Norwegian University of Science
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TMT4252
Electrochemistry
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Lecture Notes on the
Reciprocal Sum Formula

1 An Overpotential Equation for One-Electron Transfer Limited by Transport and Kinetics

For a one-electron, single-step reaction $\mathrm{O} + \mathrm{e}^- \rightleftharpoons \mathrm{R}$ the Butler-Volmer equation reads

$$\frac{I}{A} = i = i_n \left[-\frac{c_\mathrm{O}^s}{c_\mathrm{O}^b} \exp\left\{ \frac{-\alpha F}{RT} (E - E_n) \right\} + \frac{c_\mathrm{R}^s}{c_\mathrm{R}^b} \exp\left\{ \frac{(1-\alpha) F}{RT} (E - E_n) \right\} \right] \tag{1}$$

where i_n is the *exchange current density*:

$$i_\mathrm{n} = F k^{0'} \left(c_\mathrm{R}^b \right)^\alpha \left(c_\mathrm{O}^b \right)^{1-\alpha} \tag{2}$$

If $c_\mathrm{O}^s = c_\mathrm{O}^b$ and $c_\mathrm{R}^s = c_\mathrm{R}^b$ Eq. (1) is complete. In general we may not assume bulk and surface concentrations to be equal, however, and we need to take into account any differences in these in the current-overpotential relation.

In cases where the flux towards the electrode may be expressed as

$$j_i^s = m_i \left(c_i^s - c_i^b \right) \tag{3}$$

Eq. (3) applies in experiments such as potential leap experiments or steady-state voltammetry when a supporting electrolyte has been added to the solution. Faraday's law gives

$$\frac{i}{F} = -j_\mathrm{R}^s = j_\mathrm{O}^s \tag{4}$$

if we employ an axis system with the x-axis pointing away from the electrode. (Each time an R molecule reaches the electrode an electron is transferred to it from R, which results in a positive (anodic) current. However, due to the positioning of the axis system this corresponds to a negative flux. A similar reasoning applies to the relation between j_O^s and i.)

The maximum anodic current that can be drawn is, accordingly,

$$i_{lim}^{an} = -F m_\mathrm{R} \left(-c_\mathrm{R}^b \right) = F m_\mathrm{R} c_\mathrm{R}^b \tag{5}$$

since the concentration of R at the electrode, c_R^s, can never be less than zero. The most negative (i. e. cathodic) current that can be drawn is, correspondingly,

$$i_{lim}^{cath} = F m_\mathrm{O} \left(-c_\mathrm{O}^b \right) = -F m_\mathrm{O} c_\mathrm{O}^b \tag{6}$$

since the concentration of R at the electrode, c^s_{R}, can never be less than zero. Combining Eqs. (3) and (4) gives

$$\frac{i}{F} = j^s_{\mathrm{O}} = m_{\mathrm{O}}\left(c^s_{\mathrm{O}} - c^b_{\mathrm{O}}\right)$$

and

$$\frac{i}{F} = -j^s_{\mathrm{R}} = -m_{\mathrm{R}}\left(c^s_{\mathrm{R}} - c^b_{\mathrm{R}}\right)$$

which we reorganize to give

$$Fm_{\mathrm{O}}c^s_{\mathrm{O}} = i + Fm_{\mathrm{O}}c^b_{\mathrm{O}} \tag{7}$$

and

$$Fm_{\mathrm{R}}c^s_{\mathrm{R}} = -i + Fm_{\mathrm{R}}c^b_{\mathrm{R}}. \tag{8}$$

or

$$\frac{c^s_{\mathrm{O}}}{c^b_{\mathrm{O}}} = 1 + \frac{i}{Fm_{\mathrm{O}}c^b_{\mathrm{O}}} \tag{9}$$

and

$$\frac{c^s_{\mathrm{R}}}{c^b_{\mathrm{R}}} = 1 - \frac{i}{Fm_{\mathrm{R}}c^b_{\mathrm{R}}} \tag{10}$$

Use of Eqs. (5) and (6),

$$i^{cath}_{lim} = -Fm_{\mathrm{O}}c^b_{\mathrm{O}}$$
$$i^{an}_{lim} = Fm_{\mathrm{R}}c^b_{\mathrm{R}}$$

gives

$$\frac{c^s_{\mathrm{O}}}{c^b_{\mathrm{O}}} = 1 - \frac{i}{i^{cath}_{lim}} \tag{11}$$

and

$$\frac{c^s_{\mathrm{R}}}{c^b_{\mathrm{R}}} = 1 - \frac{i}{i^{an}_{lim}} \tag{12}$$

Eqs. (11) and (12) inserted into Eq. (1) gives

$$\frac{i}{i_{\mathrm{n}}} = -\left(1 - \frac{i}{i^{cath}_{lim}}\right)\exp\left(\frac{-\alpha F}{RT}\eta\right) + \left(1 - \frac{i}{i^{an}_{lim}}\right)\exp\left\{\frac{(1-\alpha)F}{RT}\eta\right\} \tag{13}$$

with $\eta = E - E_n$. Introducing

$$b = \exp\left(\frac{F}{RT}\eta\right) \tag{14}$$

we obtain

$$\frac{i}{i_{\mathrm{n}}} = -\left(1 - \frac{i}{i^{cath}_{lim}}\right)b^{-\alpha} + \left(1 - \frac{i}{i^{an}_{lim}}\right)b^{1-\alpha} \tag{15}$$

Collecting terms proportional to i gives

$$\frac{1}{i_{\mathrm{n}}} - \frac{b^{-\alpha}}{i^{cath}_{lim}} + \frac{b^{1-\alpha}}{i^{an}_{lim}} = \frac{1}{i}\left(b^{1-\alpha} - b^{-\alpha}\right) = \frac{1}{i}\frac{b-1}{b^{\alpha}} \tag{16}$$

$$\frac{b^{\alpha}}{b-1}\left[\frac{1}{i_{\mathrm{n}}} - \frac{b^{-\alpha}}{i^{cath}_{lim}} + \frac{b^{1-\alpha}}{i^{an}_{lim}}\right] = \frac{1}{i} \tag{17}$$

or finally

$$\boxed{\frac{1}{i} = \frac{1}{i_{kin}} + \frac{1}{i_{rem}} + \frac{1}{i_{lim}}} \tag{18}$$

where

$$i_{kin} = i_{\mathrm{n}}\left(b^{1-\alpha} - b^{-\alpha}\right) \tag{19}$$

$$i_{rem} = (1-b)\, i_{lim}^{cath} \tag{20}$$

$$i_{lim} = \left(\frac{b-1}{b}\right) i_{lim}^{an} \tag{21}$$

in which bulk concentrations are supposed to be used in the first equation (Butler-Volmer). In the limits of large negative ($b << 1$) or large positive potentials ($b >> 1$) the two last equations become or

$$\lim_{b\to 0} i_{rem} = i_{lim}^{cath};\ \text{cathodic limiting current if } b << 1 \tag{22}$$

$$\lim_{b\to\infty} i_{lim} = i_{lim}^{an};\ \text{anodic limiting current if } b >> 1 \tag{23}$$

2 Limiting Case for Infinitely Fast Kinetics

If the exchange current density is vary fast, i.e. $i_{\mathrm{n}} \to \infty$, one may write an approximated Eq. (17) as

$$\frac{b-1}{i} = \frac{b}{i_{lim}^{an}} - \frac{1}{i_{lim}^{cath}} \tag{24}$$

We solve Eq. (24) with respect to b,

$$b\left(\frac{1}{i} - \frac{1}{i_{lim}^{an}}\right) = \frac{1}{i} - \frac{1}{i_{lim}^{cath}} \tag{25}$$

$$\ln b = \ln\left(\frac{\frac{1}{i} - \frac{1}{i_{lim}^{cath}}}{\frac{1}{i} - \frac{1}{i_{lim}^{an}}}\right) \tag{26}$$

$$\ln b = \ln\left(\frac{1 - \frac{i}{i_{lim}^{cath}}}{1 - \frac{i}{i_{lim}^{an}}}\right) \tag{27}$$

$$\ln b = \ln\left(1 - \frac{i}{i_{lim}^{cath}}\right) - \ln\left(1 - \frac{i}{i_{lim}^{an}}\right) \tag{28}$$

and using Eq. (14) to solve for the transport overpotential[1],

$$\frac{F\eta_{\mathrm{trans}}}{RT} = \ln\left(1 - \frac{i}{i_{lim}^{cath}}\right) - \ln\left(1 - \frac{i}{i_{lim}^{an}}\right) \tag{29}$$

which can be written

$$\frac{F\eta_{\mathrm{trans}}}{RT} = \ln\left(\frac{1 - \frac{i}{i_{lim}^{cath}}}{1 - \frac{i}{i_{lim}^{an}}}\right) = \ln\left(\frac{i - i_{lim}^{cath}}{i_{lim}^{an} - 1}\right) + \ln\left(\frac{i_{lim}^{an}}{-i_{lim}^{cath}}\right) \tag{30}$$

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[1] The overpotential is now a pure transport overpotential since kinetics does not contribute.

In the last equation we have multiplied numerator and denominator in the argument of the ln-function in the first equation both with $-i_{lim}^{cath} i_{lim}^{an}$. (We multiply with $-i_{lim}^{cath}$; i_{lim}^{cath} is negative and the minus sign makes all arguments of the ln-functions positive, which is a convenient way of writing the equations.)

We can express Eq. (30) as[2]

$$E \approx E_{1/2} + \frac{RT}{F} \ln \left(\frac{i - i_{lim}^{cath}}{i_{lim}^{an} - i} \right) \tag{31}$$

in which

$$E_{1/2} = E_{\mathrm{n}} - \frac{RT}{F} \ln \left(\frac{-i_{lim}^{cath}}{i_{lim}^{an}} \right) = E_{\mathrm{n}} - \frac{RT}{F} \ln \left(\frac{m_{\mathrm{O}} c_{\mathrm{O}}^{b}}{m_{\mathrm{R}} c_{\mathrm{R}}^{b}} \right) \tag{32}$$

$E_{1/2}$ is frequently referred to as the *half-wave potential.*

3 Limiting Case for Infinitely Fast Transport

In this case Eq. (18) reduces to the Butler-Volmer equation for one-electron transfer.

4 Limiting Cases for High and Large Negative Overpotentials

These cases have already been referred to above in Eqs. (19) through Eq. (21), but are highlighted here in the box below.

$\eta >> 0 \Rightarrow b >> 1$ (anodic limits):

$$i_{kin} \approx i_n b^{1-\alpha}; \text{ anodic Tafel} \tag{33}$$

$$i_{rem} \approx -b\, i_{lim}^{cath} \tag{34}$$

$$i_{lim} \approx i_{lim}^{an} \tag{35}$$

$$\frac{1}{i} \approx \frac{1}{i_{kin}} + \frac{1}{i_{lim}} \overset{\text{ultimately}}{\rightarrow} \frac{1}{i_{lim}} \tag{36}$$

$\eta << 0 \Rightarrow b << 1$ (cathodic limits):

$$i_{kin} \approx -i_n b^{-\alpha}; \text{ cathodic Tafel} \tag{37}$$

$$i_{rem} \approx i_{lim}^{cath} \tag{38}$$

$$i_{lim} \approx -\left(\frac{1}{b}\right) i_{lim}^{an} \tag{39}$$

$$\frac{1}{i} \approx \frac{1}{i_{kin}} + \frac{1}{i_{rem}} \overset{\text{ultimately}}{\rightarrow} \frac{1}{i_{rem}} \tag{40}$$

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[2] Recall that $\eta = E - E_{\mathrm{n}}$.

In this case Eq. (18) reduces to the Butler-Volmer equation for one-electron transfer.

5 A General Overvoltage Equation for One-Electron Transfer

In supported electrolytes, a general equation for the electrode potential for one-electron transfer in the presence of ohmic, transport, and kinetic overvoltage is given (without derivation[3]) by

$$\frac{F\left[\exp\left\{F\left(\eta - iR_{\text{cell}}A\right)/RT\right\} - 1\right]}{i} = \frac{\exp\left\{\alpha F\left(\eta - iR_{\text{cell}}A\right)/RT\right\}}{k^{0'}\left(c_R^b\right)^{\alpha}\left(c_O^b\right)^{1-\alpha}} + \frac{1}{m_O c_O^b} + \frac{\exp\left\{F\left(\eta - iR_{\text{cell}}A\right)/RT\right\}}{m_R c_R^b} \tag{41}$$

In this equation, R_{cell} is the (area specific) cell resistance, $k^{0'}$ the formal rate constant, and A the electrode area. The equation is implicit and must be solved numerically. A *Python* code for doing so is provided below. The calculations are performed in terms of the following dimensionless parameters, for some of which the user is prompted:

Dimensionless anodic limiting current: $\iota_{\text{lim}}^{an} = i_{\text{lim}}^{an}/i_{\text{n}} = Fm_{\text{R}}c_{\text{R}}^{b}/i_{\text{n}}$

Dimensionless cathodic limiting current: $\iota_{\text{lim}}^{cath} = i_{\text{lim}}^{cath}/i_{\text{n}} = -Fm_{\text{O}}c_{\text{O}}^{b}/i_{\text{n}}$

Dimensionless resistance: $\rho = i_{\text{n}}FR_{\text{cell}}A/RT$

Dimensionless potential: $\Delta = FE/RT$

Dimensionless current: $\iota = i/i_{\text{n}}$

The symmetry factor also needs to be entered, but is already dimensionless

Examples of calculated results are given in Figures 1 through 3. Which corresponds to which type of control?

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[3] Eq. (41) may be derived by redefining b as $b = \exp\left\{F\left(\eta - iR_{\text{cell}}A\right)/RT\right\}$, i.e. by correcting the measured overpotential for any ohmic potential difference between the reference and the working electrodes. Eq. (41) may be written as

$$\frac{\exp\left\{F\left(\eta - iR_{\text{cell}}A\right)/RT\right\} - 1}{i} = \frac{\exp\left\{\alpha F\left(\eta - iR_{\text{cell}}A\right)/RT\right\}}{Fk^{0'}\left(c_R^b\right)^{\alpha}\left(c_O^b\right)^{1-\alpha}} + \frac{1}{Fm_O c_O^b} + \frac{\exp\left\{F\left(\eta - iR_{\text{cell}}A\right)/RT\right\}}{Fm_R c_R^b}$$

or with the re-defined b as

$$\frac{b-1}{i} = \frac{b^{\alpha}}{i_{\text{n}}} - \frac{1}{i_{lim}^{cath}} + \frac{b}{i_{lim}^{an}}$$

and finally by

$$\frac{1}{i} = \frac{b^{\alpha}}{b-1}\left[\frac{1}{i_{\text{n}}} - \frac{b^{-\alpha}}{i_{lim}^{cath}} + \frac{b^{1-\alpha}}{i_{lim}^{an}}\right]$$

which is identical to Eq. (17) and hence also to Eq. (18).

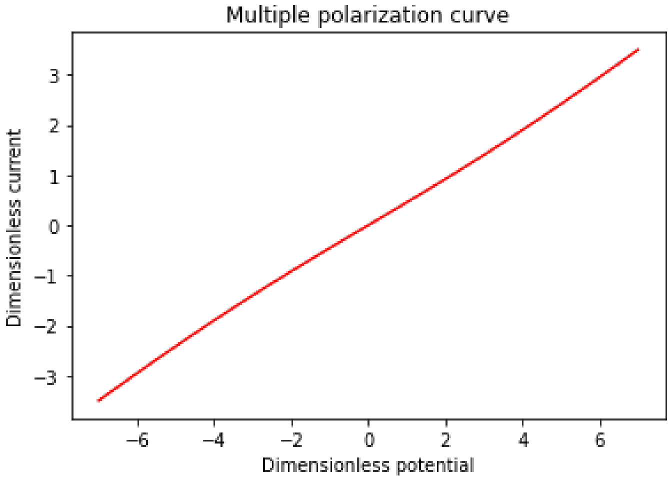

Figure 1: Computation of current-potential curve for $\alpha = 0.5$, $\iota_{\lim}^{an} = 10$, $\iota_{\lim}^{cath} = -10$, and $\rho = 1$, for which the current-potential relation is almost purely ohmic.

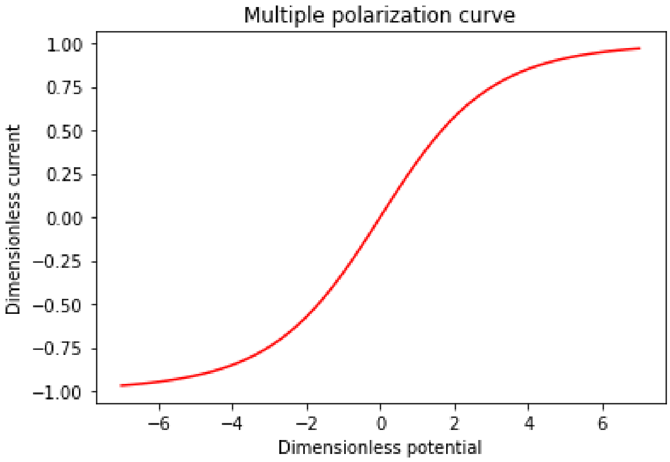

Figure 2: Computation of current-potential curve for $\alpha = 0.5$, $\iota_{\lim}^{an} = 1$, $\iota_{\lim}^{cath} = -1$, and $\rho = 0.01$, conditions corresponding to mass-trasnport limitations.

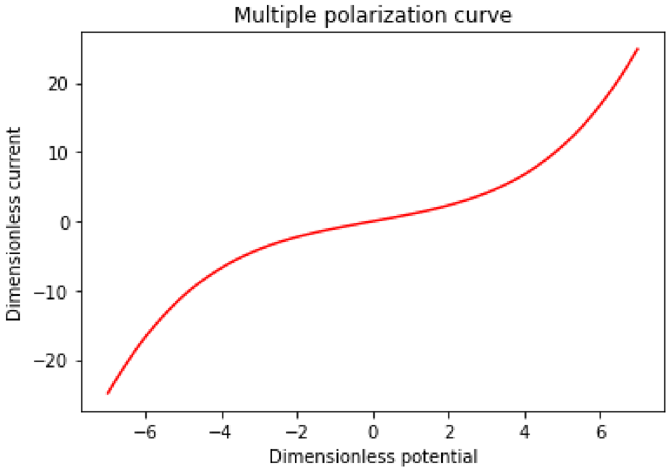

Figure 3: Computation of current-potential curve for $\alpha = 0.5$, $\iota_{\lim}^{an} = 100$, $\iota_{\lim}^{cath} = -100$, and $\rho = 0$. The current-potential relation is clearly dominated by kinetics for these parameters.

A Python code for dimensionless current vs. dimesionless potential

```
Created on Sat Apr 17 17:31:25 2021

@author: sveinsu

import math
import matplotlib.pyplot as plt

#Global constants
JMAX = 100 #Max number of iterations
NMAX = 100 #Number of points in plot
xacc = 1e-7 #Convergence criterion

def current(xi0):
    b = math.exp(theta-rho*xi0)
    xikin = b**(1.-alpha) - b**(-alpha)
    xirem = (1-b)*xilimcath
    xilim = ((b-1)/b)*xiliman
    if theta*theta < 1e-12:
        xi1 = 0.
    else:
        xi1 = 1./(1/xikin + 1./xirem + 1./xilim)
    return xi0 - xi1

def rtbis(func,x1,x2,xacc):
    #Bisection method
    fmid = func(x2)
    f = func(x1)
    if f*fmid > 0:
        print('Root must be bracketed in rtbis')
    if f < 0:
        rtbisec = x1
        dx = x2 - x1
    else:
        rtbisec = x2
        dx = x2 - x1
    j = 0
    while j < JMAX and abs(dx) > xacc and fmid != 0:
        j = j + 1
        dx = dx * .5
        xmid = rtbisec + dx
        fmid = func(xmid)
        if fmid < 0:
            rtbisec = xmid
        if j == JMAX:
            print('Too many bisections in rtbis. j = ',j,', rtbisec = ',rtbisec)
```

```
    #print(j,dx,xacc,fmid,rtbisec) #Debug statement
    return rtbisec

def main():
    global alpha,xiliman,xilimcath,rho,theta
    print('Plots current-voltage relationships for one-electron transfer.')
    print('Note. Dimensionless presentation.')
    str = input('Charge-transfer coefficient = ? ')
    alpha = float(str)
    str = input('Dimensionless anodic limiting-current density = ? ')
    xiliman = float(str)
    str = input('Dimensionless cathodic limiting-current density (< 0) = ? ')
    xilimcath = float(str)
    str = input('Dimensionless resistance = ? ')
    rho =  float(str)

    thetas = []
    xi = []

    imax=102
    for ii in range(imax):
        thetas.append(-7 + ii*14/(imax-1))
        theta=thetas[ii]
        xi.append(rtbis(current,xilimcath,xiliman,xacc))

    plt.figure()
    plt.title('Multiple polarization curve')
    linea0, = plt.plot(thetas,xi,'r-')
    plt.xlabel('Dimensionless potential')
    plt.ylabel('Dimensionless current')
    plt.show()


main()
```