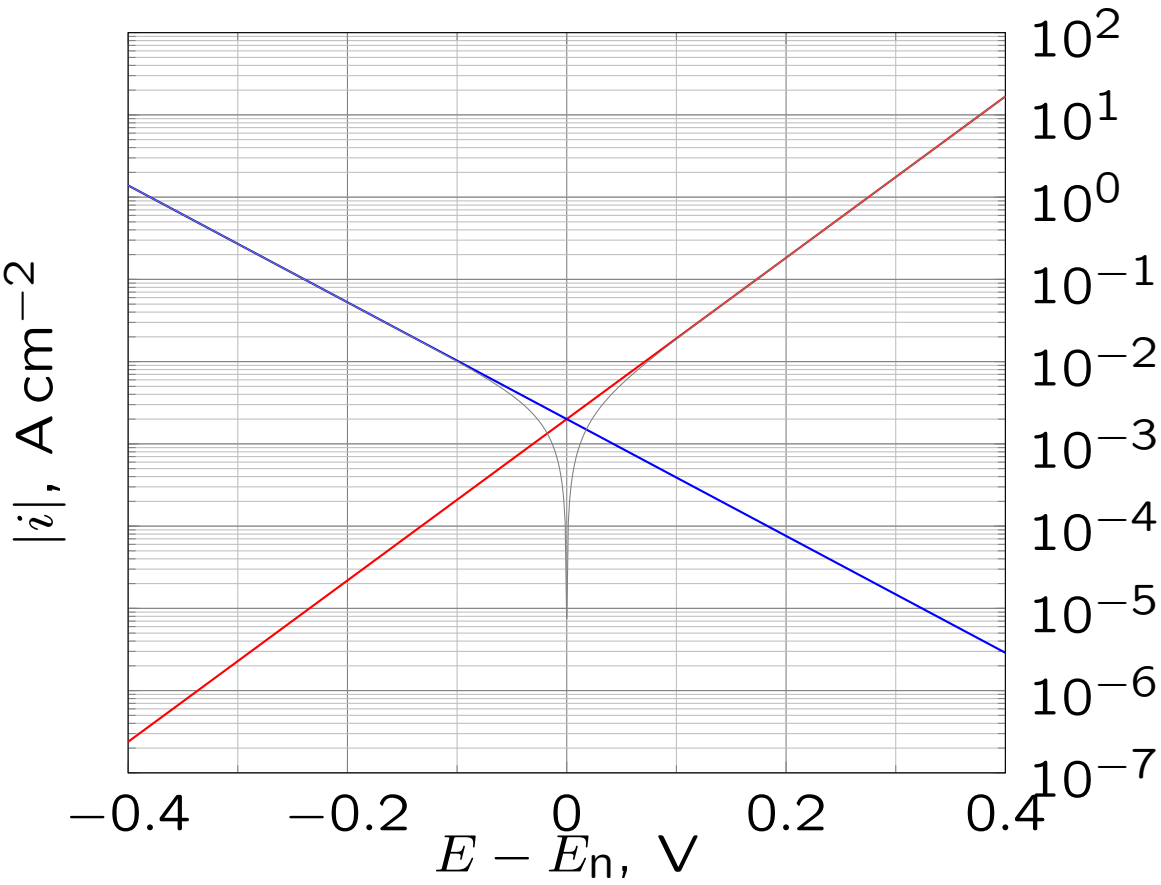
$$\boxed{i\left(\eta\right) \approx \begin{cases} i_{\mathsf{n}} e^{(1-\alpha)f\eta} & : \quad \eta >> 0 \\ -i_{\mathsf{n}} e^{-\alpha f\eta} & : \quad \eta << 0 \end{cases}} \tag{21}$$

Example

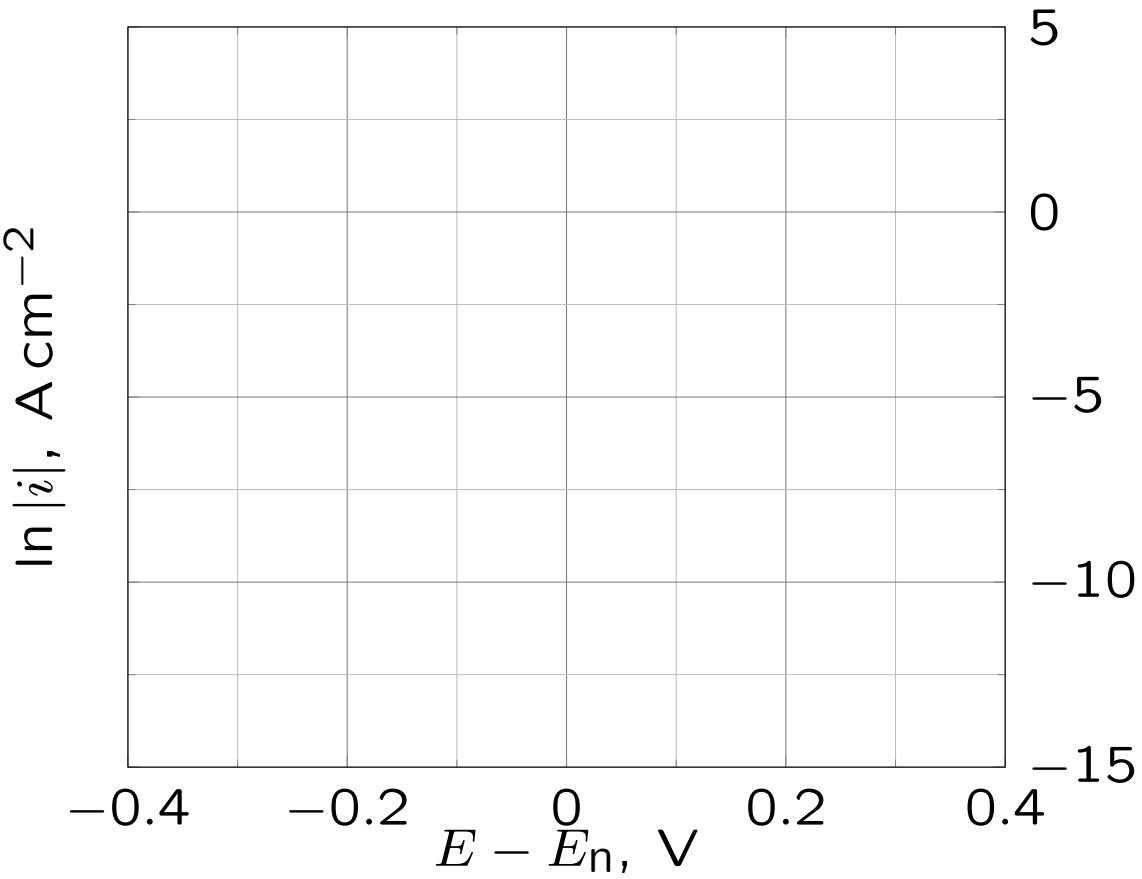
0.005 mol dm^{-3} Fe^{3+}/Fe^{2+} ($Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$) in 1 mol dm^{-3} H_2SO_4 at Pt electrodes: $\alpha = 0.42$, $i_n = 2 \times 10^{-3}$ A cm^{-2}



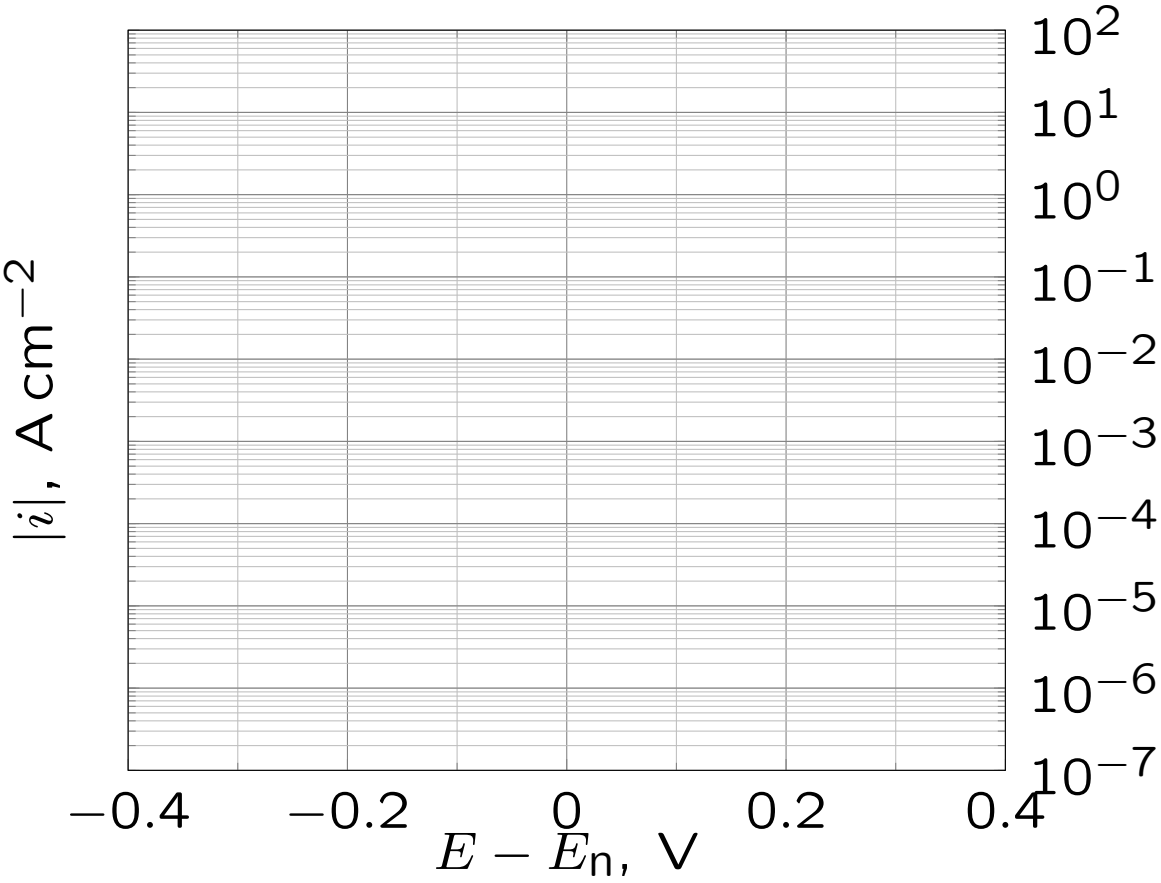
Or since $\ln x = \log 10 \log x$ . . .



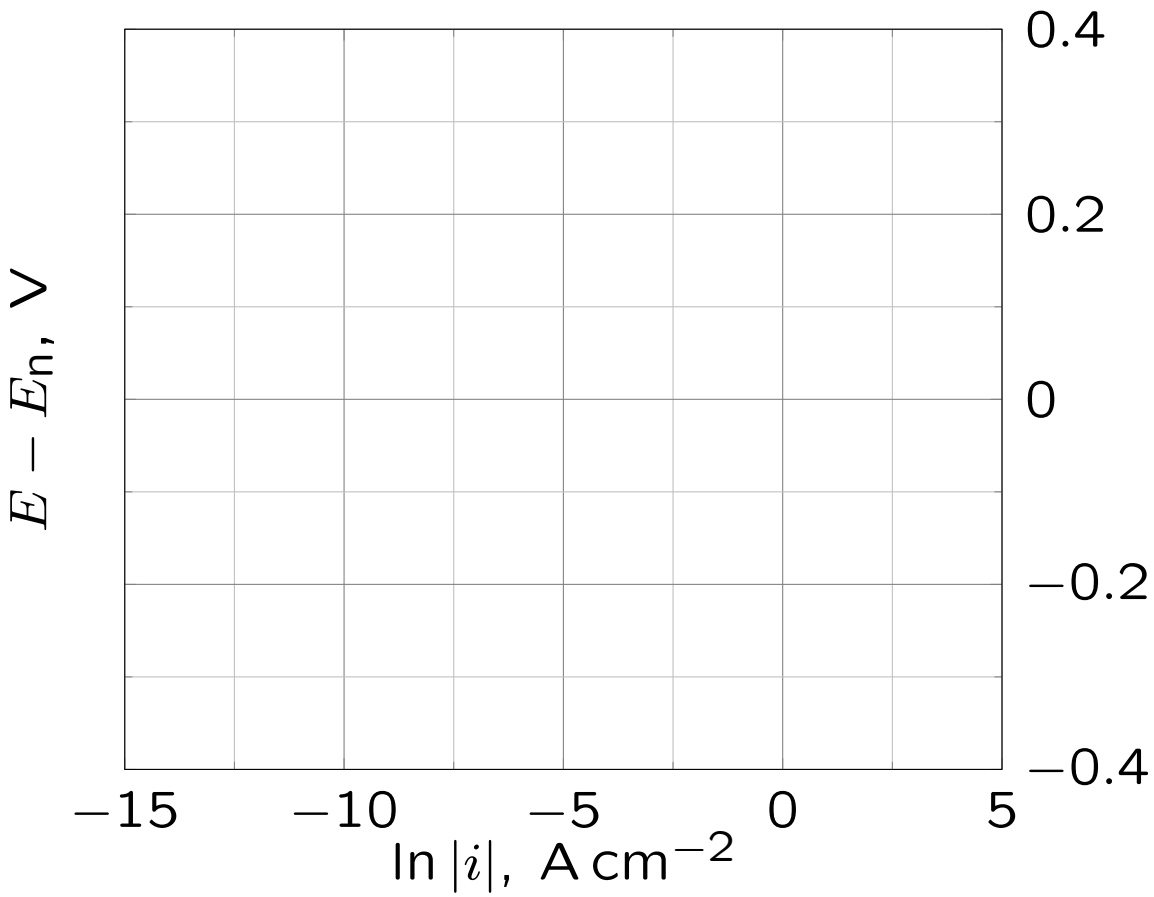
$E - \ln i$ diagram for kinetic data



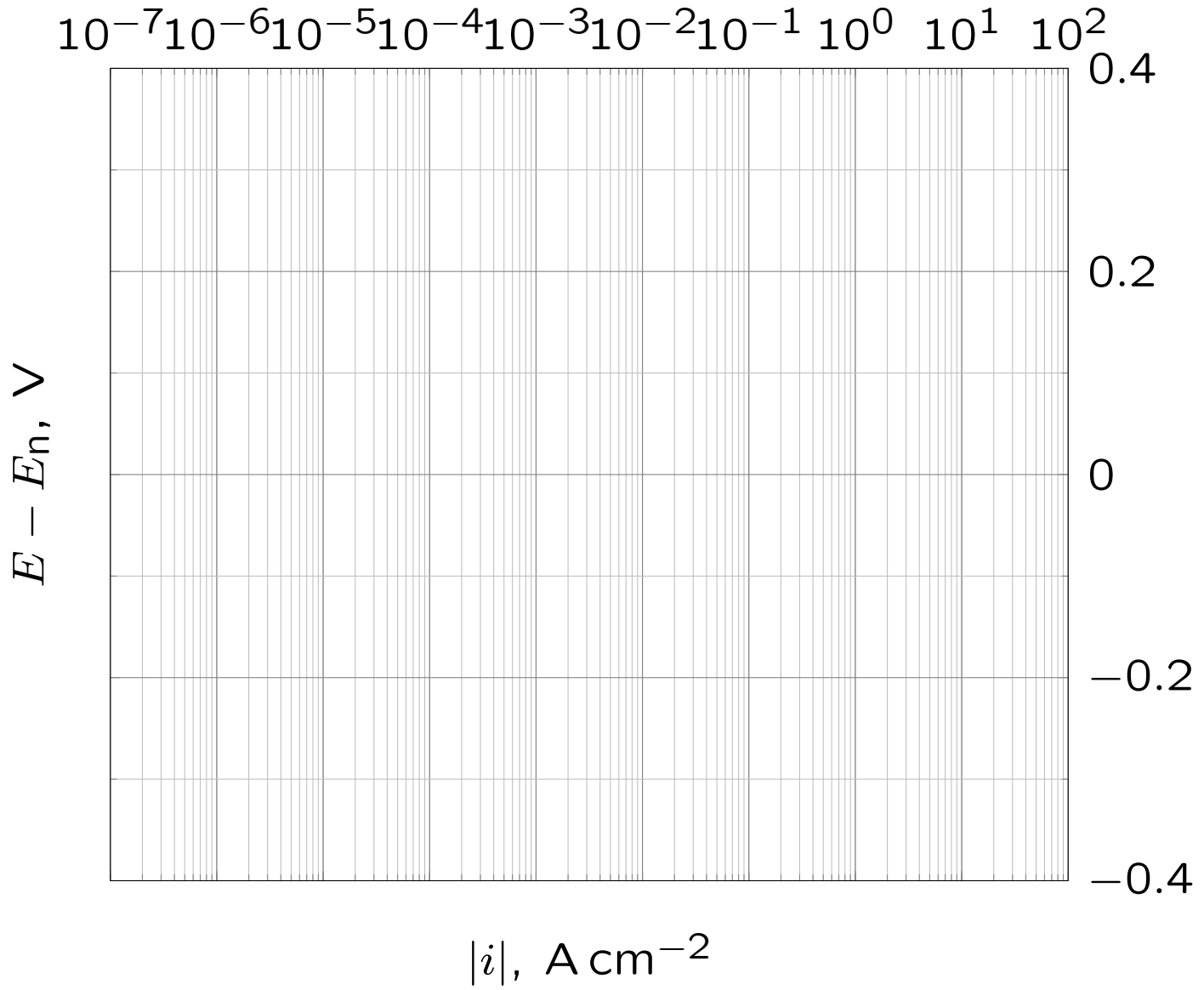
$E - \log i$ diagram for kinetic data



$\ln i - E$ diagram for kinetic data



$\log i - E$ diagram for kinetic data



$\log i - E$ diagram for kinetic data