Measurement of standard electrode potential (E^o) re-explained in detail

The electrode chosen as the ultimate standard is the standard hydrogen electrode (SHE) discussed in lecture II. This is because SHE standard electrode potential has been conventionally taken as 0.0 V. If this electrode (SHE) is connected to another electrode say $Cu^{2+}|Cu$ of unknown electrode potential as shown in Figure 12, the standard electrode potential (E^o) of the $Cu^{2+}|Cu$ can be measured as long as the copper(II) ion solution is 1 molal, and the system is operating under standard condition. The reading on the voltmeter gives the standard (reduction) electrode potential (E^o) value of the $Cu^{2+}|Cu$ since the SHE potential value has been taken as 0.0 V.
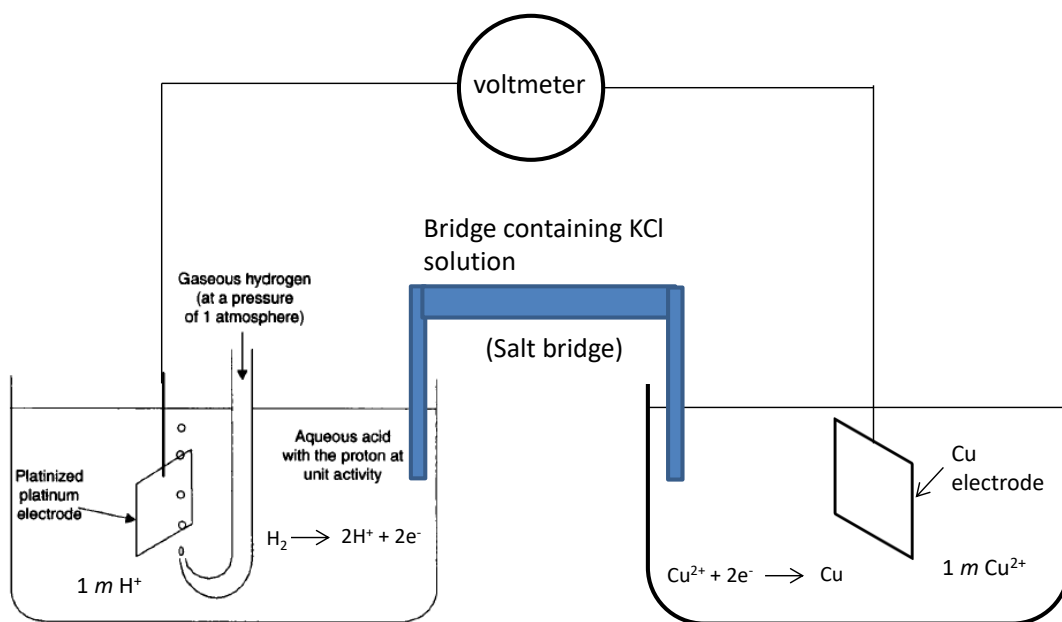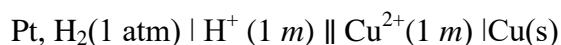

Figure 12: A voltaic cell in which a SHE has been connected to a copper electrode in a 1 m (molal) solution of $CuSO_4$. This set-up would give the standard electrode potential E^o value of the $Cu^{2+}|Cu$.

The voltaic cell shown in Figure 12 can be represented as follows:

Pt, H_2(1 atm) | H^+ (1 m) || Cu^{2+}(1 m) |Cu(s)

The observed emf of the cell is +0.34 V. The sign is positive by convention because electrons flow from left to right in the outer circuit. There is therefore a greater tendency for the process

$$Cu^{2+} + 2e^- \longrightarrow Cu(s)$$
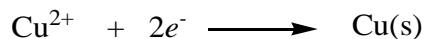
to occur than for $2H^+ + 2e^- \rightarrow H_2$ to occur. This second process is forced to go in the reverse direction instead.

By the IUPAC convention, the $Cu^{2+}|Cu$ electrode is on the right (this was mentioned in lecture II), and the standard electrode potential E^o of this electrode is +0.34 V. It is a measure of the tendency for the copper(II) ions to be reduced by the process: $Cu^{2+} + 2e^- \rightarrow Cu$. It is for this reason that these electrode potentials are also known as ***standard reduction potentials***.

Online sources for the table of standard electrode (reduction) potentials at T = 25°C

http://butane.chem.uiuc.edu/cyerkes/Chem104ACSP08/Genchemref/standpot.html

http://demo.webassign.net/question_assets/wertzcaqs3/reduction/manual.html

From the above links, it would be seen that the reactions are written as reduction processes (e.g. $Cu^{2+} + 2e^- \rightarrow Cu$). A table of standard oxidation potentials, on the other hand, would have the signs reversed and the corresponding reactions would be oxidations, for example, $Cu \rightarrow Cu^{2+} + 2e^-$.

From the tables given in the links, it would be seen that the E^o values for the two half-cell reactions in the Daniell cell, Zn(s) | ZnSO$_4$(1 m) || CuSO$_4$(1 m) |Cu(s) are as given below:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^o = +0.34 \text{ V}$$

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E^o = -0.76 \text{ V}$$

It then means that the emf of the cell would be $E^o_{emf} = E^o_R - E^o_L = +0.34 - (-0.76) = +1.10$ V

Thermodynamics of electrochemical cells

Recall that the Gibbs free energy change or maximum work done by an electrochemical process is given by $\Delta G_{rxn} = -nFE$. This is also true for the standard-cell reaction, and the change in the Gibbs free energy is given by

$$\Delta G^{\text{o}} = -nFE^{\text{o}} \tag{33}$$

Note that if E is positive, ΔG is negative; a positive E means that the cell is operating spontaneously with the reactions occurring in the forward direction (e.g. $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$), and this requires ΔG to be negative.

For any reaction,

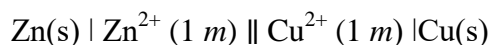$$a\text{A} + b\text{B} + \cdots \longrightarrow \cdots + y\text{Y} + z\text{Z}$$
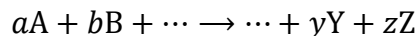
the Gibbs energy change that occurs when a mol of A at a concentration [A] reacts with b mol of B at [B], etc. is given by

$$\Delta G = -RT\left[\ln K^{\text{o}} - \ln\left(\frac{\dots[\text{Y}]^y[\text{Z}]^z}{[\text{A}]^a[\text{B}]^b\dots}\right)\right] \tag{34}$$

If the concentration of the reactants and products are unity, then

$$\Delta G = \Delta G^{\text{o}} = -RT\ln K^{\text{o}} \tag{35}$$

For any cell involving standard electrodes such as the standard Daniell cell,

$Zn(s) \mid Zn^{2+}$ (1 m) $\parallel$ Cu^{2+} (1 m) $\mid Cu(s)$

Equations 33 and 35 apply; therefore,

$$E^{\text{o}} = \frac{RT}{nF}\ln K^{\text{o}} \tag{36}$$

At 25$^{\text{o}}$C this becomes

$$E^{\text{o}}/\text{V} = \frac{0.025674}{n}\ln K^{\text{o}} \tag{37}$$

where R and F have been taken as 8.314 J mol^{-1} K^{-1} and 96 500 C mol^{-1} respectively.

This expression provides a very important method for calculating Gibbs energy changes and equilibrium constants.

The Nernst Equation

So far our discussions have been limited to standard electrode potentials E^o and to E^o values for cells in which the active species are present at $1\ m$ concentrations, and where the corresponding standard Gibbs energies have been written as ΔG^o.

Let us now remove the restriction to standard electrolytes and consider cells in which the concentrations are other than unity.

Consider, for example, the cell Pt, H_2(1 atm) | H^+ (aq) ‖ Cu^{2+}(aq) |Cu(s) in which a hydrogen electrode has been combined with a copper electrode immersed in a Cu^{2+} solution, the concentration of which is other than unity. The overall cell reaction is

$$H_2 + Cu^{2+} \rightarrow 2H^+ + Cu \qquad \text{and the Gibbs energy change is}$$

$$\Delta G = -RT\left(\ln K^o - \ln\frac{[H^+]^2}{[Cu^{2+}]}\right) \qquad \text{as proven in Eq. 34} \tag{38}$$

If Eq. 38 is opened, we have, $\Delta G = -RT\ln K^o + RT\ln\dfrac{[H^+]^2}{[Cu^{2+}]}$ \hfill (39)

and recall that $\Delta G = \Delta G^o = -nFE^o = -RT\ln K^o$,
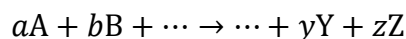
therefore, $\Delta G = -nFE^o + RT\ln\dfrac{[H^+]^2}{[Cu^{2+}]}$ by replacing $= -RT\ln K^o$ with $-nFE^o$ in Eq. 39.

$$\Delta G = -nFE^o + RT\ln\frac{[H^+]^2}{[Cu^{2+}]} \tag{40}$$

Eq. 40 can be written as $-nFE = -nFE^o + RT\ln\dfrac{[H^+]^2}{[Cu^{2+}]}$ which actually is;

$$E = E^o - \frac{RT}{nF}\ln\frac{[H^+]^2}{[Cu^{2+}]} \tag{41}$$

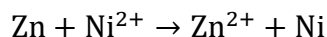In general, we may consider any cell for which the overall reactions have the general form;

$$a\text{A} + b\text{B} + \cdots \rightarrow \cdots + y\text{Y} + z\text{Z}$$

ΔG is given by $\Delta G = -nFE^o + RT\ln\left(\dfrac{\ldots[Y]^y[Z]^z}{[A]^a[B]^b\ldots}\right)$ \hfill (42)

Eq. 42 then leads to $E = E^{o} - \frac{RT}{nF} \ln \left(\frac{...[Y]^{y}[Z]^{z}}{[A]^{a}[B]^{b}...} \right)$ The Nernst Equation   (43)

Suppose that this equation is applied to the cell,

$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$ for which the overall reaction is

$Zn + Ni^{2+} \rightarrow Zn^{2+} + Ni$

The standard electrodes according to the Tables in the above links are:

$Ni^{2+} + 2e^{-} \rightarrow Ni \qquad E^{o} = -0.257$ V

$Zn^{2+} + 2e^{-} \rightarrow Zn \qquad E^{o} = -0.762$ V

and the E^{o} for the overall processes is $= -0.257 - (-0.762) = 0.505$ V. The Nernst is thus;

$E = 0.505 \text{ (V)} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Ni^{2+}]}.$

At 25°C, this equation becomes, $E/V = 0.505 \text{ (V)} - \frac{0.025674}{2} \ln \frac{[Zn^{2+}]}{[Ni^{2+}]}$ (44)

since n = 2. It can be seen from this equation that increasing the ratio $[Zn^{2+}]/[Ni^{2+}]$ decreases the cell emf. This is understandable because a positive emf means that the cell is producing Zn^{2+} and that Ni^{2+} ions are being removed.

Temperature Coefficients of Cell emfs

Since a Gibbs energy change can be obtained from the standard emf of a reversible cell according to Equation 33, the ΔS^{o} and ΔH^{o} values can be calculated if emf measurements are made over a range of temperature.

The basic relationship is shown in Eq. 45;

$S = - \left(\frac{\partial G}{\partial T} \right)_{P}$ (45)

and for an overall reaction where a change from reactant to product is measured;

$\Delta S = - \left(\frac{\partial \Delta G}{\partial T} \right)_{P}$ (46)

If Eq. 46 is sunstituted into Eq. 33, we have;

$$\Delta S = nF \left(\frac{\partial E}{\partial T}\right)_P \tag{47}$$

Recall that the enthalpy change is $\Delta H = \Delta G + T\Delta S$, therefore,

$$\Delta H = -nFE + T\left(nF\frac{\partial E}{\partial T}\right) = -nF\left(E - T\frac{\partial E}{\partial T}\right) \tag{48}$$

The measurement of emf values at various temperatures provides a very convenient method of obtaining thermodynamic values for chemical reactions and has frequently been employed for this purpose. For the results to be reliable, the temperature coefficients should be known to three significant figures, and this requires careful temperature and emf measurements.
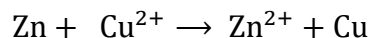
Worked examples:

1.) Calculate the equilibrium at 25°C for the reaction occurring in the Daniell cell, if the standard emf is 1.100 V.

The reaction is

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$ and n = 2 (the number of electrons transferred as shown here below)

Left (ox.): $Zn \rightarrow Zn^{2+} + 2e^-$

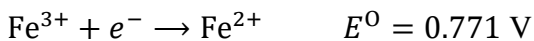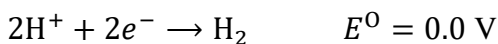Right (red.): $Cu^{2+} + 2e^- \rightarrow Cu$
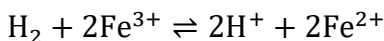
$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

$$\ln K^o = \frac{nE^o}{0.025674} = \frac{2 \times 1.100}{0.025674} = 85.6$$

and thus $K^o = e^{85.6} = 1.50 \times 10^{37}$

2.) Using the data below,

$2H^+ + 2e^- \longrightarrow H_2 \qquad E^O = 0.0 \text{ V}$

$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E^O = 0.771 \text{ V}$

calculate the equilibrium constant for the reaction;

$H_2 + 2Fe^{3+} \rightleftharpoons 2H^+ + 2Fe^{2+}$

The E^o_{emf} for the process $2Fe^{3+} + H_2 \longrightarrow 2H^+ + 2Fe^{2+}$ for which $n = 2$ is 0.771 (recall that $E^o_{emf} = E^o_R - E^o_L = 0.771 - 0.0 = 0.771\ V$).

$$\ln K^o = \frac{nE^o}{0.025674} = \frac{2 \times 0.771}{0.025674}$$

$\Rightarrow K^o = 1.14 \times 10^{26}\ mol^2\ dm^{-6}$. The unit is brought about because the equilibrium constant from the process is a ratio of the product of the square of the concentrations of the products to the square of the concentration of the reactants, i.e. $K = \frac{[H^+]^2[Fe^{2+}]^2}{[Fe^{3+}]^2}$.

It should be noted that the emf is an intensive property (i.e it does not depend on the amount of matter, the electron in this case), hence, in making this calculation, 0.771 V must not be multiplied by 2 (no. of transferred electrons). To show this assertion, the emf of 0.771 V equally applies well to the process $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$. Calculating the K^o for this process,

$\frac{1}{2}H_2 + Fe^{3+} \rightleftharpoons H^+ + Fe^{2+}$, the half-cell reactions would be written as;

$H^+ + e^- \longrightarrow \frac{1}{2}H_2\ \ E^0 = 0.0\ V$
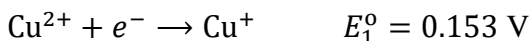
$Fe^{3+} + e^- \longrightarrow Fe^{2+}\ E^0 = 0.771\ V$
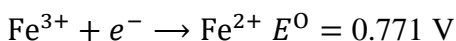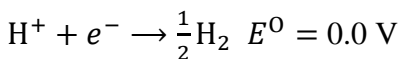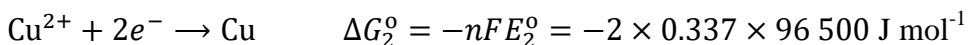
and again $E^o_{emf} = 0.771$ V but $n = 1$.

$$\ln K^o = \frac{nE^o}{0.025674} = \frac{1 \times 0.771}{0.025674} = 30.01$$

$\Rightarrow K^o = 1.10 \times 10^{13}\ mol\ dm^{-3}$

3.) Calculate E^0 for the process $Cu^+ + e^- \longrightarrow Cu$ by making use of the following E^0 values:

$Cu^{2+} + e^- \longrightarrow Cu^+ \qquad E^o_1 = 0.153\ V$

$Cu^{2+} + 2e^- \longrightarrow Cu \qquad E^o_2 = 0.337\ V$

The ΔG^o values for these two reactions are:

$Cu^{2+} + e^- \longrightarrow Cu^+ \qquad \Delta G^o_1 - nFE^o_1 = -1 \times 0.153 \times 96\ 500\ J\ mol^{-1}$

$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \Delta G^o_2 = -nFE^o_2 = -2 \times 0.337 \times 96\ 500\ J\ mol^{-1}$

The reaction $Cu^+ + e^- \rightarrow Cu$ is obtained by subtracting reaction 1 from reaction 2 and the ΔG^o value for $Cu^+ + e^- \rightarrow Cu$ is therefore obtained by subtracting ΔG_1^o from ΔG_2^o:

$\Delta G^o = [-2 \times 0.337 \times 96\,500 - (-1 \times 0.153 \times 96\,500)]$ J mol^{-1}

$= (0.153 - 0.674) \times 96500$ J mol^{-1}
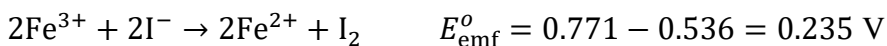
$= -0.521 \times 96500$ J mol^{-1} (compare with $-nFE^o$)

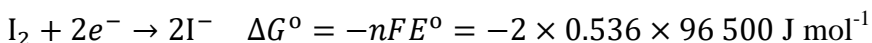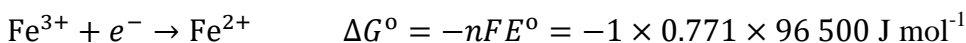Since, for $Cu^+ + e^- \rightarrow Cu$, $n = 1$, it follows that $E^o = 0.521$ V.

NOTE

It is incorrect in working example 3 which is for a single electrode (haf-cell), by combining the E_1^o and E_2^o values directly. In view of this, the student may wonder why it is legitimate to calculate E^o values for overall cell reactions by simple combination of the respective E^o values of the individual electrodes. To expatiate on this, consider for example, the following E^o values:

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^o = 0.771$ V

$I_2 + 2e^- \rightarrow 2I^-$ $E^o = 0.536$ V

The procedure we have been adopting is to combine these two E^o values:

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ $E_{emf}^o = 0.771 - 0.536 = 0.235$ V

The fact that this is justified can been seen by writing the ΔG^o values:

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\Delta G^o = -nFE^o = -1 \times 0.771 \times 96\,500$ J mol^{-1}

$I_2 + 2e^- \rightarrow 2I^-$ $\Delta G^o = -nFE^o = -2 \times 0.536 \times 96\,500$ J mol^{-1}

If the two free energy expressions are combined. This is done after multiplying the first by two and subtracting the second:

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$
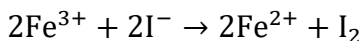
$\Delta G^o = [2(-1 \times 0.771 \times 96\,500) - (-2 \times 0.536 \times 96\,500)]$ J mol^{-1}

$\Delta G^o = -2 \times 0.235 \times 96\,500$ J mol^{-1} (comparing with $-nFE^o$), thus, $E^o = 0.235$ V. This is simply $0.771 - 0.536$. This shows the justification of simply subtracting E^o values to find E^o for an overall reaction, in which there are no left over electrons. However, to obtain an E^o for a half-reaction (as in example 3), we can in general not simply combine E^o values but must calculate the ΔG^o values as just done.

4.) Calculate the emf of the cell Co | Co^{2+} || Ni^{2+} |Ni if the concentrations are

   (a) $[Ni^{2+}] = 1\ m$ and $[Co^{2+}] = 0.1\ m$

   (b) $[Ni^{2+}] = 0.01\ m$ and $[Co^{2+}] = 1.0\ m$

   The cell reaction is $Co + Ni^{2+} \rightleftharpoons Co^{2+} + Ni$ and from the standard electrode reduction Table (links above),

   $Ni^{2+} + 2e^- \rightarrow Ni \qquad E^o = -0.257$ V

   $Co^{2+} + 2e^- \rightarrow Co \qquad E^o = -0.280$ V

   The $E^o_{emf} = -0.257 - (-0.280) = 0.023$ V, and $n = 2$. The cell emf at the concentrations specified are
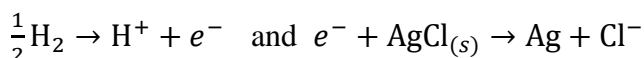
   (a) $E = 0.023 - \frac{0.025674}{2} \ln \frac{[Co^{2+}]}{[Ni^{2+}]} = 0.023 - \frac{0.025674}{2} \ln \frac{0.1}{1} = 0.023 + 0.030 = 0.053$ V

   (b) $E = 0.023 - \frac{0.025674}{2} \ln \frac{[Co^{2+}]}{[Ni^{2+}]} = 0.023 - \frac{0.025674}{2} \ln \frac{1}{0.01} = 0.023 - 0.059 = -0.036$ V
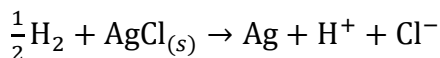
   It should be noted that the cell operates in opposite directions in the two cases.

5.) The emf of the cell Pt, H$_2$(1 atm) | HCl (0.01 m) || AgCl(s) |Ag is 0.2002 V at 25°C, and $\partial E / \partial T$ is -8.665 $\times$ 10^{-5} V K^{-1}. Write the cell reaction and calculate ΔG, ΔS and ΔH.

   The electrode reactions are:

   $\frac{1}{2} H_2 \rightarrow H^+ + e^-$ and $e^- + AgCl_{(s)} \rightarrow Ag + Cl^-$

   The cell reaction is

   $\frac{1}{2} H_2 + AgCl_{(s)} \rightarrow Ag + H^+ + Cl^-$

   The Gibbs energy change is

   $\Delta G = -96\ 500 \times 0.2002 = -19\ 320$ J mol^{-1}

   The entropy change is obtained from;

   $\Delta S = 96\ 500 \times -8.665 \times 10^{-5} = -8.36$ J K^{-1} mol^{-1}

   The enthalpy change can be calculated by using Eq. 48 or more easily from $\Delta H = \Delta G + T \Delta S$ since all the parameters therein are known.

   $\Delta H = -19\ 320 + (-8.36 \times 298.15) = -21\ 800$ J mol^{-1}

   END OF LECTURES ON ELECTROCHEMISTRY FOR THIS SEMESTER