Solutions for Electrochemistry Problem Set

Constants:

$F \equiv 96484.56 \cdot coul \cdot mole^{-1}$ $T := (273.15 + 25) \cdot K$

$R \equiv 8.31441 \cdot joule \cdot mole^{-1} \cdot K^{-1}$ $M := \frac{mole}{liter}$

Equations

$E_{std\_cell} = E_{cathode} - E_{anode}$ $E_{cell} = E_{std\_cell} - \frac{R \cdot T}{n \cdot F} \cdot \ln\left(\frac{C_{anode}}{C_{cathode}}\right)$

1 a. Calculate the cell potential and free energy available for the following electrochemical systems

Ag (*s*)| Ag^{1+} (*aq* 1.0M) || Cu^{2+} (*aq* 1.0M) | Cu(*s*)

Anode (oxidation) Ag (s) <--> Ag1+ + 1 e-
Cathode (reduction Cu2+ + 2e- <--> Cu(s)

From the table of reduction potentials, we can find

$E_{anode} := 0.7996 \cdot volt$ $E_{cathode} := 0.3402 \cdot volt$

And then calculate the standard cell potential

$E_{std\_cell} := E_{cathode} - E_{anode}$ $E_{std\_cell} = -0.4594 \circ volt$

Next determine the cell potential at the concentrations given

Balance the oxidation and reduction reactions

2 Ag (*s*) + Cu^{2+}(*aq*) <--> 2 Ag^{1+}(*aq*) + Cu (*s*)

The number of electrons exchanged

$n := 2$

Calculate Q

$$Q = \frac{(C_{Ag})^2}{(C_{Cu})}$$

Anode: Cathode:

$C_{Ag} := 1.0$ $C_{Cu} := 1.0$

Calcuations:

$E_{cell} := E_{std\_cell} - \frac{R \cdot T}{n \cdot F} \cdot \ln\left[\frac{(C_{Ag})^2}{C_{Cu}}\right]$ $E_{cell} = -0.4594 \circ volt$

1.b This is the same reaction for everything except the concentrations so:

Anode: $C_{Ag} := 0.1$

Cathode: $C_{Cu} := 0.1$

Calcuations:

$$E_{cell} := E_{std\_cell} - \frac{R \cdot T}{n \cdot F} \cdot \ln\left[\frac{\left(C_{Ag}\right)^2}{C_{Cu}}\right] \qquad E_{cell} = -0.4298 \, volt$$

1.c This is the same reaction for everything except the concentrations so:

Anode: $C_{Ag} := 1.0$

Cathode: $C_{Cu} := 0.1$

Calcuations:

$$E_{cell} := E_{std\_cell} - \frac{R \cdot T}{n \cdot F} \cdot \ln\left[\frac{\left(C_{Ag}\right)^2}{C_{Cu}}\right] \qquad E_{cell} = -0.489 \, volt$$

1.d This is the same reaction for everything except the concentrations so:

Anode: $C_{Ag} := 1$

Cathode: $C_{Cu} := 0.01$

Calcuations:

$$E_{cell} := E_{std\_cell} - \frac{R \cdot T}{n \cdot F} \cdot \ln\left[\frac{\left(C_{Ag}\right)^2}{C_{Cu}}\right] \qquad E_{cell} = -0.5186 \, volt$$

1.e This is the same reaction for everything except the concentrations so:

Anode: $C_{Ag} := 0.1$

Cathode: $C_{Cu} := 1.0$

Calcuations:

$$E_{cell} := E_{std\_cell} - \frac{R \cdot T}{n \cdot F} \cdot \ln\left[\frac{\left(C_{Ag}\right)^2}{C_{Cu}}\right] \qquad E_{cell} = -0.4002 \, volt$$

1 f In this problem the cell is reversed so that:

Cu(*s*) | Cu^{2+} (*aq* 1.0M) || Ag^{1+} (*aq* 1.0M) | Ag (*s*)

Anode (oxidation) Cu (s) <--> Cu2+ + 2e-
Cathode (reduction Ag1+ + 1 e- <--> Ag(s)

From the table of reduction potentials, we can find

$E_{anode} := 0.3402 \cdot volt$ $E_{cathode} := 0.7996 \cdot volt$

And then calculate the standard cell potential

$E_{std\_cell} := E_{cathode} - E_{anode}$ $E_{std\_cell} = 0.4594 \circ volt$

Next determine the cell potential at the concentrations given

Balance the oxidation and reduction reactions

2 Ag^{1+}(*aq*) + Cu (*s*) <--> 2 Ag (*s*) + Cu^{2+}(*aq*)

The number of electrons exchanged

$n := 2$

Calculate Q

$$Q = \frac{(C_{Cu})}{(C_{Ag})^2}$$

Anode: Cathode:

$C_{Ag} := 1.0$ $C_{Cu} := 1.0$

Calcuations:

$$E_{cell} := E_{std\_cell} - \frac{R \cdot T}{n \cdot F} \cdot \ln\left[\frac{C_{Cu}}{(C_{Ag})^2}\right]$$ $E_{cell} = 0.4594 \circ volt$

Notice that in this reaction the cell potential is positive, this electrochemical cell is spontaneous (the reactions are going the way they want to). So this is the voltage produced by the cell. It is acting like a battery here. In the previous examples, the reactions were all going in the non-spontaneous direction. The voltage was negative, indicating that this is the voltage that must be applied to the system to push it backwards. The previous cells were electrolytic, they were being charged.

2. If the electrochemical cell discussed is used as a battery and begins with 10.0 g electrodes and 150 mL of 1.0 M solution. Identify the limiting reagent and calculate the moles of electrons exchanged when the reaction goes to completion.

We use the balanced chemical equation from 1f, where the reaction was spontaneous.

$2\ Ag^{1+}(aq) + Cu\ (s) \text{ <--> } 2\ Ag\ (s) + Cu^{2+}(aq)$

So, silver ions and copper metal are the reactants.

$$\text{moles}_{\text{Ag\_ion}} := (0.250 \cdot L) \cdot (1.0 \cdot M)$$

$$\text{moles}_{\text{Ag\_ion}} = 0.25\ \text{mol}$$

$$\text{moles}_{\text{Cu\_solid}} := \frac{10 \cdot gm}{63.546 \cdot \frac{gm}{mole}}$$

$$\text{moles}_{\text{Cu\_solid}} = 0.1574\ \text{mol}$$

Since the balanced equation shows that two moles of silver ions are required for each mole of copper solid, silver is the limiting reagent.

$$\text{moles}_{\text{Cu\_solid\_used}} := \frac{\text{moles}_{\text{Ag\_ion}}}{2}$$

$$\text{moles}_{\text{Cu\_solid\_used}} = 0.125\ \text{mol}$$

Each silver ion requires one electron to be reduced. So the moles of electrons are the same as the moles of silver.

$$\text{moles}_{\text{electron}} := \text{moles}_{\text{Ag\_ion}}$$

$$\text{moles}_{\text{electron}} = 0.25\ \text{mol}$$