Applications to Butler-Volmer equation, Chapter 3

Practical numerical application :

$|\eta|$ > 0.1 V Tafel:

Anodic current for +ve η; $i = i_o \exp\{(1-\alpha)\eta F/RT\}$

Cathodic current for -ve η; $i = i_o \exp\{-\alpha\eta F/RT\}$

$|\eta|$ < 0.01 V Charge transfer resistance

$i = 2i_o \sin(F\eta/2RT) \approx 2i_o (F\eta/2RT) = i_o (F\eta/RT)$

For $\eta \approx$ 0.01 V - 0.1V

=> Use the BV-equation. The BV equation can be used as is for any case.

Exercise 1

Calculate the ratio of the rates of the reaction: $Ag^+ + e^- \rightarrow Ag$ at:

a) η = - 0.15V & η = 0.15 V.
b) η = - 0.2V & η = 0.2 V.

Assume room temperature at 25°C.

Exercise 2

For an overpotential of η = 10 mV, a current I = 0.62 mA is passed through a 2 cm^2 Pt electrode for a H^+/H_2 half reaction given as: $H^+ + e^- \rightarrow \frac{1}{2} H_2$.

What will be the current density i for (a) η = 100 mV? (b) η = -100 mV?

Assume the symmetry factor as 0.5 and a room temperature of 25°C

Exercise 3

The exchange current density of a Pt electrode for the H^+/H_2 half reaction is $i_o = 0.79\ mA.cm^{-2}$ at 25°C.

Calculate the current density across it when the over potential is (a) η = 10 mV (b) η = –200 mV.

Exercise 4

Calculate the effective resistance across 1 cm^2 of

a) Pt, H_2, H^+ ; i_o = 0.79 $mA.cm^{-2}$
b) Hg, H_2, H^+ ; i_o = 0.79 x 10^{-12} $A.cm^{-2}$

What conclusion you can draw from the result?

Exercise 5

In an experiment involving Pt, H_2, H^+ electrode, the following data were obtained at 298 K.
Determine α and i_0

η/mV	50	100	150	200	250
i / $mA{\cdot}cm^{-2}$	3.19	10.69	35.88	120.00	402.00

Exercise 6

For the system Pt /Fe^{3+}, Fe^{2+} at 298K the i were measured as shown below:
Determine α and i_0

η/mV	-50	-80	-100	-120	-150	-200
i / $mA{\cdot}cm^{-2}$	-8.01	-16.1	-25.17	-41	-82.4	-264
η/mV	50	80	100	120	150	200
i / $mA{\cdot}cm^{-2}$	5.50	8.78	11.91	16.30	26.00	56.60

Exercise 9

The exchange current density of Pt /Fe^{3+}, Fe^{2+} is 2.5 $mA{\cdot}\ cm^{-2}$.
Calculate the current density across the electrode at 25 °C maintained at 1 V when [Fe^{2+}] = 0.1 M and [Fe^{+3}]= 0.2 M
(Standard reduction potential = 0.77I V, β = 0.58)