Exercises

Exercise 1

Calculate the probability of finding an electron which has energy of 4.8 eV in metallic lithium at temperatures: a) 0 K, b) -200 °C, c) 25 °C, d) 200°C. The Fermi level in Li has energy of 4.72 eV.

Plot curves $f(E)$ versus E at these temperatures.

For details of calculations see Exercise.xslx, sheet Ex1. All the calculations one can be obtained using Eq. (1.15).

t / °C	T / K	$F(E)$
-273.15	0.00	0.00
-200	73.15	3.08E-06
25	298.15	4.25E-02
200	473.15	1.23E-01

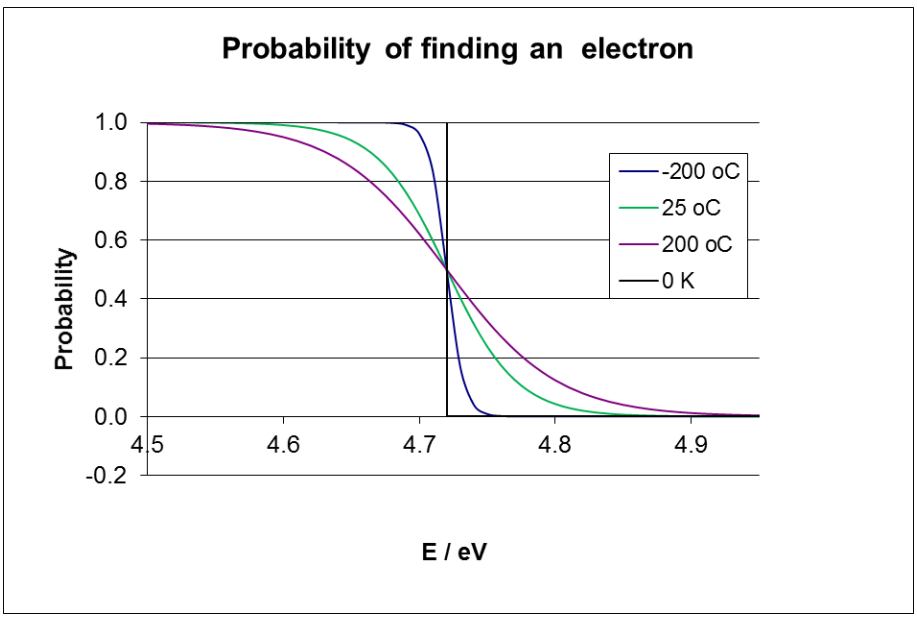


Fig. 1. Probability of finding an electron in the metal having Fermi Level of 4.72 eV.

Exercise 2

Calculate V, V_b, V_s and μ_e^M (in eV and kJ mol^{-1}) for sodium and cadmium and make a graph of the energy diagrams for these metals (as in Fig. 1.19)using the following data:

Work function	Na: 2.7 eV ;	Cd: 4.12 eV
Fermi level	Na: 3.23 eV;	Cd: 7.46 eV
Surface potential	Na: 0.6 V;	Cd: 1.9 V

For details of calculations see Exercise.xslx, sheet Ex2. The necessary values may be calculated using Eqs. (1.17)-(1.21). For example for Na:

$$V = -(\Phi^{\mathrm{M}} + \varepsilon_{\mathrm{F}}) = -(2.7 + 3.23) = 5.93 \ \ \mathrm{eV}$$

$$V_{\mathrm{s}} = -e\chi = -0.6 \ \ \mathrm{eV}$$

$$V_{\mathrm{b}} = V + \chi = -5.93 + 0.6 = -5.33 \ \ \mathrm{eV}$$

$$\mu = -\Phi^{\mathrm{M}} - V_{\mathrm{s}} = -2.7 + 0.6 = -2.1 \ \ \mathrm{eV}$$

The values in kJ mol^{-1} are obtained using relation: 1 eV = 1.60217653×10^{-19} J electron^{-1}= 96.485 kJ mol^{-1}.

Exercise 3.

Plot external, image, and total potential vs. log of the distance (in cm) from the metallic sphere of radius r = 1 cm possessing electrical charge of 1.11×10^{-12} C (in the vacuum).

The solution is found in see Exercise.xslx, sheet Ex3. Calculations are carried out using Eqs. (1.9), (1.12), and (1.13), see Example 1.1.

Exercise 4.

Calculate absolute potential of the following systems:
Li^+/Li, Zn^{2+}/Zn, Cd^{2+}/Cd, Cu^{2+}/Cu and Ag^+/Ag
Assuming the absolute potential of the standard hydrogen electrode is 4.35 V.

Solution is presented in Exercise.xslx, sheet Ex4.

Exercise 5.

Calculate potential ϕ_2 for 0.1 M and 0.001 M KF solution when the electrode charge is σ^M = -10 μC cm^{-2}.

Potential ϕ_2 is calculated using Eq. (4.50), see Exercise.xslx, sheet Ex5. The units should be uniformed:
σ^M = -10^{-5} C cm^{-2}, c^* = 10^{-4} mol cm^{-3}, ε_0 = 8.8542×10^{-14} F cm^{-1}.
The values of ϕ_2 are:

0.1 M	-0.0884 V
0.001 M	-0.2050 V

Exercise 6.

Calculate potential ϕ in the diffuse layer as a function of distance from the electrode for 0.1 M electrolyte 1:1 in aqueous solution for ϕ_2 a) -0.1 V and b) -0.01 V assuming that the distance of the closest approach (outer Helmholtz plane) is x_2 = 0.5 nm. Show the plot in a graph.

The distribution of the potential is described by Eq. (4.31). First, $\tanh(zF\phi/4RT)$ must be calculated, from which ϕ is easily obtained, see Exercise.xslx, sheet Ex6.

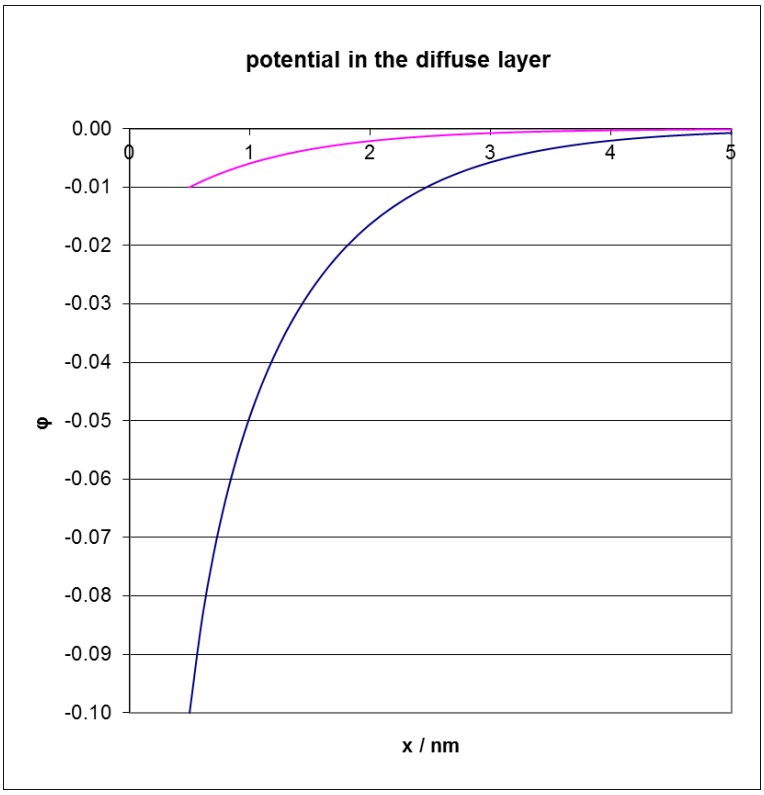


Fig. 2. Plot of the potential in the double layer.

Exercise 7.

Compare values of σ^M and C_D calculated using Guy-Chapman and Guy-Chapman-Stern theories for E - E_{PZC} = -0.20 V, ϕ_2 = -0.02 V.

For the Guy-Chapman theory Eqs. (4.25) and (4.28) are used with ϕ_0 = -0.20 V while for Guy-Chapman-Stern theory Eqns. (4.47)-(4.48) should be used. Calculations are presented in Exercise.xslx, sheet Ex7. The following values are obtained:

G-Ch
σ^M = -288 μC cm^{-2} C_D = 5602 μF cm^{-2}
G-Ch-S
σ^M = -4.69 μC cm^{-2} C_D = 246 μF cm^{-2}

Exercise 8.

Calculate the charge of Cl^- adsorbed at Hg electrode in 0.2 M HCl at 25 °C using the following data obtained from thermodynamic measurements:
a) σ^M= 0, σ_{Cl-} = -3.1 μC cm^{-2}
b) σ^M = 8 μC cm^{-2}, σ_{Cl-} = -11.5 μC cm^{-2}
where σ_{Cl-} is the total charge of chloride ions (adsorbed and in the double layer).

Details of calculations are displayed in Exercise.xslx, sheet Ex8.
a) The H^+ ions are located only in the double layer as they are not adsorbed at mercury (see also Exercise 4.1 in the book). Their charge is:
b)

$$\sigma^{\mathrm{M}} = -(\sigma_{\mathrm{H}^+} + \sigma_{\mathrm{Cl}^-})$$

$$\sigma_{\mathrm{H}^+} = -\sigma^{\mathrm{M}} - \sigma_{\mathrm{Cl}^-} = 3.1\ \mu\mathrm{C\ cm}^{-2}$$

The total metal charge is:

$$\sigma^{\mathrm{M}} = -\left(\sigma^{\mathrm{d}}_{\mathrm{H}^+} + \sigma^{\mathrm{d}}_{\mathrm{Cl}^-} + \sigma^{1}_{\mathrm{Cl}^-}\right)$$

The amounts of H^+ and Cl^- in the diffuse part of the double layer are determined by the potential ϕ_2 at the OHP. It can be estimated from the amount of H^+ in the double layer:

$$\sigma^{\mathrm{d}}_{\mathrm{H}^+} = \sqrt{2RT\varepsilon\varepsilon_0\, c^*}\left[\exp\left(-\frac{zf\phi_2}{2}\right)-1\right] = A\left[\exp\left(-\frac{zf\phi_2}{2}\right)-1\right]$$

$$\phi_2 = \frac{-2}{zf}\ln\left(\frac{\sigma^{\mathrm{d}}_{\mathrm{H}^+}}{A}+1\right) \quad A = 2.63\times10^{-6}\,\mathrm{C\,cm}^{-2}$$

$$\phi_2 = -0.0401\ \mathrm{V}$$

From which the charge of Cl^- in the double layer can be calculated:

$$\sigma^{\mathrm{d}}_{\mathrm{Cl}^-} = -A\left[\exp\left(\frac{zf\phi_2}{2}\right)-1\right] = 1.42\times10^{-6}\,\mathrm{C\ cm}^{-2} = 1.42\ \mu\mathrm{C\ cm}^{-2}$$

Positive value means that the concentration of Cl^- ions in the double layer is lower than in the bulk of solution. Now, the amount of Cl^- adsorbed can be calculated:

$$\sigma_{\mathrm{Cl}^-} = \sigma^{1}_{\mathrm{Cl}^-} + \sigma^{\mathrm{d}}_{\mathrm{Cl}^-}$$

$$\sigma^{1}_{\mathrm{Cl}^-} = \sigma_{\mathrm{Cl}^-} - \sigma^{\mathrm{d}}_{\mathrm{Cl}^-} = (-3.1-1.42)\,\mu\mathrm{C\,cm}^{-2} = -4.52\ \mu\mathrm{C\,cm}^{-2}$$

b)
$$\sigma^{\mathrm{M}} = -(\sigma_{\mathrm{H}^+} + \sigma_{\mathrm{Cl}^-})$$
$$\sigma_{\mathrm{H}^+} = -\sigma^{\mathrm{M}} - \sigma_{\mathrm{Cl}^-} = 3.5\ \mu\mathrm{C\ cm}^{-2}$$
$$\phi_2 = \frac{-2}{zf}\ln\left(\frac{\sigma^{\mathrm{d}}_{\mathrm{H}^+}}{A} + 1\right) \quad A = 2.63\times10^{-6}\,\mathrm{C\,cm^{-2}}$$
$$\phi_2 = -0.04354\ \mathrm{V}$$
$$\sigma^{\mathrm{d}}_{\mathrm{Cl}^-} = -A\left[\exp\left(\frac{zf\phi_2}{2}\right) - 1\right] = 1.50\times10^{-6}\,\mathrm{C\ cm^{-2}} = 1.50\,\mu\mathrm{C\ cm^{-2}}$$
$$\sigma^{1}_{\mathrm{Cl}^-} = \sigma_{\mathrm{Cl}^-} - \sigma^{\mathrm{d}}_{\mathrm{Cl}^-} = (-11.5 - 1.50)\,\mu\mathrm{C\,cm^{-2}} = -13.00\ \mu\mathrm{C\,cm^{-2}}$$

Charge of Cl^- in the double layer might also be evaluated using

$$\sigma^{\mathrm{d}}_{-} = \frac{A\sigma^{\mathrm{d}}_{+}}{A + \sigma^{\mathrm{d}}_{+}}$$

which can easily obtained from Eqs. (4.41) and (4.42) by eliminating ϕ_2.

Exercise 9.

Calculate the surface excess of amyl alcohol from solution containing 0.031 M of this compound in 0.1 M $HClO_4$ at the potential of -0.6 V vs. SCE at 25 °C if $(\partial\gamma/\partial \ln c)_E$ = -25 mN m^{-1}.

From Eq. (3.28) the surface excess is easily obtained:

$$\Gamma_{\mathrm{M(H_2O)}} = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln a_{\mathrm{M}}}\right)_{\mathrm{E}} \approx -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln c_{\mathrm{M}}}\right)_{\mathrm{E}} = 1.008\times10^{-9}\ \mathrm{mol\ cm^{-2}}$$

Exercise 10.

Calculate concentrations of ions Na^+ and F^- at the outer Helmholtz plane in the aqueous solution of NaF using the following data:

E (V vs. ECS)	C_{NaF} (M)	ϕ_2 (V)
-1.75	0.001	-0.241
	0.1	-0.128
-0.55	0.001	-0.066
	0.1	-0.021

From Eq. (4.4) the concentrations might be easily obtained, see Exercises I.xlsx, sheet Ex10.

$$c_{\mathrm{i}} = c^*_{\mathrm{i}} \exp\left(-\frac{z_{\mathrm{i}}F\phi}{RT}\right)$$

The results are presented below:

E (V vs. ECS)	C_{NaF} (M)	$[Na^+]$ (M)	$[F^-]$ (M)
-1.75	0.001	11.79	8.48×10^{-8}
	0.1	14.54	6.88×10^{-4}
-0.55	0.001	0.0130	7.67×10^{-5}
	0.1	0.226	4.42×10^{-2}

Exercise 11.

In 0.1 M solution of $(C_2H_5)_4NClO_4$ in DMSO at 25°C at mercury electrode the double layer capacitance C_d = 22.96 μF cm^{-2} (at the electrode potential -1.00 V vs. 0.05 M Ag^+/Ag in the same nonaqueous solution) and the electrode charge density σ_M = -2.46 μC cm^{-2}. Calculate potential ϕ_2, capacity of the diffuse layer, C_D and capacity of the compact Helmholtz layer, C_H. There is no specific adsorption in that electrolyte and ε (DMSO) = 46.7.

The solution is shown in Exercise I.xlsx Ex11. First, the potential at the OHP is calculated, Eq. (4.34):

$$\phi_2 = \frac{2RT}{zF}\sinh^{-1}\left(\frac{\sigma^{\mathrm{M}}}{2\sqrt{2RT\varepsilon\varepsilon_0 c^*}}\right) = -0.0400\ \mathrm{V}$$

The capacitance of the diffuse layer is determined as:

$$C_{\mathrm{D}} = zF\sqrt{\frac{2\varepsilon\varepsilon_0 c}{RT}}\cosh\left(\frac{zF\phi_2}{2RT}\right) = 73.5\ \mu\mathrm{F\ cm}^{-2}$$

And the inner layer capacitance from the total capacitance:

$$\frac{1}{C_{\mathrm{d}}} = \frac{1}{C_{\mathrm{H}}} + \frac{1}{C_{\mathrm{D}}} \quad\Rightarrow\quad C_{\mathrm{H}} = \left(\frac{1}{C_{\mathrm{d}}} - \frac{1}{C_{\mathrm{D}}}\right)^{-1} = 33.4\ \mu\mathrm{F\ cm}^{-2}$$

Exercise 12.

Give equations for the electromotive force of the following cells using electrochemical potentials:

a) Pt'|MnO_2|Mn_2O_3| KOH | $Zn(OH)_2$ | Zn | Pt
b) Ni | Ni_2O_3 | NiO | KOH | FeO | Fe | Ni'
c) Pt | TiO^{2+},Ti^{3+}, H^+ || V^{2+}, H^+ | V_2O_3(s) | Pt'

Write the half-cell and total redox reactions.

First, redox reactions on both sides must be written using forts mass balance and then charge balance, finally the total reactions must be balanced and simplified.

Re a) This is a cell without the liquid junction potential.
Left
$2\ MnO_2 + H_2O + 2e$ (Pt') = $Mn_2O_3 + 2OH^-$
Right
$Zn(OH)_2 + 2e$ (Pt) = $Zn + 2\ OH^-$
Total
$Zn(OH)_2 + Mn_2O_3 + 2e$ (Pt) = $Zn + 2\ MnO_2 + H_2O + 2e$ (Pt')

Or as it is written without electrons:
$Zn(OH)_2 + Mn_2O_3 = Zn + 2\ MnO_2 + H_2O$

Electrochemical potentials might substituted for each species:

$$\bar{\mu}^{Zn(OH)_2}_{Zn(OH)_2} + \bar{\mu}^{Mn_2O_3}_{Mn_2O_3} + 2\bar{\mu}^{Pt}_{e} = \bar{\mu}^{Zn}_{Zn} + 2\bar{\mu}^{MnO_2}_{MnO_2} + \bar{\mu}^{s}_{H_2O} + 2\bar{\mu}^{Pt'}_{e}$$

$$\mu^0_{Zn(OH)_2} + \mu^0_{Mn_2O_3} + 2\mu^{Pt}_{e} - 2F\phi^{Pt} = \mu^0_{Zn} + 2\mu^0_{MnO_2} + \mu^0_{H_2O} + RT\ln a_{H_2O} + 2\mu^{Pt}_{e} - 2F\phi^{Pt'}$$

where electrochemical potential of noncharged species equals to the chemical potential and that of pure sold phases equals to the standard chemical potential. Rearranging one can obtain:

$$2F\left(\phi^{Pt} - \phi^{Pt'}\right) = -\mu^0_{Zn} - 2\mu^0_{MnO_2} - \mu^0_{H_2O} - RT\ln a_{H_2O} + \mu^0_{Zn(OH)_2} + \mu^0_{Mn_2O_3}$$

$$E = \phi^{Pt} - \phi^{Pt'} = \frac{\left(\mu^0_{Zn(OH)_2} - \mu^0_{Zn}\right) - \left(2\mu^0_{MnO_2} + \mu^0_{H_2O} - \mu^0_{Mn_2O_3}\right)}{2F} - \frac{RT}{2F}\ln a_{H_2O}$$

$$E = E^0_{cell} - \frac{RT}{2F}\ln a_{H_2O} \approx E^0 = E^0_{MnO_2|Mn_2O_3} - E^0_{Zn(OH)_2|Zn}$$

If the solutions are diluted the water activity is one and the cell potential equals to the standard potential of the cell.

Re b) This is a cell without diffusion potential

Left

$Ni_2O_3 + H_2O + 2\ e\ (Ni) = 2\ NiO + 2\ OH^-$

Right

$FeO + H_2O + 2\ e\ (Ni') = Fe + 2\ OH^-$

Total

$FeO + 2\ e\ (Ni') + 2\ NiO + = Fe + Ni_2O_3 + 2\ e\ (Ni)$

Proceeding as in a) one obtains:

$$2F(\phi^{Ni'} - \phi^{Ni}) = 2FE = \left(\mu^0_{FeO} - \mu^0_{Fe}\right) - \left(\mu^0_{Ni_2O_3} - \mu^0_{NiO}\right)$$

$$E = \frac{\left(\mu^0_{FeO} - \mu^0_{Fe}\right) - \left(\mu^0_{Ni_2O_3} - \mu^0_{NiO}\right)}{2F} = E^0_{FeO|Fe} - E^0_{Ni_2O_3|NiO} = E^0_{cell}$$

Re c) This is a cell separated by a membrane and the concentrations (and pH) on both sides are different. One can proceed as in a) and b) to determine the electrode electromotive force

Left

$TiO^{2+}(l) + 2\ H^+(l) + e\ (Pt) = Ti^{3+}(l) + H_2O(l)$

Right

$V_2O_3 + 6\ H^+(r) + 2\ e\ (Pt') = 2\ V^{2+}(r) + 3\ H_2O\ (r)$

Total

$V_2O_3 + 6\ H^+(r) + 2\ e\ (Pt') + 2Ti^{3+}(l) + 2H_2O(l) = 2\ V^{2+}(r) + 3\ H_2O\ (r) + 2TiO^{2+}(l) + 4\ H^+(l) + 2e\ (Pt)$

$$E = \phi^{\mathrm{Pt'}} - \phi^{\mathrm{Pt}} = \underbrace{\frac{\mu^0_{\mathrm{V_2O_3}} + 2\mu^0_{\mathrm{H^+}} + 2\mu^0_{\mathrm{Ti^{3+}}} - 2\mu^0_{\mathrm{V^{2+}}} - 2\mu^0_{\mathrm{TiO^{2+}}} - \mu^0_{\mathrm{H_2O}}}{2F}}_{E^0_{\mathrm{V_2O_3|V^{3+}}} - E^0_{\mathrm{TiO^{2+}|Ti^{3+}}}}$$

$$+ \frac{RT}{2F} \ln \frac{a^6_{\mathrm{H^+}(r)} a^2_{\mathrm{Ti^{3+}}(l)} a^2_{\mathrm{H_2O(l)}}}{a^2_{\mathrm{V^{3+}}(r)} a^3_{\mathrm{H_2O(r)}} a^2_{\mathrm{TiO^{2+}}(l)} a^4_{\mathrm{H^+}(l)}}$$

Exercise 13.

Give equations for the electromotive force of the following cells using the Nernst law:

a) Cu' | $Cu(CN)_2^-$, CN^- || Cl^- | Cl_2 | Pt | Cu

b) Pt' | CrO_4^{2-}, CrO_2^-, OH^- | HgO | Hg | Pt

c) Pt' | Hg | HgEDTA , CaEDTA , Ca^{2+} | CaC_2O_4(s) | ZnC_2O_4(s) | Zn | Pt

d) Pt' | I_3^-, I^- || CO_3^{2-} | $CdCO_3$ | Cd | Pt

Write the half-cell and total redox reactions.

Re. a)

Right

$Cl_2 + 2\,e = 2\,Cl^-$

$$E_r = E^0_{\mathrm{Cl_2|Cl^-}} + \frac{RT}{2F} \ln \frac{a_{\mathrm{Cl_2}}}{a^2_{\mathrm{Cl^-}}}$$

Left

$Cu(CN)_2^- + e = Cu + 2\,CN^-$

$$E_l = E^0_{\mathrm{Cu(CN)_2^-|Cu}} + \frac{RT}{F} \ln \frac{a_{\mathrm{Cu(CN)_2^-}}}{a^2_{\mathrm{Cl^-}}}$$

Total

$Cl_2 + 2Cu + 4\,CN^- = 2\,Cl^- + 2Cu(CN)_2^-$

$$E = E_r - E_l = E^0_{\mathrm{Cl_2|Cl^-}} + \frac{RT}{2F} \ln \frac{a_{\mathrm{Cl_2}}}{a^2_{\mathrm{Cl^-}}} - E^0_{\mathrm{Cu(CN)_2^-|Cu}} - \frac{RT}{F} \ln \frac{a_{\mathrm{Cu(CN)_2^-}}}{a^2_{\mathrm{CN^-}}}$$

$$= \left(E^0_{\mathrm{Cl_2|Cl^-}} - E^0_{\mathrm{Cu(CN)_2^-|Cu}} \right) + \frac{RT}{2F} \ln \frac{a_{\mathrm{Cl_2}} a^4_{\mathrm{CN^-}}}{a^2_{\mathrm{Cl^-}} a^2_{\mathrm{Cu(CN)_2^-}}}$$

Re b)

Right

$HgO + H_2O + 2e = Hg + 2\,OH^-$

$$E_r = E^0_{\mathrm{HgO|Hg}} + \frac{RT}{2F}\ln\frac{a_{\mathrm{H_2O}}}{a^2_{\mathrm{OH^-}}} \approx E^0_{\mathrm{HgO|Hg}} - \frac{RT}{2F}\ln a^2_{\mathrm{OH^-}}$$

Left

$CrO_4^{2-} + 2H_2O + 3e = CrO_2^- + 4OH^-$

$$E_l = E^0_{\mathrm{CrO_4^{2-}|CrO_2^-}} + \frac{R}{3F}\ln\frac{a_{\mathrm{CrO_4^{2-}}}a^2_{\mathrm{H_2O}}}{a_{\mathrm{CrO_2^-}}a^4_{\mathrm{OH^-}}} \approx E^0_{\mathrm{CrO_4^{2-}|CrO_2^-}} + \frac{R}{3F}\ln\frac{a_{\mathrm{CrO_4^{2-}}}}{a_{\mathrm{CrO_2^-}}a^4_{\mathrm{OH^-}}}$$

Total

$3\ HgO + 2\ CrO_2^- + 2\ OH^- = 3\ Hg + 2\ CrO_4^{2-} + H_2O$

$$E = E_r - E_l = E^0_{\mathrm{HgO|Hg}} - \frac{RT}{2F}\ln a^2_{\mathrm{OH^-}} - E^0_{\mathrm{CrO_4^{2-}|CrO_2^-}} - \frac{R}{3F}\ln\frac{a_{\mathrm{CrO_4^{2-}}}}{a_{\mathrm{CrO_2^-}}a^4_{\mathrm{OH^-}}} =$$

$$= \left(E^0_{\mathrm{HgO|Hg}} - E^0_{\mathrm{CrO_4^{2-}|CrO_2^-}}\right) + \frac{RT}{6F}\ln\frac{a^2_{\mathrm{CrO_2^-}}a^2_{\mathrm{OH^-}}}{a^2_{\mathrm{CrO_4^{2-}}}}$$

Re c)

Right

$Ca^{2+} + 2e + ZnC_2O_4 = CaC_2O_4 + Zn$

$$E = E^0_{\mathrm{Ca^{2+}|CaC_2O_4|ZnC_2O_4|Zn}} + \frac{RT}{2F}\ln a_{\mathrm{Ca^{2+}}}$$

Left

$Ca^{2+} + HgEDTA + 2e = CaEDTA + Hg$

$$E = E^0_{\mathrm{Ca^{2+}|CaEDTA|HgEDTA|Hg}} + \frac{RT}{2F}\ln\frac{a_{\mathrm{Ca^{2+}}}a_{\mathrm{HgEDTA}}}{a_{\mathrm{CaEDTA}}}$$

Total

$CaEDTA + Hg + ZnC_2O_4 = CaC_2O_4 + Zn + HgEDTA$

$$E = \left(E^0_{\mathrm{Ca^{2+}|CaC_2O_4|ZnC_2O_4|Zn}} - E^0_{\mathrm{Ca^{2+}|CaEDTA|HgEDTA|Hg}}\right) + \frac{RT}{2F}\ln\frac{a_{\mathrm{CaEDTA}}}{a_{\mathrm{HgEDTA}}}$$

Re d)

Right

$CdCO_3 + 2e = Cd + CO_3^{2-}$

$$E_r = E^0_{\mathrm{CdCO_3|Cd}} - \frac{RT}{2F}\ln a_{\mathrm{CO_3^{2-}}}$$

Left

$I_3^- + 2e = 3\ I^-$

$$E_l = E^0_{I_3^-|I^-} + \frac{RT}{2F}\ln\frac{a_{I_3^-}}{a^3_{I^-}}$$

Total

$CdCO_3 + 3\ I^- = Cd + CO_3^{2-} + I_3^-$

$$E = \left(E^0_{CdCO_3|Cd} - E^0_{I_3^-|I^-}\right) + \frac{RT}{2F}\ln\frac{a^3_{I^-}}{a_{CO_3^{2-}}a_{I_3^-}}$$

Exercise 14

Consider reaction: $O + ne \rightleftarrows R$ with $C_R^* = C_O^* = 1$ mM, $k^0 = 10^{-7}$ cm s^{-1}, $\alpha = 0.3$, and $n = 1$.

a) Calculate the exchange current density j_0 in μA cm^{-2}
b) Make a plot of current density versus overpotential for this reaction until the anodic and cathodic current reaches 600 μA cm^{-2}. Neglect the mass transfer effects.
c) Make a plot of log|j| vs. η, i.e. Tafel plot, using data from (b).

The calculations are presented in the Excel sheet Ex14.

Exercise 15

Current density versus overpotential for reaction: Ox + e = R is displayed below:

η / V	j / A cm^{-2}
-0.04	1.32×10^{-6}
-0.03	1.01×10^{-6}
-0.02	6.99×10^{-7}
-0.01	3.66×10^{-7}

Determine the exchange current density and the transfer coefficient α (the plot should be linear).

Because the overpotentials are very small one cannot neglect the backward reaction and the following form of the Butler-Volmer equation must be used:

$$\ln\left(\frac{i}{1-\exp[f\eta]}\right) = \ln(i_0) - \alpha f \eta$$

Using the linear regression the intercept -6.001 and the slope -5.603 is obtained which give: $j_0 = 9.97\times10^{-7}$ A cm^{-2} and $\alpha = 0.33$, see Sheet Ex15.

Exercise 16

Berzins et Delahay [*J. Am. Chem. Soc.*, **77**, 6448 (1955)] have studied reaction:

$$Cd^{2+} + 2e \overset{Hg}{\rightleftarrows} Cd(Hg)$$

And obtained the following results for $C_{Cd(Hg)}$ = 0.40 M :

$C_{Cd^{2+}}$ (mM)	1.0	0.50	0.25	0.10
j_0 (mA cm^{-2})	30.0	17.3	10.1	4.94

a) Determine the transfer coefficient α
b) Determine k^0_{app}.

Dependence of j_0 on concentration is given by Eq. (6.61):

$$j_0 = nFk^0_{app} C_O^{(1-\alpha)} C_R^{\alpha}$$

$$\left(\frac{\partial \ln j_0}{\partial \ln C_O}\right)_{C_R} = 1 - \alpha$$

Linear regression gives k_s = 0.0430 cm s^{-1} and α = 0.22, see Sheet Ex16.

Exercise 17

In solution containing 2 mM Zn(II) and 0.025 M $Ba(ClO_4)_2$ at the electrode Zn(Hg) containing 0.048 M Zn, the apparent exchange current density is 9.1 mA cm^{-2}. At the equilibrium potential ϕ_2 = -60.8 mV. Calculate $i_{0,t}$ and $k_{0,t}$ if α = 0.60 and z = +2.

From relations (5.37)-(5.39) one can obtain: $k_0 = k_0^t \exp\left[(\alpha n - z) f \phi_2\right]$ and $j_0 = j_0^t \exp\left[(\alpha n - z) f \phi_2\right]$. Calculations give: j_0^t = 1.37×10^{-3} A cm^{-2} and k_0^t = 5.28×10^{-4} cm s^{-1}, see Sheet Ex17.

Exercise 18

Plot:
a) log k_f versus potential
b) the above curve corrected for the double layer effects

for the irreversible reaction: A^{2-} + 2e = 2 B^{2-} in 0.1 M NaF at the mercury electrode. Determine the transfer coefficient and the rate constant of the electron transfer corrected for the double layer effects at the potential of zero charge using the following data:

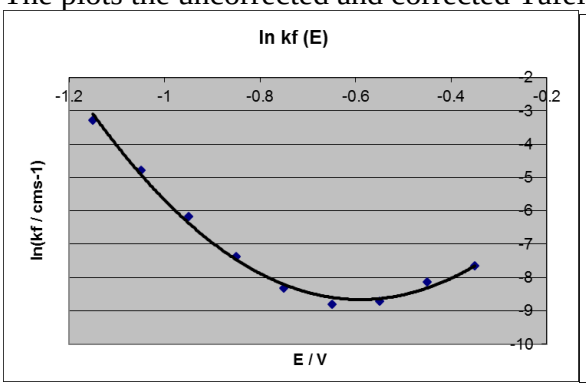
E (V vs. ECS)	ln k_f	ϕ_2 / V
-0.35	-7.652	0.0344
-0.45	-8.142	0.0067
-0.55	-8.723	-0.0210
-0.65	-8.805	-0.0437
-0.75	-8.309	-0.0606

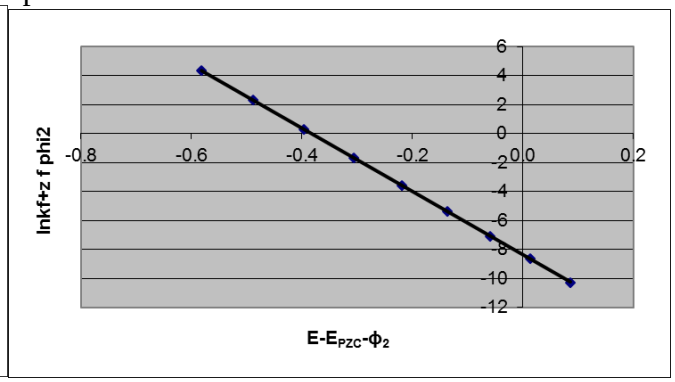
-0.85	-7.375	-0.0731
-0.95	-6.172	-0.0829
-1.05	-4.780	-0.0908
-1.15	-3.278	-0.0976

Explain the obtained results, E_{PCN} = -0.470 V vs. SCE.

The linear relation corrected for the double layer effects is analog to Eq. (5.39):
$\ln k_f + zf\phi_2 = \ln k_f(E_{PZC}) - \alpha nf(E - E_{PZC} - \phi_2)$

The plots the uncorrected and corrected Tafel plots are shown below.





The details are shown in Exercise 5.1 and Sheet Ex18. Linear regression according to the above equation gives the intercept ln $k_f(E_{PZC})$ = -8.399 , i.e. $k_f(E_{PZC}) = 2.25\times10^{-4}$ cm s^{-1} and the slope αnf = -21.879, i.e. α = 0.28.

Exercise 19

Solve the following differential equations using Laplace transform:
a) y' + y = 0 y(0) = 1

$$s\bar{y} - y_0 + \bar{y} = 0$$
$$\bar{y} = \frac{y_0}{s+1} = \frac{1}{s+1}$$
$$y = \exp(-t)$$

b) y'' + ky = 0 y(0) = a y'(0) = b

$$s^2\bar{y} - sy_0 - y_0' + k\bar{y} = 0$$
$$\bar{y} = \frac{sy_0 + y_0'}{s^2+k} = \frac{as+b}{s^2+k} = a\frac{s}{s^2+k} + b\frac{1}{s^2+k}$$
$$y = a\cos\left(\sqrt{k}t\right) + \frac{b}{\sqrt{k}}\sin\left(\sqrt{k}t\right)$$

c) y'' – ky = 0 y(0) = a y'(0) = b

$$\bar{y} = \frac{as+b}{s^2-k} = a\frac{s}{s^2-k} + \frac{b}{s^2-k}$$

$$y = a\cosh\left(\sqrt{k}t\right) + \frac{b}{\sqrt{k}}\sinh\left(\sqrt{k}t\right)$$

$$y = \left(\frac{a}{2} + \frac{b}{2\sqrt{k}}\right)\exp(\sqrt{k}t) + \left(\frac{a}{2} - \frac{b}{2\sqrt{k}}\right)\exp\left(-\sqrt{k}t\right)$$

d) y'' – y' – 2y = 1 y(0)=1 y'(0) = 0

$$s^2\bar{y} - sy(0) - y'(0) - s\bar{y} + y(0) - 2\bar{y} = \frac{1}{s}$$

$$s^2\bar{y} - s - s\bar{y} - 2\bar{y} = \frac{1}{s}$$

$$\bar{y} = \frac{s^2-s+1}{s\left(s^2-s-2\right)} = \frac{s^2-s+1}{s(s+1)(s-2)} = \frac{A}{s} + \frac{B}{s+1} + \frac{C}{s-2} =$$

$$= \frac{s^2(A+B+C) + s(-A-2B+C) - 2A}{s\left(s^2-s-2\right)}$$

$$A = -1/2;\ B = 1;\ C = 1/2$$

$$y = -\frac{1}{2} + \mathrm{e}^{-t} + \frac{1}{2}\mathrm{e}^{2t}$$

Exercise 20

Derive current-potential, *i* – *E*, equation for the reversible reaction in chronoamperometry when the bulk concentrations of ox and red are different from zero.

Answer: $E = E_{1/2} + \frac{RT}{nF}\ln\left(\frac{i_{l,c} - i}{-i_{l,a} + i}\right)$

$$a = \frac{C_{\mathrm{O}}}{C_{\mathrm{O}}^*} \qquad b = \frac{C_{\mathrm{R}}}{C_{\mathrm{O}}^*}$$

$$\frac{d^2\bar{a}}{dy^2} - s\bar{a} + 1 = 0$$

$$\frac{1}{\xi^2}\frac{d^2\bar{b}}{dy^2} - s\bar{b} + b(y,0) = 0$$

$$\frac{d^2\bar{b}}{dy^2} - s\xi^2\bar{b} - k\xi^2 = 0$$

$$\bar{a} = A\mathrm{e}^{-\sqrt{s}y} + \frac{1}{s}$$

$$\bar{b} = B\mathrm{e}^{-\sqrt{s}\xi y} + \frac{k}{s}$$

$$A = -\frac{B}{\xi} \qquad A + \frac{1}{s} = \upsilon\left(B + \frac{k}{s}\right)$$

$$A = -\frac{1}{s}\frac{1-\upsilon k}{1+\upsilon\xi}$$

$$B = \frac{\xi}{s}\frac{1-\upsilon k}{1+\upsilon\xi}$$

$$\bar{a} = -\frac{1}{s}\frac{1-\upsilon k}{1+\upsilon\xi}\mathrm{e}^{-\sqrt{s}y} + \frac{1}{s}$$

$$\bar{b} = \frac{\xi}{s}\frac{1-\upsilon k}{1+\upsilon\xi}\mathrm{e}^{-\sqrt{s}\xi y} + \frac{k}{s}$$

$$\frac{\partial\bar{a}}{\partial y} = \frac{1}{\sqrt{s}}\frac{1-\upsilon k}{1+\upsilon\xi}$$

$$\frac{\partial\bar{b}}{\partial y} = -\frac{\xi^2}{\sqrt{s}}\frac{1-\upsilon k}{1+\upsilon\xi}$$

$$\frac{\partial(a,t)}{\partial y} = \frac{1}{\sqrt{\pi t}} \frac{1-\upsilon k}{1+\upsilon\xi}$$

$$i = nFAC_o^* D_O^{1/2} \frac{\partial a}{\partial y}$$

$$i = \frac{nFAC_o^* D_O^{1/2}}{\sqrt{\pi t}} \frac{1-\upsilon k}{1+\upsilon\xi} = \frac{nFAC_o^* D_O^{1/2}}{\sqrt{\pi t}} \frac{1}{1+\upsilon\xi} - \frac{nFAC_R^* D_R^{1/2}}{\sqrt{\pi t}} \frac{\upsilon\xi}{1+\upsilon\xi}$$

$$\upsilon \to 0 \quad i \to i_{l,c}$$

$$\upsilon \to \infty \quad i \to i_{l,a}$$

$$i = i_{l,c} \frac{1}{1+\upsilon\xi} + i_{l,a} \frac{\upsilon\xi}{1+\upsilon\xi}$$

$$\upsilon\xi = \exp\left[\frac{nF}{RT}\left(E - E^{o'}\right)\right]\sqrt{\frac{D_O}{D_R}} = \exp\left[\frac{nF}{RT}\left(E - E^{o'} - \frac{RT}{nF}\ln\sqrt{\frac{D_R}{D_O}}\right)\right] = \exp\left[\frac{nF}{RT}\left(E - E_{1/2}\right)\right]$$

$$\upsilon\xi = \frac{i_{l,c} - i}{i - i_{l,a}}$$

$$E = E_{1/2} + \frac{RT}{nF}\ln\left(\frac{i_{l,c} - i}{i - i_{l,a}}\right)$$

Exercise 21

Derive equation for the ratio of the chronoamperometric current in the presence of chemical reaction to the diffusion limited current i_k / i_d as a function of time for the DISP1 reaction mechanism:

$$\mathrm{A} + \mathrm{ne} = \mathrm{B}$$

$$\mathrm{B} \xrightarrow{k} \mathrm{C}$$

$$\mathrm{B} + \mathrm{C} \xrightarrow{k_d} \mathrm{A} + \mathrm{D} \qquad \text{fast}$$

These two last reactions correspond to: $2B \to A + D$ 2 B $\xrightarrow{k}$ A. This system corresponds is described by the following equations:

$$\frac{\partial C_a}{\partial t} = D\frac{\partial^2 Ca}{\partial x^2} + kC_b$$

$$\frac{\partial C_b}{\partial t} = D\frac{\partial^2 C_b}{\partial x^2} - 2kC_b$$

Note: Use the auxiliary variable: $C_u = 2C_a + C_b$ and solve the system of differential equations for C_u and C_b. Keep in mind that:

$$L^{-1}\left\{\sqrt{s-a}-\sqrt{s-b}\right\}=\frac{1}{2\sqrt{\pi t^3}}\left(\mathrm{e}^{bt}-\mathrm{e}^{at}\right)$$

$$a=\frac{C_a}{C_a^*};\quad b=\frac{C_b}{C_a^*};\quad T=\frac{t}{\tau};\quad y=\frac{x}{\sqrt{D\tau}}$$

$$\begin{cases}\dfrac{\partial a}{\partial T}=\dfrac{\partial^2 a}{\partial y^2}+k\tau b\\[2ex] \dfrac{\partial b}{\partial T}=\dfrac{\partial^2 b}{\partial y^2}-2k\tau b\end{cases}$$

$$\begin{cases}T=0 & a=1\quad b=0\\ T>0\quad y\to\infty\end{cases}$$

$$T>0\quad y=0\quad a=0\quad a_y+b_y=0$$

$$u=2a+b$$

$$u_T=u_{yy}$$

$$b_T=b_{yy}-2k\tau b$$

$$\begin{cases}T=0 & u=2\quad b=0\\ T>0\quad y\to\infty\end{cases}$$

$$T>0\quad u=b,\quad u_y=2a_y+b_y=a_y=-b_y$$

$$\lambda=2k\tau$$

$$\begin{cases}s\bar{u}-u(0)=\bar{u}_{yy}\\ s\bar{b}-0=\bar{b}_{yy}-\lambda\bar{b}\end{cases}$$

$$\begin{cases}\bar{u}_{yy}-s\bar{u}+2=0\\ \bar{b}_{yy}-(s+\lambda)\bar{b}=0\end{cases}$$

$$\begin{cases}\bar{u}=\dfrac{2}{s}+C_1\mathrm{e}^{-\sqrt{s}\,y}\\[2ex] \bar{b}=C_2\mathrm{e}^{-\sqrt{s+\lambda}\,y}\end{cases}$$

$$\bar{u}_y(y=0) = -C_1\sqrt{s}$$

$$\bar{b}_y(y=0) = -C_2\sqrt{s+\lambda}$$

$$\bar{u}_y = -\bar{b}_y$$

$$-\sqrt{s}C_1 = \sqrt{s+\lambda}C_2$$

$$y=0, \quad \bar{u} = \bar{b}$$

$$\frac{2}{s} + C_1 = C_2$$

$$C_1 = -\frac{2\sqrt{s+\lambda}}{s\left(\sqrt{s}+\sqrt{s+\lambda}\right)} \qquad C_2 = \frac{2}{\sqrt{s}\left(\sqrt{s}+\sqrt{s+\lambda}\right)}$$

$$\bar{u}_y = -\sqrt{s}C_1 = \frac{2\sqrt{s+\lambda}}{\sqrt{s}\left(\sqrt{s}+\sqrt{s+\lambda}\right)} = 2\left[\frac{1}{\sqrt{s}} + \frac{1}{\lambda}\left(\sqrt{s}-\sqrt{s+\lambda}\right)\right]$$

$$u_y = 2\left[\frac{1}{\sqrt{\pi T}} + \frac{1}{2\sqrt{\pi T^3}\lambda}\right] = \frac{\sqrt{\tau}}{\sqrt{\pi t}}\left[\frac{4kt-1+\mathrm{e}^{-2kt}}{2kt}\right]$$

$$a_y = \frac{\sqrt{\tau}}{\sqrt{\pi t}}$$

$$\frac{i_k}{i_d} = \frac{4kt-1+\mathrm{e}^{-2kt}}{2kt}$$

Exercise 22

Derive equation for $i_\mathrm{k} / i_\mathrm{d}$ as a function of time for the catalytic reaction of the pseudo first order in chronoamperometry i.e. when $C_\mathrm{Z} >> C_\mathrm{B}$:

$$\mathrm{A} + ne = \mathrm{B}$$

$$\mathrm{B} + \mathrm{Z} \xrightarrow{k} \mathrm{A} + \mathrm{X}$$

Note: write equations for $C_u = C_a + C_b$ and C_b,

$$L^{-1}\left\{\frac{\sqrt{s+k}}{s}\right\} = \frac{1}{\sqrt{\pi t}}\left(\mathrm{e}^{-kt} + \sqrt{\pi kt}\,\mathrm{erf}\,\sqrt{kt}\right)$$

$$\begin{cases} \dfrac{\partial a}{\partial T} = \dfrac{\partial^2 a}{\partial y^2} - \lambda b \qquad \lambda = k\tau \\ \dfrac{\partial b}{\partial T} = \dfrac{\partial^2 b}{\partial y^2} - \lambda b \end{cases}$$

$$u = a + b$$

$$\begin{cases} \dfrac{\partial u}{\partial T} = \dfrac{\partial^2 u}{\partial y^2} \\ \dfrac{\partial b}{\partial T} = \dfrac{\partial^2 b}{\partial y^2} - \lambda b \end{cases}$$

$$T = 0 \;\; a = 1 \;\; b = 0 \;\; u = 1$$

$$T > 0 \;\; y = 0 \quad a_y + b_y = 0 \quad \frac{\partial u}{\partial y} = 0 \quad a = 0$$

$$\bar{u} = \frac{1}{s} + C_1 \mathrm{e}^{-\sqrt{s}y}$$

$$\bar{b} = C_2 \mathrm{e}^{-\sqrt{s+\lambda}y} \quad \bar{b}(0,s) = C_2$$

$$\bar{u}_y = 0 \;\; C_1 = 0 \quad \bar{u} = \frac{1}{s}$$

$$\bar{a}(0,s) + \bar{b}(0,s) = \frac{1}{s} \quad C_2 = \frac{1}{s}$$

$$\bar{b} = \frac{1}{s}\mathrm{e}^{-\sqrt{s+\lambda}y}$$

$$\frac{\partial \bar{b}(y=0)}{\partial y} = -\frac{\sqrt{s+\lambda}}{s}$$

$$\frac{\partial b(y=0)}{\partial y} = -\frac{1}{\sqrt{\pi T}}\left(\mathrm{e}^{-\lambda T} + \sqrt{\pi\lambda\tau}\ \mathrm{erf}\sqrt{\lambda\tau}\right)$$

$$i = -nFAD\left(\frac{\partial C_B}{\partial x}\right) = \frac{nFADC_O^*}{\sqrt{D\tau}}\left(\frac{\sqrt{\tau}\mathrm{e}^{-\lambda T}}{\sqrt{\pi t}} + \sqrt{\pi\lambda\tau}\ \mathrm{erf}\sqrt{k\tau}\right)$$

$$i_\mathrm{k} = \frac{nFAD^{1/2}C_O^*}{\sqrt{Dt}}\left(\mathrm{e}^{-kt} + \sqrt{\pi kt}\ \mathrm{erf}\sqrt{kt}\right)$$

$$\frac{i_\mathrm{k}}{i_\mathrm{d}} = \mathrm{e}^{-kt} + \sqrt{\pi kt}\ \mathrm{erf}\sqrt{kt}$$

Exercise 23

Determination of the kinetics of the reduction of Zn^{2+} in 0.5 M tetrabutylammonium perchlorate in DMSO was carried out chronoamperometrically. Chronoamperometric current was measured after 9 ms form the application of the potential step in function of the step potential:

Chronoampérométrie, temps = 9 ms.

$-E$ / V	i/i_{lim}
1.420	0.185
1.441	0.270
1.459	0.354
1.480	0.453
1.500	0.586

Determine the kinetic parameters k_f, k_s and α if: $E^{rev}_{1/2}$ = -1.331 V, $D_{ox} = 1.29 \cdot 10^{-6}$ cm^2/s, $D_{red} = 1.6 \cdot 10^{-5}$ cm^2/s and t = 25°C.

Solution is shown in Sheet Ex23.
First, the reversible formal potential must be calculated using:

$$E_{1/2} = E^{o'} - \frac{RT}{nF}\ln\sqrt{\frac{D_O}{D_R}}$$, $E^{o'}$ = -1.3472 V.

Dependence of the current on the kinetic parameters is displayed in Eq. (8.143):

$$\frac{i}{i_{rev}} = \frac{i\left\{1+\exp\left[nf\left(E-E_{1/2}\right)\right]\right\}}{i_l} = F(\lambda) = \pi^{1/2}\,\lambda\exp\left(\lambda^2\right)\mathrm{erfc}\left(\lambda\right)$$

Function $F(\lambda) = \dfrac{i\left\{1+\exp\left[nf\left(E-E_{1/2}\right)\right]\right\}}{i_l}$ is easily calculated, see table below:

E / V	i/i_l	E-$E^{0'}$ / V	$F(\lambda)$	λ	k_f / cm s^{-1}	ln k_f
-1.42	0.185	-0.07284	0.1856	0.1192	1.42E-03	-6.55552
-1.441	0.27	-0.09384	0.2702	0.1858	2.23E-03	-6.10759
-1.459	0.354	-0.11184	0.3541	0.2625	3.14E-03	-5.76251
-1.48	0.453	-0.13284	0.4530	0.3715	4.45E-03	-5.41534
-1.50	0.586	-0.15284	0.5860	0.5674	6.79E-03	-4.99185

Next, the value of the parameter λ must be found. It might be evaluated by preparing the table of $\pi^{1/2}\lambda\exp(\lambda^2)\mathrm{erfc}(\lambda)$ vs. λ using Excel or even better by solving equation:

$\pi^{1/2}\,\lambda\exp\left(\lambda^2\right)\mathrm{erfc}\left(\lambda\right) - F(\lambda) = 0$ for λ using Excel Solver. Knowing values of λ the forward rate constant, k_f, might be evaluated from:

$$\lambda = Ht^{1/2} = \frac{k_f}{\sqrt{D_O}}\left\{1+\exp\left[nf\left(E-E_{1/2}\right)\right]\right\}t^{1/2}$$

Exercise 24

Voltammetric method was used for determination of the kinetic parameters of the reduction of Cr^{3+} to Cr^{2+} in 2 M $NaClO_4$.
From the linear sweep voltammogram ay the sweep rate of v = 0.05 V s^{-1} the cathodic peak and half-peak potentials were obtained: E_{pc} = -0.975 V and $E_{pc/2}$ = -0.888 V. Determine αn_α and k^o if $E^{o'}$ = -0.637 V, D_{ox} = 5.6•10^{-6} cm^2 s^{-1} knowing that the system is totally irreversible.

Parameter αn_α is obtained from Eq. (10.44):

$$E_p - E_{p/2} = -1.857\frac{RT}{\alpha n_\alpha F} = -\frac{0.0477}{\alpha n_\alpha} \text{ V at } 25\,^\circ\text{C}, \ \alpha n_\alpha = 0.548.$$

The rate constant is estimated form Eq. (10.41):

$$E_p = E^{0'} + \frac{RT}{\alpha n_\alpha F}\left[-0.780 + \ln\frac{k^0}{\sqrt{D_O}} + \ln\left(\frac{RT}{\alpha n_\alpha F\ v}\right)^{1/2}\right], \ k^0 = 3.90\times10^{-6} \text{ cm s}^{-1}.$$

Exercise 25

The potential difference between anodic and cathodic peak in cyclic voltammetry is 100 mV at the scan rate of 100 V s^{-1}. Estimate the standard rate constant knowing that D_O = 4•10^{-6} cm^2 s^{-1}, n=1, $\alpha \approx 0.5$, and t = 25 °C.

In order to determine the rate constant one must use the dependence of $E_{pa} - E_{pc}$ on the kinetic parameter ψ, Table 10.3, where ψ is described by Eq. (10.59):

$$\psi = \frac{\left(\frac{D_O}{D_R}\right)^{\alpha/2} k^0}{\left(\pi D_O f v\right)^{1/2}}$$

The value of ψ might be obtained by linear interpolation between the values of 92 and 105 mV or by polynomial interpolation using e.g. four point around the value of 100 mV.
The value of ψ = 0.594 and the rate constant k^0 = 0.13 cm s^{-1}, assuming that $D_O = D_R$, see Sheet Ex25.

Exercise 26

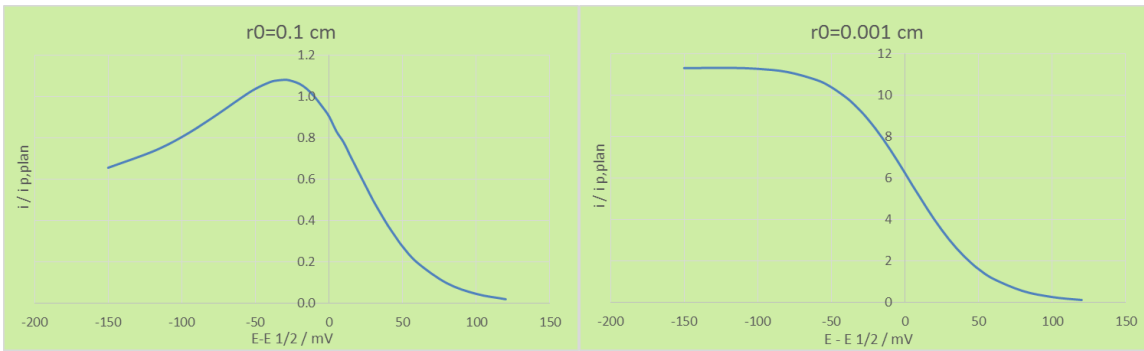
Plot the voltammetric curves of the one electron reduction of 1 mM anthracene in acetonitrile on the spherical mercury electrode of the radius 0.1 cm and 0.001 cm at the scan rate v = 0.01 V s^{-1} and using D_O = 9×10^{-6} cm^2 s^{-1}. Plot $i/i_{peak,plane}$ versus $E - E_{1/2}$.

Solution is shown in the Sheet Ex26. To simulate these curves one must use the numerical data from Table 10.1. Eqs. (10.18) and (10.23) might be rearranged to:

$$i = nFAD_{\mathrm{O}}^{1/2} c_{\mathrm{O}}^{*} \sigma^{1/2} \Psi(\xi) + \frac{nFAD_{\mathrm{O}} c_{\mathrm{O}}^{*}}{r_0 \left\{1 + \exp\left[nf\left(E - E_{1/2}\right)\right]\right\}}$$ or dividing by the peak current at plane electrode of the same dimensions:

$$\frac{i}{i_{\mathrm{p,plane}}} = \frac{\Psi(E)}{0.446} + \frac{D_{\mathrm{O}}^{1/2}}{0.446 r_0 (nfv)^{1/2} \left\{1 + \exp\left[nf\left(E - E_{1/2}\right)\right]\right\}}$$

The obtained plots are displayed below.



Exercise 27

Electroreduction reaction $M^{2+} + e = M^{+}$ was studied using rotating disk electrode. At the potential $E - E_{1/2} = 0.02$ V the following results were obtained:

Rotation rate (s^{-1})	$i \cdot 10^3$ (A)
10	0.786
30	1.215
100	1.835
300	2.483

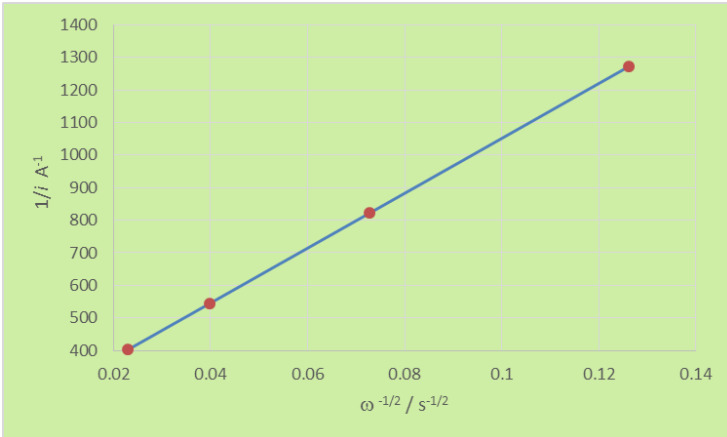
Calculate the rate constant of this process, k_f, if the concentration of M^{2+} is 1 mM, the disk radius $r_0 = 1$ cm and $D_{M2+} = 10^{-5}$ cm^2 s^{-1}.

Relations between current and rotation rate is described by Eq. (12.68)-(12.69):

$$i_{\mathrm{k}} = nFA\, k_{\mathrm{f}}\, c_{\mathrm{O}}^{*}$$

$$\frac{1}{i} = \frac{1}{i_{\mathrm{k}}} + \frac{1}{i_{\mathrm{l,c}}} = \frac{1}{i_{\mathrm{k}}} + \underbrace{\frac{1}{0.620\, nFAD_{\mathrm{O}}^{2/3} \nu^{-1/6} c_{\mathrm{O}}^{*}}}_{\text{slope}} \frac{1}{\omega^{1/2}}$$

The plot of $1/i$ vs. $\omega^{-1/2}$ gives $i_k = 4.79$ mA, which, using linear regression, gives $k_f = 1.58 \times 10^{-2}$ cm s^{-1}. See details in Sheet Ex24. The plot is also displayed below.



Exercise 28

Develop an equation current-potential for oxidation of copper from the rotating disk electrode in the presence of NaCl. The reaction proceeds according to:

$Cu - e + 2\ Cl^- = CuCl_2^-$

Suppose that the reaction is reversible and concentration of NaCl is sufficiently high.

$$i = -0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}\left(\left[CuCl_2^-\right]^* - \left[CuCl_2^-\right]_{x=0}\right)$$

$$\left[CuCl_2^-\right]^* = 0,\ \ [Cl^-]_{x=0} = [Cl^-]^* = [Cl^-]$$

$$E = E^{0'} + \frac{RT}{F}\ln\frac{\left[CuCl_2^-\right]_{x=0}}{[Cl^-]} \ \Rightarrow\ \left[CuCl_2^-\right]_{x=0} = [Cl^-]^2\exp\left[f\left(E - E^{0'}\right)\right]$$

$$i = 0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}[Cl^-]^2\exp\left[f\left(E - E^{0'}\right)\right]$$

Exercise 29

Chronopotentiometry with current reversal was used to determine the kinetics of the benzidine rearrangement of hydrazobenzene into benzidine. In the solution of 1 mM azobenzene in 0.25 M $HCLO_4$ the following results were obtained:

t_{red} / s	τ_{ox}/t_{rex}
2	0.277
3	0.255
5	0.217
10	0.156

Calculate the rate constant of the pseudo first order of benzidine rearrangement.

For the first order following reaction

$$\mathrm{O} + e = \mathrm{R}$$

$$\mathrm{R} \xrightarrow{k} \mathrm{Z}$$

Eq. (9.50) should be used

$$2\ \mathrm{erf}[(\tau_2 / t_1) k_\mathrm{f} t_1]^{1/2} = \mathrm{erf}[k_\mathrm{f} t_1 (\tau_2 / t_1 + 1)]^{1/2}$$

The values of $k_f t_1$ vs. τ_2/t_1 might be obtained by solving the above equation using Excel Solver, see Sheet Ex29. The obtained results are shown below:

$\log(\tau_2/t_1)$	$\boldsymbol{\tau_2/t_1}$	fun	$\boldsymbol{k_f t_1}$
-1	**0.1**	1.06172E-10	**2.114**
-0.95	**0.112202**	2.16127E-12	**1.828**
-0.9	**0.125893**	1.37637E-11	**1.564**
-0.85	**0.141254**	1.09124E-12	**1.321**
-0.8	**0.158489**	8.71203E-12	**1.097**
-0.75	**0.177828**	5.66045E-11	**0.888**
-0.7	**0.199526**	-5.8155E-11	**0.6964**
-0.65	**0.223872**	-8.2487E-12	**0.5182**
-0.6	**0.251189**	-2.4644E-12	**0.3533**
-0.55	**0.281838**	-2.7286E-11	**0.2009**
-0.5	**0.316228**	-1.1884E-11	**0.06044**

The values of $k_f t_1$ for the experimental values of τ_2/t_1 might be found using linear interpolation between the points or using a polynomial approximation (here using 5-th order polynomial and calculating the values using the polynomial coefficients. The Results using linear interpolation are shown below.

t_1 / s	τ_2/τ_1	$k_f t_1$
2	0.277	0.225
3	0.255	0.334
5	0.217	0.568
10	0.156	1.129

Next, the plot of $k_f t_1$ vs. t_1 is made, see below. The slope of this plot gives the rate constant (using linear regression). It gives $k_f = 0.113\ \mathrm{s}^{-1}$.

kf*t1 versus t1
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
12