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.

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

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).

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.

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}.

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.

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.

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) $\sigma^M = 0$, $\sigma_{Cl-} = -3.1\ \mu C\ cm^{-2}$

b) $\sigma^M = 8\ \mu C\ cm^{-2}$, $\sigma_{Cl-} = -11.5\ \mu C\ cm^{-2}$

where σ_{Cl-} is the total charge of chloride ions (adsorbed and in the double layer).

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 $(\partial\gamma/\partial \ln c)_E = -25\ mN\ m^{-1}$.

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

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 $C_d = 22.96\ \mu F\ cm^{-2}$ (at the electrode potential -1.00 V vs. 0.05 M Ag^+/Ag in the same nonaqueous solution) and the electrode charge density $\sigma_M = -2.46\ \mu C\ cm^{-2}$. 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.

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.

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.

Exercise 14

Consider reaction: $O + ne \rightleftarrows R$ with $C_R^* = C_O^* = 1\ \text{mM}$, $k^0 = 10^{-7}$ 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).

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).

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 $C_{Cd(Hg)} = 0.40\ \text{M}$:

$C_{Cd^{2+}}$ (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_{app}^0.

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 $\alpha = 0.60$ and $z = +2$.

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.

Exercise 19

Solve the following differential equations using Laplace transform:
a) y' + y = 0 y(0) = 1
b) y'' + ky = 0 y(0) = a y'(0) = b
c) y'' – ky = 0 y(0) = a y'(0) = b
d) y'' – y' – 2y = 1 y(0)=1 y'(0) = 0

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

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:

$$A + ne = B$$

$$B \xrightarrow{k} C$$

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

These two last reactions correspond to: $2B \rightarrow A + D$ 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:

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

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,

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

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: $E^{\mathrm{rev}}_{1/2}$ = -1.331 V, D_{ox} = 1.29•10^{-6} cm^2/s,

D_{red} = 1.6•10^{-5} cm^2/s and t = 25°C.

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.

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 ^{o}C.

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 $E - E_{1/2}$.

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•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}.

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.

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

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