Electrochemical Analysis Methods

M.Sc. Analytical chemistry

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ELECTRODE POTENTIALS

- The **cell potential (E_{cell})** is the **electromotive force (emf)** driving electrons through the external circuit of a galvanic cell. it uses to measure the **tendency** for the reaction (**occur spontaneously or not**).

$$E_{cell} = E_{cathode} - E_{anode}$$

- Units: volts (**V**)
- $E_{cell} > 0$ **(+positive) → spontaneous** reaction
- $\Delta G < 0$ **(- negative) → spontaneous** reaction

1) $E_{cell} = E^{\circ}_{cell}$, where E°_{cell} is measured under **standard** conditions :

- **At 25°C = T=298 K , α=1 =(≈ 1.0 M for solutes), standard hydrogen electrode as reference P=1 atm, Pure solids/liquids.**

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

- $E^{\circ}_{cell} > 0 \Rightarrow \Delta G^{\circ} < 0$ ***(spontaneous)***
- $E^{\circ}_{ox} = -(E^{\circ}_{red})$

2) **Under Non-Standard** Conditions (**Nernst Equation apply**)

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n}\log Q \quad = \quad E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n}\log K_{eq}$$

Example: 1- Determine E_{cell} of classical Daniell cell at Standard Conditions?

$$Zn_{(s)}\,|Zn^{2+}_{(aq)}||Cu^{2+}_{(aq)}|Cu_{(s)}$$

Oxidation (**anode**): $Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$ $E^\circ_{Zn^{2+}/Zn} = -0.76$ V

Reduction (**cathode**): $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ $E^\circ_{Cu^{2+}/Cu} = +0.34$ V

net eq. $Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} + Cu_{(s)}$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{cell} = +0.34 - (-0.76)$$

$$E_{cell} = E^\circ_{cell} = +1.10\ v\ \textit{spontaneous}$$

2- Determine E_{cell} of classical Daniell cell Under Non-Standard conditions, when concentrations of Cu^{2+}(0.01M) & Zn^{2+}(1.0M) ions ≠ 1 M (**Apply Nernst eq.)**

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log Q \quad = \quad E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log K_{eq}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log\frac{[Zn^{2+}]\,[Cu_{(s)}]}{[Zn_{(s)}]\,[Cu^{2+}]} = E_{cell} = 1.1 - \frac{0.0592}{2}\log\frac{[1]\,[1]}{[1]\,[0.01]}$$

$$E_{cell} = 1.1 - \frac{0.0592}{2}\log 100 = \quad E_{cell} = 1.1 - 0.0592 = \ E_{cell} = +1.04\ v$$

Determination of Cell Potential

Apparatus

- Two half-cells
- Salt bridge
- High-impedance voltmeter (very high resistance) prevent electrons to flow.

Procedure

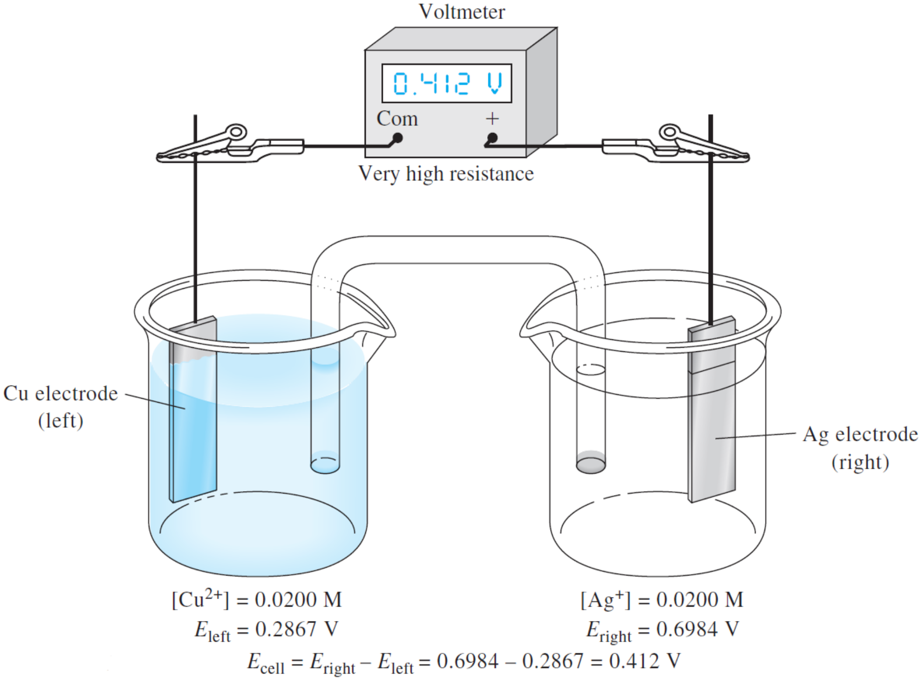
- Connect **anode** (**oxidation**) to **negative terminal** (on the **left** side of cell)
- Connect **cathode** (**reduction**) to **positive terminal** (on **right** side of cell)
- Measure open-circuit voltage (no reaction occurs) measure the spontaneity.
- Measured voltage ≈ Ecell (minimal current flow)
- Electrical current flows from the anode to the cathode due to a difference in electrical potential energy between the electrodes
- Measured current called the **overall cell potential** (**E_{cell}**) is the difference between the electrical potentials at the two electrodes (the two half-cell potentials)
- varies with concentration, temperature, metals/ions used.

Calculate the E_{cell} of the galvanic cell: $Cu_{(s)}| Cu^{2+}(0.02M)|| Ag^{+}(0.02M)| Ag_{(s)}$?
If $E^{\circ}_{Ag^{+}/Ag} = +0.799$ v , $E^{\circ}_{Cu^{2+}/Cu} = +0.337$ v.

This galvanic cell is not

At st. condition, so **Nernst eq.**

is applying here.



$$E_{cell} = E_{cathode} - E_{anode}$$

Anode : $Cu_{(s)} \leftrightharpoons Cu^{2+}_{(l)} + 2e^{-}$

Cathode : $\underline{Ag^{+}_{(l)} + e^{-} \leftrightharpoons Ag_{(s)}}$

Net eq. $Cu_{(s)} + 2Ag^{+}_{(l)} \leftrightharpoons Cu^{2+} + 2Ag_{(s)}$

$$E_{anode} = E^{\circ}_{anode} - \frac{0.0592}{n}\log\frac{[Cu^{2+}]}{[Cu_{(s)}]}$$

$$E_{anode} = -0.337 - \frac{0.0592}{2}\log\frac{[0.02]}{[1]}$$

$$E_{anode} = +0.2867 \text{ v}$$

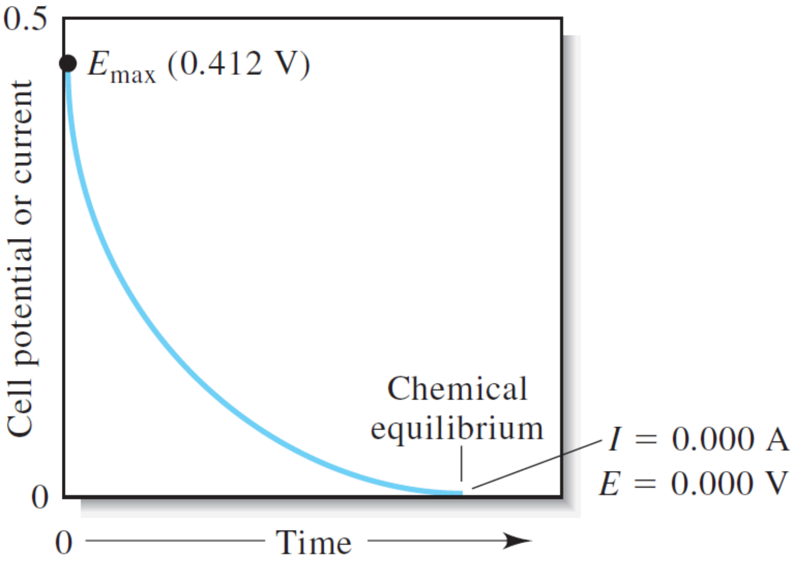
$$E_{cathode} = E^{\circ}_{cathode} - \frac{0.0592}{n}\log\frac{[Ag_{(s)}]}{[Ag^{+}]} = E_{cathode} = +0.799 - \frac{0.0592}{1}\log\frac{[1]}{[0.02]} = E_{cathode} = +0.6984 \text{ v}$$

- $E_{cell} = E_{cathode} - E_{anode} = E_{cell} = +0.6984 - (+0.2867) = E_{cell} \approx +0.412\ v$

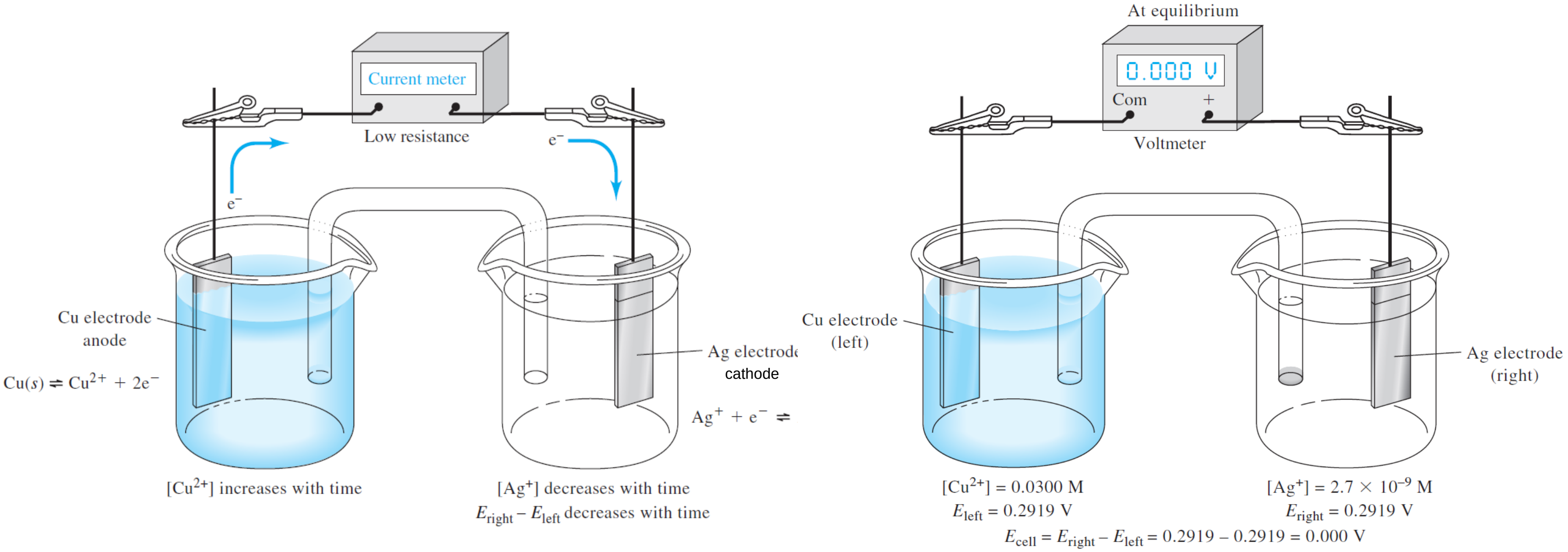
In this cell the **oxidation** of **Cu** and reduction of Ag^{+} will occur spontaneously when the cell is connected to a device and allowed to do so.

Discharging a Galvanic Cell

- At a **high-resistance voltmeter open circuit potential (OCP)**, the cell is at **non- equilibrium** and **no significant reaction occurs and also no current flow**.
- The measured cell potential represents the **tendency of the reaction**, not actual discharge. For the example of Cu/Ag cell, the open-circuit potential $\mathbf{E_{cell}}$= + 0.412 V.
- At **low-resistance ammeter** allows the
- The **current is initially high** and **decreases exponentially** with time.
- At **equilibrium**:
- **net current (*I*)**= 0 A
- **Overall cell potential $\mathbf{E_{cell}}$** = 0 V
- **Gibbs free energy ΔG** = 0 KJ/mol.



After equilibrium of a Galvanic Cell

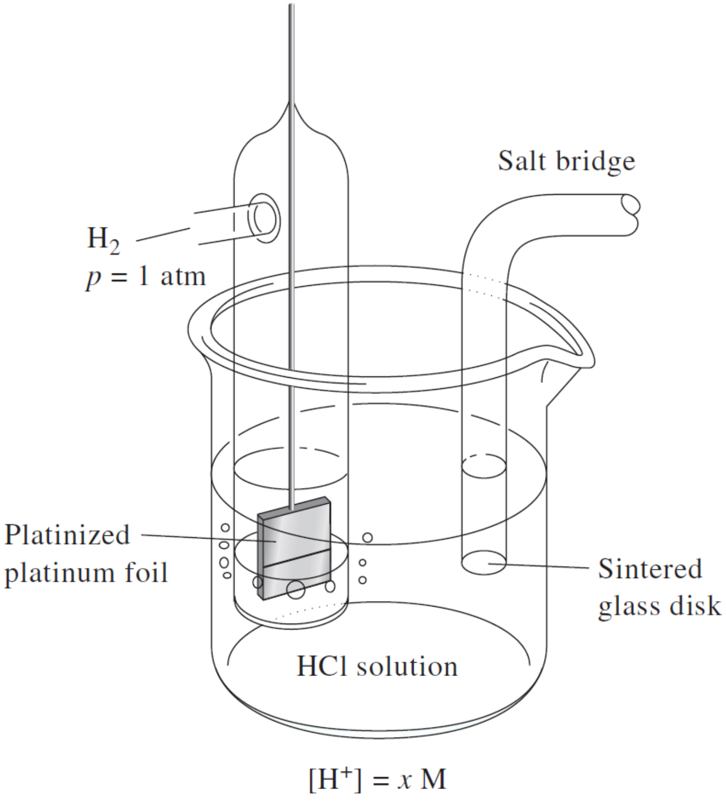


- Figure on the left illustrates the cell discharges with time until eventually equilibrium is reached when voltmeter is replaced with a low-resistance current meter.
- Figure on the right describes the cell after equilibrium is reached, the cell potential is again measured with a voltmeter and found to be $E_{cell} = 0.000$ V.
- The concentrations in the cell are now those at equilibrium as shown.
- At equilibrium E_{cell} is related to ΔG.

The Standard Hydrogen Reference Electrode (SHE) or (NHE)

Standard hydrogen reference electrode (SHE) is a universal reference half-cell is required to make electrode potentials comparable. This reference electrode is **easy to construct**, **reversible**, and **highly reproducible**. It is a gas electrode & used worldwide.

- SHE Consists of platinized Pt electrode, H^+ solution, and H_2 gas at 1 atm. Electrode is immersed in an acidic aqueous solution of known H^+ activity.
- Hydrogen gas is bubbled over the electrode at constant pressure.
- Platinum acts only as an electron transfer surface (not chemically involved).
- Half reaction: $2H^{+}{}_{(\text{`p})} + 2e^{-} \leftrightharpoons H_{2(\text{f})}$
  Pt | H_2 (g, 1 atm)| H^{+}(aq, a=1)
- $E^{\circ}_{SHE} = E_{SHE} = 0.000\ V$
- SHE is a reversible electrode.
- E°_{SHE} depends on T, $a\ H^{+} = 1$, $P_{H_2} = 1$ atm



Electrode Potential vs. Standard Electrode Potential

Example: Calculate the ***standard potential*** of copper electrode *Cu^{2+}(a =1) versus SHE, where the reading of voltmeter* = +0.337 V ?

- Connect the **Cu electrode** to the **+ positive terminal** of **OCP** cathode (reduction occurs).
- Connect **SHE H_2** to the **– negative potential** of **OCP** anode (oxidation occurs).
- The potential deference of the electrodes using voltmeter E_{cell} = +0.337 V
- Cathode (reduction): $Cu^{2+}_{(aq)} + 2e^- \leftrightharpoons Cu_{(s)}$
- Anode (oxidation) : $H_{2(f)} \leftrightharpoons 2H^+_{(`p)} + 2e^-$ E = 0.000V
  - $\mathbf{E^\circ_{cell\ at\ OCP} = E_{positive\ terminal\ (cathode)} - E_{nagative\ terminal\ (anode)}}$
- $E_{cell} = E^\circ_{cell}$ because using SHE and α =1 ≈ concentration of Cu^{2+} ion = 1M

  $E^\circ_{cell} = E_{cathode} - E_{anode} \Rightarrow + 0.337 = E_{Cu^{2+}/Cu} - 0.000$
- $E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} = + 0.337$ V this **+ positive** value of Cu electrode that means the **spontaneous** cell reaction is oxidation in the left-hand compartment and reduction in the right-hand compartment.

Example: Calculate the standard potential of zinc electrode Zn^{2+}(ɑ =1) versus SHE, where the voltmeter = -0.763 V ?

$E_{cell} = E^{\circ}_{cell}$ because using SHE and ɑ =1 ≈ concentration of Zn^{2+} ion = 1M

- The standard electrode potential, ***E*°**, of a half-reaction is defined as its electrode potential when the **activities of the reactants and products are all unity**.
- Cathode (reduction) : $Zn^{2+} + 2e^{-} \leftrightharpoons Zn_{(s)}$
- Anode (oxidation): $H_{2(f)} \leftrightharpoons 2H^{+}_{(`p)} + 2e^{-}$ E = 0.000V

$E^{\circ}_{cell} = E_{cathode} - E_{anode} \Rightarrow -0.763 = E_{Zn^{2+}/Zn} - 0.000 \Rightarrow E^{\circ}_{Zn^{2+}/Zn} = -0.763\ V$

- Because the cell potential is **- negative**, the spontaneous cell reaction is not the reaction as written (**that is, oxidation on the left and reduction on the right**). Rather, the spontaneous reaction is in the opposite direction.

$$Zn_{(s)} + 2H^{+}_{(`p)} \leftrightharpoons Zn^{2+} + H_{2(f)}$$

- When connecting two half-cells *E*° for each half-reaction can be used to predict the redox reactions
- E° half-reaction with **more +positive** will go as **reduction (cathode).**
- other half-reaction (E° half-reaction with **less +positive** will go as **oxidation (anode).**
- $E°_{cell}$ is *always* **positive for a spontaneous** reaction. $E°_{cell}$ **negative** is opposite.
- **Exp.:** Calculate the overall cell reaction $E°_{cell}$ of a galvanic cell made of a Cd electrode in a 1.0 M $Cd(NO_3)_2$ solution and a Pb electrode in a 1.0 M $Pb(NO_3)_2$ solution. $E°_{Cd2+/Cd}$ = -0.40 V and $E°_{Pb2+/Pb}$ = -0.13 V?

E° of Pb is (less –negative it means more + positive), so Pb can oxidize Cd will therefore Pb go as a reduction, and Cd as an oxidation.

Anode (oxidation): $Cd_{(s)} \leftrightharpoons Cd^{2+}_{(l)} + \cancel{2e}^-$ $E° = -0.40$ V

Catthode (reduction): $Pb^{2+}_{(l)} + \cancel{2e}^- \leftrightharpoons Pb_{(s)}$ $E° = -0.13$ V

$$Cd_{(s)} + Pb^{2+}_{(l)} \leftrightharpoons Cd^{2+}_{(l)} + Pb_{(s)}$$

Ecell = E°cell because the concentration of solution =1 M

E°cell = E°cathode – E°anode → E°cell = -0.13 –(-0.4) → E°cell = + 0.27 V

Effect of Concentration on Electrode Potentials: The Nernst Equation

$$\boxed{\Delta G = \Delta G^\circ + RT \ln K_{eq}}$$

- ΔG is the maximum useful work that can be obtained.
- In a galvanic cell, the work is supplied by the electric current (moving electrons through a wire).

$$\boxed{\Delta G = -nFE_{cell}} \qquad \boxed{\Delta G^\circ = -nFE^\circ_{cell}}$$

- **At equilibrium $E_{cell} = 0$ and $\Delta G = 0$, but $\Delta G^\circ \neq 0$**

$$\boxed{\Delta G^\circ = -RT \ln K_{eq}}$$

$$- nFE_{cell} = - nFE^{\circ}_{cell} + RT\ln K_{eq} \div -nF$$

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF}\ln K_{eq} \quad \textbf{(Nernst Equation)}$$

$$aA + bB + ne^{-} \leftrightharpoons cC + dD$$

$$K_{eq} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \quad \Rightarrow \quad E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF}\ln \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

- *E° = standard electrode potential*, which is characteristic for each half-reaction
- *R* = ideal gas constant, **8.314** J K^{-1} $mol.^{-1}$
- *T* = temperature, K
- *n* = number of moles of electrons that appears in the half-reaction.
- ***F*** = faraday constant = **96,485** C/mol. (coulombs)/mole of electrons.
- ln = natural logarithm = **2.303** log
- [A], [B], [C] and [D] = concentration in molarity mol./L
- If A is a gas, [A] in above equation then will replaced by *p*A, the partial pressure
- of A in atmospheres.
- If A is a pure liquid, a pure solid, or the solvent, its activity is unity.

Conditions for application of Nernst eq.

- **The Nernst equation applies only when the electrode system is at thermodynamic equilibrium:**

$$\mathbf{E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ at } 25\ ^{\circ}C = 298\ K}$$

- **Electrochemical equilibrium**
  - No net current flows ($i = 0$)
  - Forward and reverse electrode reaction rates are equal, its **reversible potential**
- **No kinetic limitations**
  - Electron-transfer kinetics are fast (Nernstian behavior)
  - No activation over potential
- **No mass-transport limitations**
  - Concentration at the electrode surface equals bulk concentration
  - No concentration polarization
- **Thermodynamic control**
  - Describes **state variables**, not reaction rates, independent of time and scan rate
- **Activities are well defined**
  - Ideally dilute solutions (**activities ≈ concentrations**)
- **Constant temperature**
  - Usually assumed 25 °C unless explicitly corrected

Validation of Nernst eq.

1. Reversible Electrodes at OCP:

$$M^{n+} + ne^{-} \leftrightharpoons M_{(s)} \Longrightarrow M_{(s)} \mid M^{n+}$$

- Gas electrodes (H_2, O_2, Cl_2) under equilibrium pressure
- Used to calculate **open-circuit potential (OCP)**

2. Half-Cell Potentials in Electrochemical Cells:

- Calculation of individual electrode potentials
- Cell EMF determination: $\mathbf{E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln K_{eq}}$ Used in:
- **Daniell cell**
- **Concentration cells** (Identical electrodes, different activities)
- **Galvanic cells at equilibrium**

3. Ion-Selective Electrodes (ISEs)

- Direct practical application of Nernstian response:
- $\mathbf{E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln a_{\text{ion}}}$
- pH electrode (H^+ activity), and F^-, Cl^-, Ca^{2+} electrodes

4. Equilibrium Potentials in Corrosion Science to calculation of:

- Corrosion potentials.
- Pourbaix (E–pH) diagrams

5. Reference Electrodes, Used to define stable reproducible potentials:

- Saturated Hydrogen reference electrode SHE
- Ag/AgCl
- Calomel electrode

Note:

1. **Nernst equation defines the maximum possible driving force.**
2. **It is the boundary condition for kinetic models.**
3. **In voltammetry, the formal potential approximates the Nernst potential only for reversible system.**

Limitations of Nernst eq.

1. Under Current Flow, any non-zero current introduces:

- Activation over potential.
- Concentration over potential
- Ohmic drop

2. Irreversible or Quasi-Reversible Systems, slow electron-transfer kinetics

Observed in:

- Many organic redox systems
- Surface-confined reactions

3. Dynamic Techniques

- Cyclic voltammetry (except formal potential extraction)
- Chronoamperometry
- Polarography under diffusion control

- **Here, Butler–Volmer or kinetic models dominate.**

Example: Calculate ΔG° for the following reaction at 25°C,

$$\mathbf{Pb_{(s)} + Ni^{2+}_{(aq)} \leftrightharpoons Pb^{2+}_{(aq)} + Ni_{(s)}}$$

Solution:

Anode (oxidation): $Pb_{(s)} \rightarrow Pb^{2+} + 2e^{-}$, E° = -0.13 V

Cathode (reduction): $Ni^{2+} + 2e^{-} \rightarrow Ni_{(s)}$, E° = -0.25 V

- The given reaction runs nickel as a reduction and lead as an
- oxidation reaction, thus $E^{\circ}_{cell} = -0.25\ V - (-0.13\ V) = -0.12\ V$.
- Since $E^{\circ}_{cell} < 0$ this reaction is **not spontaneous** and ΔG° > 0.

$$\mathbf{\Delta G^{\circ} = - nFE^{\circ}_{cell} \rightarrow \quad \Delta G^{\circ} = - 2 \times 96485 \times -0.12}$$

ΔG° =23.1 KJ/mol.

Example: Calculate the equilibrium constant for the following reaction at 25°C, $2Ag_{(s)} + Fe^{2+}{}_{(aq)} \leftrightharpoons 2Ag^{+}{}_{(aq)} + Fe_{(s)}$

Solution:

Anode (oxidation): $Ag_{(s)} \rightarrow Ag^{+} + e^{-}$, $E° = +0.80$ V

Cathode (reduction): $Fe^{2+} + 2e^{-} \rightarrow Fe_{(s)}$, $E° = -0.44$ V

The given reaction runs silver as an oxidation and iron as a reduction, thus $E°_{cell} = -0.44 - 0.80 = -1.24$ V.

From $\Delta G° = -RT\ln \boldsymbol{K_{eq}}$ and $\Delta G° = -nF\mathbf{E°_{cell}}$

$$-nF\mathbf{E°_{cell}} = -RT\ln \boldsymbol{K_{eq}} \qquad \mathbf{E°_{cell}} = \frac{2.303RT}{nF}\log K_{eq}$$

$$\mathbf{-1.24} = \frac{0.0592}{2}\log K_{eq} \quad \Rightarrow \quad K_{eq} = 1.28 \times 10^{-42}$$

Example: Calculate the electrode potential of a silver electrode immersed in a 1 M solution of NaCl using $E^{\circ}_{Ag+/Ag}$ = +0.799 V, K_{sp} AgCl = 1.82 x 10^{-10}

We get [Cl$^-$] from NaCl = 1.00 M

$K_{sp} = [Ag^+]\,[Cl^-]$, So $[Ag^+] = \frac{K_{sp}}{[Cl^-]}$

$Ag^+ + e^- \leftrightharpoons Ag_{(s)}$ $\quad E^{\circ}_{Ag+/Ag}$ = +0.799 V

$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-$

$$\mathbf{E_{Ag} = +\,0.799 - \frac{0.0592}{1} \log \frac{1}{[Ag+]}}$$

$$\mathbf{E_{Ag} = E^{\circ}_{Ag+/Ag} - \frac{0.0592}{n} \log \frac{[Cl^-]}{K_{sp}}} \qquad \mathbf{E_{Ag} = E^{\circ}_{Ag+/Ag} + \frac{0.0592}{n} \log K_{sp} - \log[Cl^-]}$$

$$\mathbf{E_{Ag/AgCl} = +\,0.799 + \frac{0.0592}{1} \log 1.82\ x\ 10^{-10} - \log[1]}$$

$$\mathbf{E_{Ag/AgCl} = +\,0.799 + (-0.577) - 0.000}$$

$$\mathbf{E_{Ag/AgCl} = +\,0.222\ V}$$

References

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