Electrochemistry involves redox reactions.

Terminology:

Red-ox reaction – a chemical reaction where one species undergoes a loss of electrons another species gains electrons.

$$\text{Cu(II)}^+ + \text{Zn} \rightarrow \text{Cu(II)} + \text{Zn(II)}$$

Further, the reaction can be carried out so that oxidation and reduction occur at physically different locations – electrodes - in electrochemical set-ups. The electrode reactions are,

$$\text{Zn} \rightarrow \text{Zn(II)} + 2e$$
$$2e + \text{Cu(II)} \rightarrow \text{Cu}$$

Two electrodes, coupled, constitute an electrochemical cell.

The electron movement: q = quantity of charge, i = rate of movement of charge. The electrical potentials of the electrodes, $E_a$ and the potential difference of the electrodes $E_{cell}$ that are involved and can be measured.
Two types of cells are studied:

a. **Galvanic (Voltaic) cell**: Galvanic cell uses **spontaneous** red-ox chemical reactions to produce electrical energy; that would result in a flow of electrons. \( \Delta G < 0 \).

b. **Electrolytic cell**: An electrolytic cell decomposes chemical compounds by red-ox processes **using** electrical energy from an outside source - electrolysis. This is an energy demanding process – **non-spontaneous**. \( \Delta G > 0 \).

In any type of cell: Anode – oxidation occurs
Cathode – reduction occurs

**Half Cell**

M(s) immersed in an aqueous solution of M\(^{2+}\)(aq) establishes an equilibrium between on the two phases. Depending on the position of equilibrium there would be an accumulation or depletion of electrons from the metal(s).

e.g. Zn/Zn\(^{2+}\)(aq) system (half-cell), electrons accumulate (standard state) on the Zn electrode.

\[
\text{Zn(s) } \xrightarrow{} \text{Zn}^{2+}(aq) + 2e^-
\]

A negative charge builds up on the Zn electrode and positive charge builds up in the surrounding solution. This charging separation leads to a difference in the electrical potential difference between the metal (electrode) and the solution (~1V); half-cell potential, electrode potential.

The electrical potential, \( \phi \), developed affects the chemical potential (energy) of the charged species.

The potential energy of the charged species would have an additional term in addition to the normal chemical potential, \( \mu \); **electrochemical (energy) potential** \( \bar{\mu} \).

\[
\bar{\mu} = \mu + \phi(zF)
\]
\[
\bar{\mu} = \mu + \phi zF \quad \Rightarrow \quad \bar{\mu} = \mu \quad \text{for } \phi = 0 \text{ and/or } z = 0.
\]
Electrochemical potential $\mu$ is a thermodynamic measure of chemical potential that that takes into account the energy contribution from the electrical potential.

For an electrochemical reaction; $\Delta G_e = \sum_i \bar{\mu}_i$

For an electrochemical reaction @ equilibrium; $\Delta G_e = \sum_i \bar{\mu}_i = 0$

In this example the Zn(II) ion do not exist in isolation, but with a counter ion. That will be true for all compounds in solution.

The $\phi$ affects all ions, in the solution, regardless of their participation in the redox equilibrium half reaction.

Note: The overall reaction include the ‘non-participating’ counter ions as well.

Therefore for electrochemical reaction ;

$$\Delta G_e = \sum_i \bar{\mu}_i + \bar{\mu}_i + \sum_z (\phi F)$$

For any ionic compound in solution

Therefore considering all species present in the solution; we can set $\phi = 0$, and as a result.

$$\bar{\mu}_i = \bar{\mu}_i \text{ (ions in solution)}$$

Half Cell

\[
\begin{align*}
Zn & \rightarrow Zn^{2+} \\
\phi & \\
Zn^{2+}(aq) + 2e & \rightleftharpoons Zn(s)
\end{align*}
\]

At equilibrium the chemical/electrochemical potentials of the ‘reactant side’ and ‘product’ side are equal.

$$\mu_{2n+} + z\mu_e = \mu_{2n}$$

$$\bar{\mu}_e = -\phi F \text{ per electron in metal.}$$

$$\bar{\mu}_{2n+} = \mu_{2n+} \text{ considering the counter ions}$$

$$\mu_{2n+} + z\bar{\mu}_e = \mu_{2n} \text{ for } Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s); \ z = 2$$

$$\mu_{2n+}^{\circ} + RT \ln a_{2n+} - zF\phi_{2n+2/2n} = \mu_{2n}$$

$$\phi_{2n+2/2n} = \frac{\left(\mu_{2n+}^{\circ} + RT \ln a_{2n+} \right) - \mu_{2n}}{zF}$$

$$\phi_{2n+2/2n} = \frac{\left(\mu_{2n+}^{\circ} - \mu_{2n} \right) + RT \ln a_{2n+1}}{zF}$$

$$E_{2n+2/2n} = E_{2n+2/2n}^{\circ} + \frac{RT}{zF} \ln a_{2n+2}$$

$$E_{el} = E_{el}^{\circ} + \frac{RT}{zF} \ln Q_{el}$$

Electrode Potential
\( \mu_{\text{Zn}^{2+}} = \mu_{\text{Zn}^{2+}} \) considering the counter ions

\( \mu_{\text{Zn}^{2+}} = \mu_{\text{Zn}^{2+}} + z\mu_+ = \mu_{\text{Zn}} \) for \( \text{Zn}^{2+}(aq) + 2e^- = \text{Zn}(s); z = 2 \)

\( \mu_{\text{Zn}^{2+}} = \mu_{\text{Zn}^{2+}} + RT \ln a_{\text{Zn}^{2+}} - zF\phi_{\text{Zn}^{2+}/\text{Zn}} = \mu_{\text{Zn}} \)

\( \mu_{\text{Zn}^{2+}} + RT \ln a_{\text{Zn}^{2+}} - zF\phi_{\text{Zn}^{2+}/\text{Zn}} = \mu_{\text{Zn}} \)

\( \phi_{\text{Zn}^{2+}/\text{Zn}} = \left( \frac{\mu_{\text{Zn}^{2+}} + RT \ln a_{\text{Zn}^{2+}}}{zF} - \frac{\mu_{\text{Zn}}}{zF} \right) \)

\( \phi_{\text{Zn}^{2+}/\text{Zn}} = \left( \frac{\mu_{\text{Zn}^{2+}} - \mu_{\text{Zn}}}{zF} \right) + RT \ln \frac{1}{a_{\text{Zn}^{2+}}} \)

\( E_{\text{Zn}^{2+}/\text{Zn}} = E'_{\text{Zn}^{2+}/\text{Zn}} - \frac{RT}{zF} \ln \frac{1}{a_{\text{Zn}^{2+}}} \)

\( E_{\text{Zn}^{2+}/\text{Zn}} = E'_{\text{Zn}^{2+}/\text{Zn}} - \frac{RT}{zF} \ln Q_{\text{Zn}^{2+}/\text{Zn}} \)

Electrode Potential, Nernst Equation

**Primary Reference Electrode: Standard Hydrogen Electrode**

However the absolute electrical potential of an individual half cell cannot be measured. Therefore, it is convenient to choose one half-cell as a reference and arbitrarily assign an electrical potential of zero to this half-cell.

Coupling with the reference electrode the electrical potential associated with any other half cell, the new cell potential difference can be determined.

The standard hydrogen electrode fulfills the role of a reference half-cell of zero potential. The reaction in the standard hydrogen electrode is,

\( \text{H}^+(aq) + e^- \rightarrow \frac{1}{2}\text{H}_2(g) \Rightarrow \mu_{\text{H}^+}(aq) + \mu_e^- = \frac{1}{2}\mu_{\text{H}_2(g)} \)

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\( \mu_H + RT \ln a_H - F\phi_{H^+/H_2} = \frac{1}{2} \mu_H^+ + \frac{1}{2}RT \ln f_{H_2} \)

\( \phi_{H^+/H_2} = \frac{\mu_H^+ - \frac{1}{2} \mu_H^+}{F} + \frac{RT}{F} \ln \frac{f_{H_2}^{1/2}}{a_H} \)

Setting unit activities for all species;

\( \phi_{H^+/H_2} = \frac{\mu_H^+}{F} \quad \phi_{H^+/H_2} = 0 \)

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**Standard Hydrogen Electrode: SHE**

\( E_{\text{SHE}} = 0.00V @ 25^\circ\text{C} \) by definition.
pH meter is very close to an ideal voltmeter. Impedance $\to \infty$
Draws negligible current.

Negative terminal
- reference electrode slot.
- BNC – outer connector

For Cell: $\text{Zn} | \text{Zn}^{2+} (a_1) \ || \ \text{Cu}^{2+} (a_2) | \text{Cu}$

Overall: $\text{Zn}(s) + \text{Cu}^{2+} (aq) \longrightarrow \text{Zn}^{2+} (aq) + \text{Cu}(s)$

$$Q_{eq} = \frac{a_{\text{Zn}^{2+}} a_{\text{Cu}^{2+}}}{a_{\text{Cu}^{2+}} a_{\text{Zn}^{2+}}}$$

$$\Delta G_k = \mu_{Zn^{2+}} + \mu_{Cu^{2+}} - \mu_{Zn^{2+}} - \mu_{Cu^{2+}} + RT \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$$

$$\Delta G_R = -nF \Delta \phi$$

$$-2FE = \Delta G_k + RT \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$$

Cell Potential, Nernst Equation

$$E = E^* - \frac{RT}{2F} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$$

$$E_{eq} = E^* - \frac{RT}{nF} \ln Q_{eq}$$
**Electrode potential** $E_{el}$:

Calculation of (half cell) electrode potential $E_{el}$ as a reduction potential (convention).

a. Write charged and mass balanced *half* reaction as a reduction reaction, note the # electrons $n$

b. Write the *reaction quotient* $(Q_{el})$, associated with $n$

c. Obtain the Standard Electrode Potential for the half reaction $E^0_{el}$, i.e. $E^0_{M+n/M}$

$$E_{M^{n+}M} = E^0_{M^{n+}M} - \frac{RT}{nF} \ln Q_{el}$$

If $Q = 0$, i.e. all activities at standard states $= 1$

$$E_{M^{n+}M} = E^0_{M^{n+}M}$$

Using Nernst equation - electrodes:

$$Fe^{+1} + e = Fe^{+2}$$

$$MnO_2 + 8H^+ + 5e = Mn^{+2} + 4H_2O$$

Using Nernst equation:

$$E_{\text{red}} = E_{\text{ox}} - \frac{RT}{nF} \ln \frac{a_{\text{red}}}{a_{\text{ox}}}$$

**Cell potential (EMF) $E_{cell}$:**

Calculation of (half cell) electrode potential $E_{cell}$ as a reduction potential (convention).

a. Write charged and mass balanced *full* reaction as a reduction reaction, note the # electrons $n$, for the full reaction.

b. Write the *reaction quotient* $(Q_{cell})$, associated with $n$ electrons.

c. Obtain the Standard Cell Potential for the cell reaction $E^0_{cell}$, i.e. $E^0_{\text{full reaction}} - E^0_{\text{oxidation reaction}}$

$$E_{cell} = (E^0_{\text{full reaction}} - E^0_{\text{oxidation reaction}}) - \frac{RT}{nF} \ln Q_{cell}$$

If $Q = 0$, i.e. all activities at standard states $= 1$

$$E_{cell} = E^0_{cell}$$

By convention half reactions are written as reduction reactions.

Larger the electrode potential calculated (determined) for the reduction process, higher the propensity for that to occur.

Then the reverse of the reaction has less or no propensity to occur. That is the oxidation of the is unlikely if reduction is the naturally preferred process.

And vice versa.

**Standard (reduction) potential** values compare the inherent propensity (spontaneously) of a reduction to occur. Large and positive favors (spontaneous) the reduction process; large and negative values indicative of non-spontaneous process, but reverse process, oxidation is spontaneous.
Using Nernst equation — Electrochemical cell.

\[ E_{\text{cell}} = E_{\text{cell}}^0 + \frac{RT}{nF} \ln \left( \frac{a_{Mn^{2+}} a_{Fe^{3+}}^{\alpha}}{a_{MnO_4} a_{H^+}^{5a}} \right) \]

\[ E_{\text{cell}} = E_{\text{cell}}^0 + \frac{RT}{nF} \ln \left( \frac{a_{Mn^{2+}} a_{Fe^{3+}}^{\alpha}}{a_{MnO_4} a_{H^+}^{5a}} \right) \]

\[ E_{\text{cell}} = E_{\text{cell}}^0 + \frac{RT}{nF} \ln \left( \frac{a_{Mn^{2+}} a_{Fe^{3+}}^{\alpha}}{a_{MnO_4} a_{H^+}^{5a}} \right) \]

\[ E_{\text{cell}} = E_{\text{cell}}^0 + \frac{RT}{10F} \ln \left( \frac{a_{Mn^{2+}} a_{Fe^{3+}}^{\alpha}}{a_{MnO_4} a_{H^+}^{5a}} \right) \]

\[ E_{\text{cell}} = (1.51 - 0.49) - \frac{RT}{10F} \ln \left( \frac{a_{Mn^{2+}} a_{Fe^{3+}}^{\alpha}}{a_{MnO_4} a_{H^+}^{5a}} \right) \]

\[ E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q_{\text{cell}} \]

\[ \frac{E_{\text{cell}} - E_{\text{cell}}^0}{(RT/F)} = \frac{1}{n} \ln Q_{\text{cell}} \]

Experimental determination of \( n \).
Larger and positive the cell potential indicative of a higher the propensity (spontaneous) for the reaction to occur.

Then the reverse of the reaction has less or no propensity (non-spontaneous) to occur.

Standard cell potential values compare the inherent propensity (spontaneity) of a reaction to occur.

Large and positive favors (spontaneous) the reaction; large and negative values indicative of non-spontaneous reaction, but reverse reaction is spontaneous.

Energetics:

\[ \Delta G_e = -nF \varepsilon_{cell} \]
\[ \Delta G_r = nF \varepsilon_{cell} - RT \ln Q_{cell} \]

At equilibrium \( \Delta G_e = 0 \) and \( Q = K \)
\[ 0 = nF \varepsilon_{cell} - RT \ln K \]

\[ \ln K = \frac{nF \varepsilon_{cell}}{RT} \] spontaneity prediction, reaction

\[ \Delta G_e^0 = -nF \varepsilon_{cell}^0 \]
\[ \Delta G_r^0 = -nF \varepsilon_{cell}^0 \]

Standard Gibbs Energy and Entropy Change of reactions

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]
\[ \Delta G^0 = -nF \varepsilon_{cell}^0 \]

\[ \left( \frac{\partial \Delta G^0}{\partial T} \right)_p = \left( \frac{\partial \Delta H^0}{\partial T} \right)_p - \left( \frac{\partial (T \Delta S^0)}{\partial T} \right)_p \]

\[ \left( \frac{\partial (-nF \varepsilon_{cell}^0)}{\partial T} \right)_p = -\Delta S^0 \]

\[ \Delta S^0 = nF \left( \frac{\partial \varepsilon_{cell}^0}{\partial T} \right)_p \]

Determination of \( E^0 \) and Activity Coefficients of Electrolytes:

Standard electrode by definition has the activities of all reaction components as unity.

Unlike most other solutions electrolyte activities are deviates concentration even at low concentrations. Construction of a standard electrode is not as direct as expected.

Experimental determination of standard electrode potentials much difficult and a non direct experimental approach is required.
Example

For Cell: Pt | H₂(p=1atm) | HCl(a=1) || AgNO₃(m) | Ag(s)

Cell Reaction: Ag⁺(aq,m) + 1/2 H₂(p=1atm) → Ag(s) + H⁺(aq,a = 1)

\[ \frac{Q_{\text{cell}}}{\gamma_{\text{cell}}} = \frac{a_{Ag}^{0}}{a_{Ag}^{0}}; R = 1 \]

\[ E_{\text{cell}} = E_{\text{cell}}^{0} - \frac{RT}{nF} \ln \frac{a_{Ag}^{0}}{a_{Ag}^{0}} = E_{\text{cell}}^{0} - \frac{RT}{F} \ln a_{Ag}^{0} \]

\[ E_{\text{cell}} = E_{\text{Ag}^{+}/Ag}^{0} - \frac{RT}{F} \ln \frac{a_{Ag}^{0}}{a_{Ag}^{0}} = E_{\text{Ag}^{+}/Ag}^{0} - \frac{RT}{F} \ln \frac{1}{\gamma_{Ag}^{0} \cdot m_{Ag}^{0}} \]

not possible to determine by expt.

Mean activity \( a_{x} \) is defined as \( a_{x}^{0} = a_{x}^{0} \cdot a_{x}^{\gamma} \)

\[ a_{x}^{0} = \gamma_{x} \cdot m_{x} \quad \text{and} \quad a_{x}^{0} = \gamma_{x} \cdot m_{x} \]

\[ a_{x}^{0} = \gamma_{x} \cdot m_{x} \quad \text{and} \quad a_{x}^{0} = \gamma_{x} \cdot m_{x} \]

\[ a_{Ag}^{0} = \gamma_{Ag} \cdot m_{Ag} \]

EMF of cell: Pt | H₂(p=1atm) | HCl(a=1) || AgNO₃(m) | Ag(s)

\[ E_{\text{cell}} = E_{\text{Ag}^{+}/Ag}^{0} - 0.05916 \log m - 0.03011 \sqrt{m} \]

\[ E_{\text{cell}} = E_{\text{Ag}^{+}/Ag}^{0} - 0.05916 \log m + 0.05916 \log \gamma_{z} \]

\[ \log \gamma_{z} = -0.5092 \mid z, \gamma_{z} \mid \sqrt{T} = -0.5092 \mid z, \sqrt{m} \quad \text{DHE} \]

\[ E_{\text{cell}} = E_{\text{Ag}^{+}/Ag}^{0} + 0.05916 \log m + 0.05916 \log \gamma_{z} \]

\[ E_{\text{cell}} = E_{\text{Ag}^{+}/Ag}^{0} - 0.05916 \log m - 0.03011 \sqrt{m} \]
Applications:

a. Solubility product of sparingly soluble salts, e.g. AgBr

Use half-cells involving the solubility equilibrium. Both of known standard electrode potential. Calculate standard cell potential.

\[ \Delta G^o = -nF \Delta E^o_{\text{cell}} \]
\[ \Delta G^o = -nF \Delta E^o_{\text{el}} \]

\[ \text{AgBr}(s) + e^- \rightarrow \text{Ag}(s) + \text{Br}^- (aq) \quad E^o = 0.07133 \text{ V} \quad \text{and} \]
\[ \text{Ag}(s) \rightarrow \text{Ag}^+(aq) + e^- \quad E^o = -0.7996 \text{ V} \]

\[ \text{ln} \ K_{sp} = \frac{nF}{RT} E^o = \frac{1 \times 96,485 \text{ C mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times (0.07283 \text{ V}) = 28.35 \]

Deceptive because n=1 is the same for half reactions.

Alternate approach.

\[ \text{Ag(s)|AgNO}_3(o) \ || \text{Ag(NO}_3(o)) \ || \text{Ag(s)} \]

Add Cl\(^{-}\) so that precipitate Ag\(^{+}\). At end point EMF, \(E_{\text{cell}}\):

\[ \text{AgCl}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq) \quad a_{\text{Ag}^{+}} \cdot a_{\text{Cl}^{-}} = K_{sp} \]

\[ a_{\text{Ag}^{+}} = K_{sp}, \quad a_{\text{Ag}^{+}} = \sqrt{K_{sp}} \]

Considering both electrodes as Ag(s)/Ag\(^{+}\)(aq) electrodes.

\[ E_{\text{cell}} = \left( E_{\text{cell}}^{\text{H}} - \frac{RT \ln \frac{1}{a_{\text{Ag}^{+}}}}{F} \right) - \left( E_{\text{cell}}^{\text{H}} - \frac{RT \ln \frac{1}{a_{\text{Ag}^{+}}}}{F} \right) \]

Potentials are not additive except in special situations, intensive property. Energy values are additive – extensive property.

\[ \text{PbSO}_4(s) \rightleftharpoons \text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \quad K_{sp} = a_{\text{Pb}^{2+}} \cdot a_{\text{SO}_4^{2-}} \]

\[ \text{PbSO}_4(s) + 2e^- \rightleftharpoons \text{Pb}(s) + \text{SO}_4^{2-}(aq) \quad E^o_1 \Rightarrow \Delta G^o_1 = -2F E^o_1 \]
\[ \text{Pb(s)} \rightleftharpoons \text{Pb}^{2+}(aq) + 2e^- \quad E^o_2 \Rightarrow \Delta G^o_2 = -(2F E^o_2) \]

\[ \Delta G^o = 2FE_{\text{cell}} = -RT \ln K_{sp} \]

\[ K_{sp} = \left( \frac{2F E_{\text{cell}}}{RT} \right) \]

Reference Electrodes – secondary standard electrodes

The SHE is cumbersome to construct. Other half-cells are being used as secondary standards.

Silver/silver chloride: AgCl(s) + e\(^{-}\) = Ag(s) + Cl\(^{-}\) (aq)

<table>
<thead>
<tr>
<th>Potential @ 25(^{\circ})</th>
<th>vs. SHE</th>
<th>vs. SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/AgCl, KCl (0.1M)</td>
<td>0.288</td>
<td>0.047</td>
</tr>
<tr>
<td>Ag/AgCl, KCl (3M)</td>
<td>0.210</td>
<td>-0.032</td>
</tr>
<tr>
<td>Ag/AgCl, KCl (3.5M)</td>
<td>0.205</td>
<td>-0.039</td>
</tr>
<tr>
<td>Ag/AgCl, KCl (sat'd)</td>
<td>0.199</td>
<td>-0.045</td>
</tr>
<tr>
<td>Ag/AgCl, NaCl (0.1M)</td>
<td>0.209</td>
<td>-0.035</td>
</tr>
<tr>
<td>Ag/AgCl, NaCl (sat'd)</td>
<td>0.197</td>
<td>-0.047</td>
</tr>
</tbody>
</table>