

INSTRUMENTAL ANALYSIS I



Part II- Chapter 5

ELECTROANALYTICAL METHODS

**Course Instructor: Ermias Haile
(Ass.Prof.)**

5. Introduction to Electroanalytical Methods

- Electroanalytical method is a method in which **measurement or electrical signal** (potential, current and charge) is used to perform the qualitative and quantitative analysis.
- It uses measurement **of electrical properties in analysis**, like current, potential/voltage, resistance, conductivity, charge, etc.
- Electroanalytical methods encompass a wide range of quite diverse methods, for example some of the methods are **selective** (for instance **potentiometry**) while some of them almost **nonspecific** (for instance **conductometry**).
- Moreover variations in **dynamic range** and **detection limit** are observed.

Peculiar properties of electroanalytical methods

- Provide a **unique means** for analysis or used as an alternatives;
- Physical signal is obtained directly in electronic form amenable for further processing by the instrument;
- **No detectors** other than electrodes are required;
- **Instrumentation** is simple and less expensive;
- Used as detection methods in chromatography, capillary electrophoresis and flow-injection analysis;
- Generally **low sample consumption** (also without altering the sample);
- **Possible to differentiate oxidation** or complexation state (specific analysis may be performed).

Limitation of electroanalytical methods

- Response to activity rather than to the concentration of the analyte so difficult to characterize activity;
- Rely in almost cases on reactions on electrode surface;
- Signal doesn't necessarily represent the bulk of the solution;
- Electrode reaction itself may alter the composition in the vicinity;
- Often reference electrode required, which are the potential source of measurement error.

5.1 ELECTRO-CHEMICAL CELLS

- An electrochemical cell consists of two metallic electrodes immersed in either the same electrolyte solution or in two different solutions that are in electrolytic contact.
- An electrochemical cell can operate to convert chemical energy into electrical energy or vice-versa depending on whether the cell reaction is spontaneous or forced to occur in the non-spontaneous direction.

❖ Cell Potential

- The potential difference between the two electrodes (half-cells) connected properly to form a galvanic cell, under conditions when no current flows through the system, is called the *emf of the cell* or *cell potential*.

Electrochemical cells

- ❖ A **dc** electrochemical cell **consists of two electrical conductors** called **electrodes**, each immersed in a suitable electrolyte solution.

For a current to develop in a cell, it is necessary

1. The electrodes be **connected** externally by means of a **metal conductor**,
2. The **two electrolyte solutions be in contact** to permit movement of ions from one to the other, and
3. An **electron transfer rxn can occur** at each of the two electrodes.

Faradaic and Nonfaradaic Currents

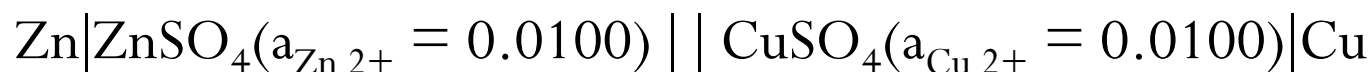
- ❖ Two types of processes can conduct currents across an electrode/solution interface.
- ❖ One kind involves a direct transfer of e^- via an oxidation rxn at one electrode and a reduction rxn at the other.
- ❖ Processes of this type are called **faradaic processes** because they are governed by Faraday's law, which states that the amount of chemical rxn at an electrode is proportional to the current;
- ❖ the resulting currents are called **faradaic currents**.
- ❖ To understand the basic difference between a faradaic and a nonfaradaic current, imagine an e^- traveling down the external circuit to an electrode surface.
- ❖ When the e^- reaches the solution interface, it can do 1 of only 2 things.
- ❖ It can remain at the electrode surface and increase the charge on the double layer, which constitutes a nonfaradaic current, no charge-transfer, external currents can flow.
- ❖ Alternatively, it can leave the electrode surface and transfer to a species in the solution, thus becoming a part of a faradaic current.

Anodes and Cathodes

- ❖ The **cathode** of an electrochemical cell is the electrode at which **redⁿ occurs**, while the **anode** is the electrode where **oxidⁿ takes place**.
- The **Cu** electrode is the **cathode** and the Zn electrode is the anode. (**Galvanic**)
- In contrast, where this same cell is operated as an **electrolytic cell**, the **Cu** electrode would be the **anode** & the Zn electrode the cathode.

Schematic Representation of Cells

- To simplify the description of cells, chemists often employ a shorthand notation, e.g. the cell shown in Fig. 5-1 can be described by



- By convention, the **anode** and information about the solution with which it is in contact is always listed **on the left**.
- **Single vertical lines** represent phase **boundaries across** which potential differences may develop.

The Thermodynamics of Cell Potentials

- From thermodynamics the change in free energy ΔG for a cell rxn is given by

$$\Delta G = RT \ln Q - RT \ln K = RT \ln Q/K$$

where, **R** is the gas constant ($8.316 \text{ J mol}^{-1} \text{ K}^{-1}$) and
T is the temperature in Kelvin's.

- The cell potential E_{cell} is related to the free energy of the rxn by the relationship

$$\Delta G = -nFE_{\text{cell}}$$

where, **F** is the faraday (96,485 coulombs per mole of es) and
n is the # of moles of es associated with the oxidation/reduction process.

Upon rearrangement, $E_{\text{cell}} = -RT/nF \ln Q + RT/nF \ln K$
 $= -RT/nF \ln [(a_{\text{H}^+})_i^2 (a_{\text{Cl}^-})_i^2] + RT/nF \ln K$

- The last term in this equation is a constant, which is called the **standard electrode potential**, E_{cell}^0 for the cell. That is

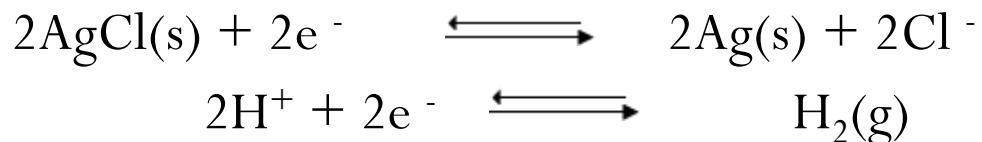
$$E_{\text{cell}}^0 = RT/nF \ln K$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - RT/nF \ln [(a_{\text{H}^+})_{\text{i}}^2 (a_{\text{Cl}^-})_{\text{i}}^2]$$

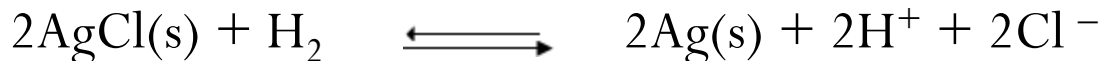
- The standard potential is equal to the cell potential when the reactants and products are at unit activity and pressure.
- This equation is a form of the Nernst equation.

ELECTRODE POTENTIALS

- ❖ The cell rxn of an electrochemical cell as being made up of 2 half-cell rxns, each of which has a characteristic electrode potential associated with it.
- ❖ By convention, they are both written as reductions.



- ❖ To obtain the cell rxn, the 2nd half-rxn is subtracted from the 1st to give



$$\text{That is, } E_{\text{cell}} = E_{\text{AgCl}} - E_{\text{H}^+}$$

A more general statement of the last relationship is

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

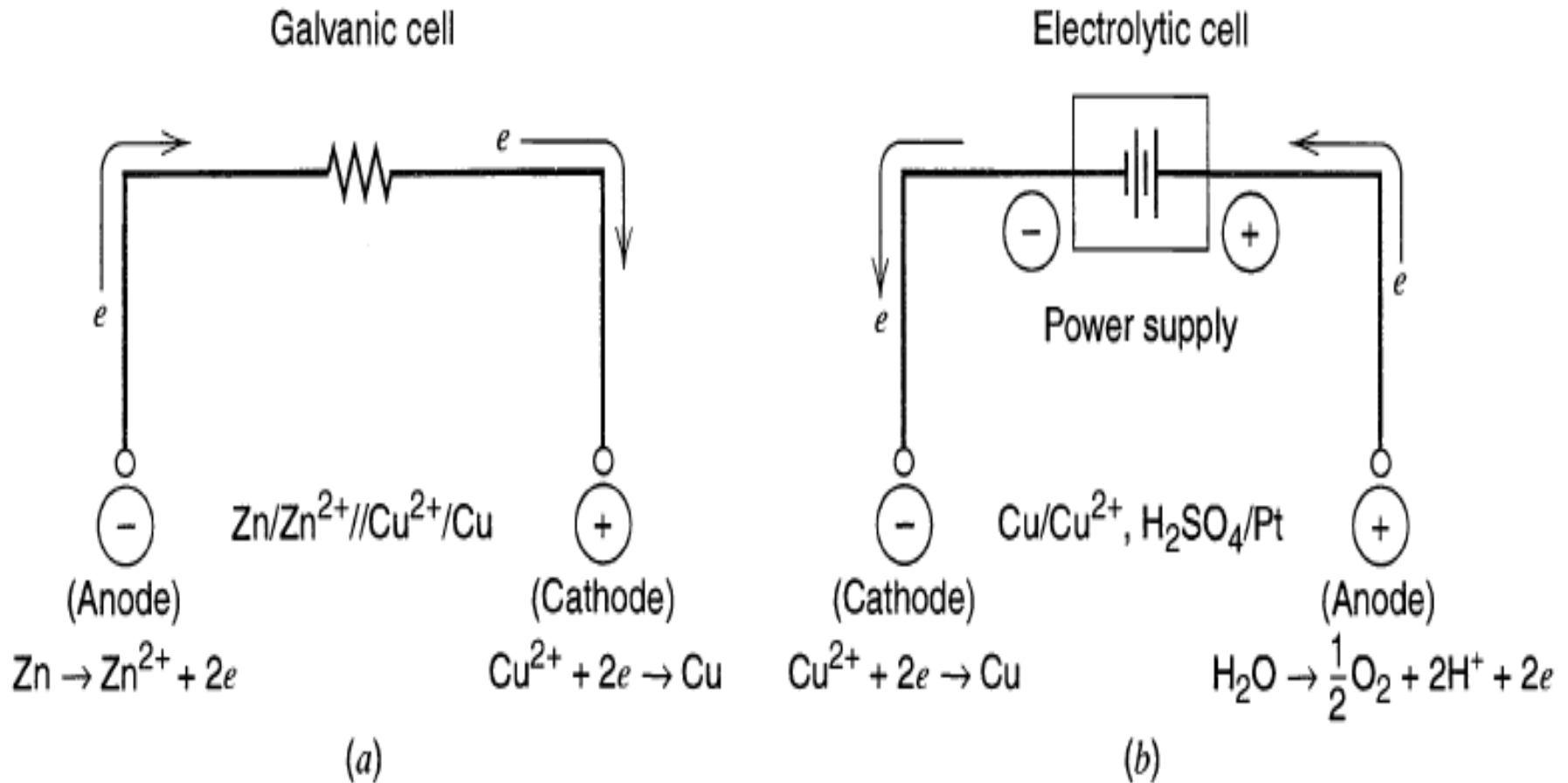
where, E_{cathode} and E_{anode} are the electrode potentials for the cathodic and anodic half-rxns.

- 5.2 Current in Electrochemical Cells

Electrochemical Cells

- **Electrochemical Cells** are of two basic types:
 - Galvanic Cells – a *spontaneous* chemical reaction generates an electric current
 - Electrolytic Cells – an electric current drives a *non-spontaneous* reaction
- Basically, the two cells are opposites of one another.
- We will be focused on the Galvanic cells for this Chapter.
- The spontaneous reaction that drives these cells is a redox reaction!

(a) Galvanic and (b) electrolytic cells.



➤ Here, the battery (not a chemical reaction) serves as the electron pump

➤ Processes in an electrolytic cell are the *reverse* of those in a galvanic cell.

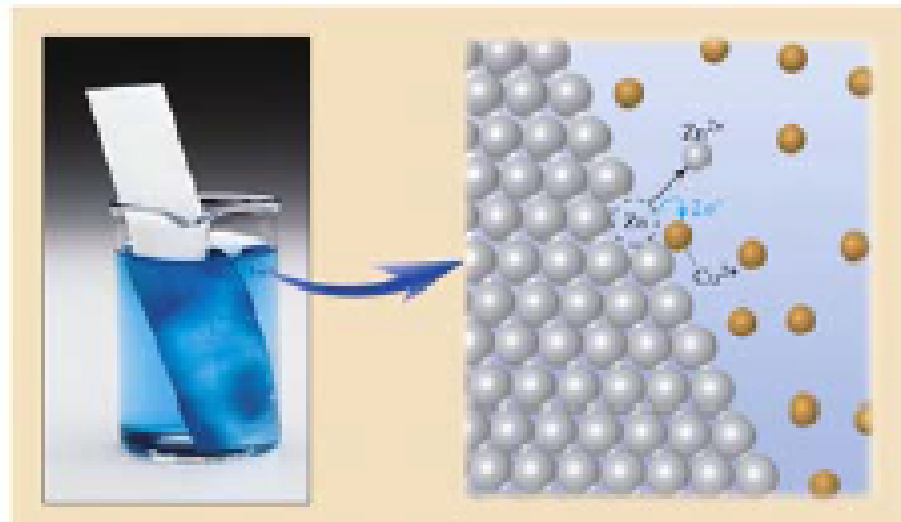
Oxidation–Reduction Reactions

LEO the lion goes **GER**

Lose $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
Electrons
Oxidation

If the electron(s) is on the product side of the reaction, it is an oxidation reaction!

A substance which loses electrons (oxidized) is called a *reducing agent*. Its oxidation number *increases*.



Oxidation–Reduction Reactions

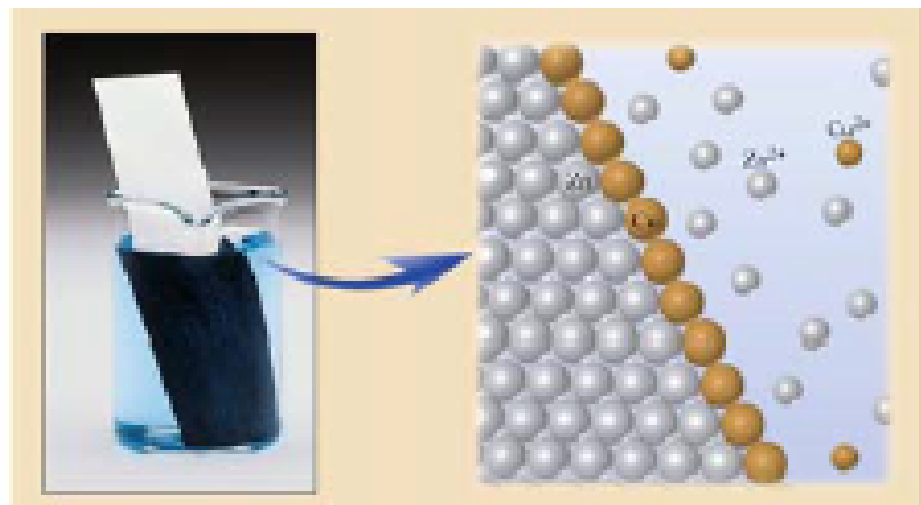
LEO the lion goes **GER**

Gain
Electrons
Reduction

$\text{Cu}^{2+} (\text{aq}) + 2 \text{e}^{-} \rightarrow \text{Cu}(\text{s})$

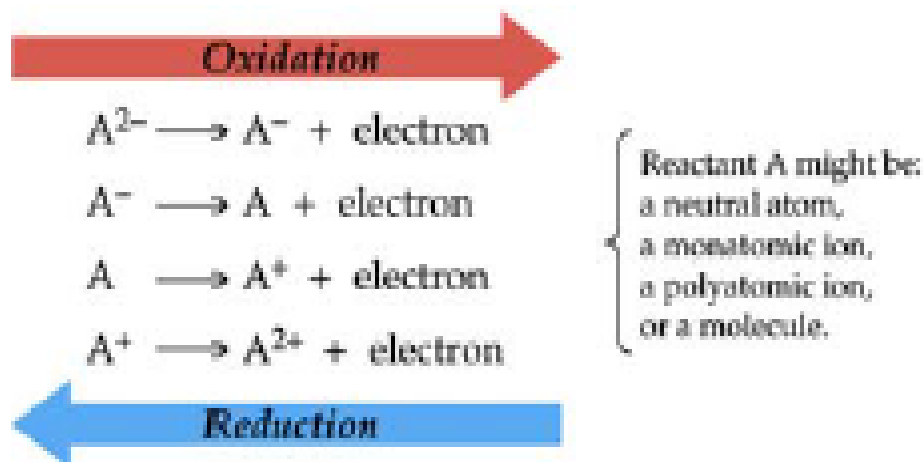
If the electron(s) is on the reactant side of the reaction, it is a reduction reaction!

A substance which gains electrons (reduced) is called the *oxidizing agent*. Its oxidation number *decreases*.



Oxidation–Reduction Reactions

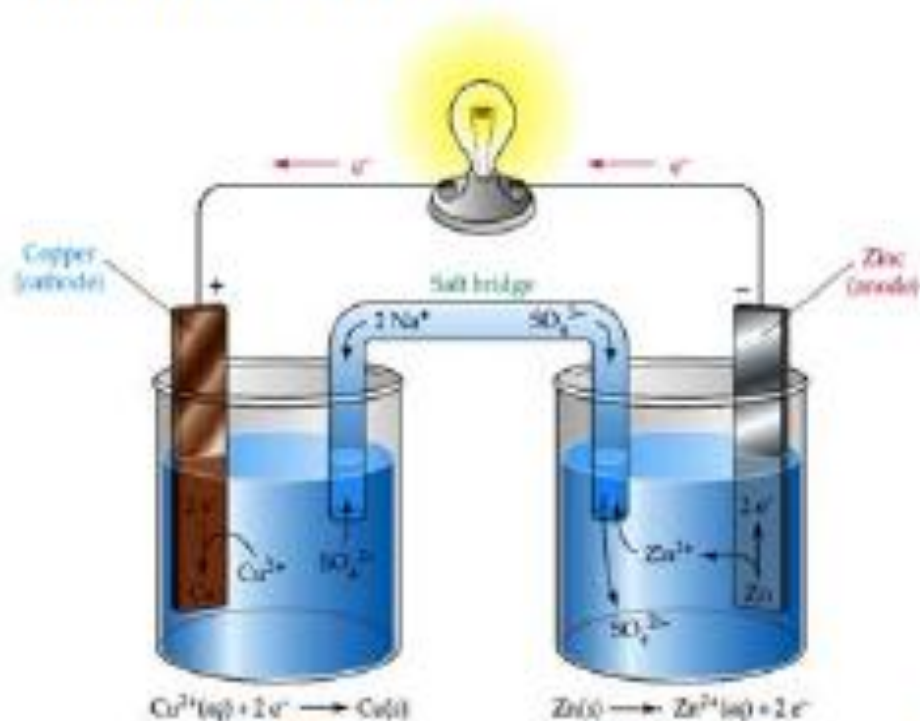
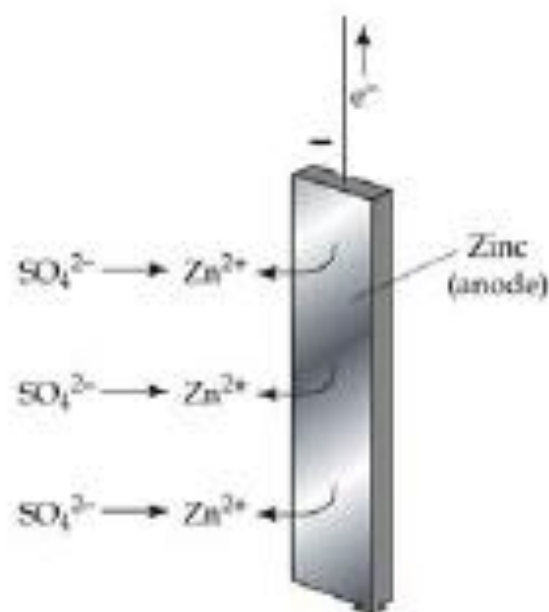
- The transfer of electrons between or among reactants is called the oxidation or reduction of species depending on which way the electrons are flowing.



- Oxidation and reduction must occur together. They cannot exist alone.
- Therefore, a redox reaction can be broken into two half-reactions, one a reduction and the other an oxidation

Electrochemical Cells -Terms

- **Salt Bridge**: is a U-shaped tube that contains a gel permeated with a solution of an inert
- These ions do not react with the other ions and they are not reduced or oxidized
- The salt bridge completes the electrical circuit by neutralizing any growing charge in the solutions.
- Anions flow into the anode and cations flow to the cathode

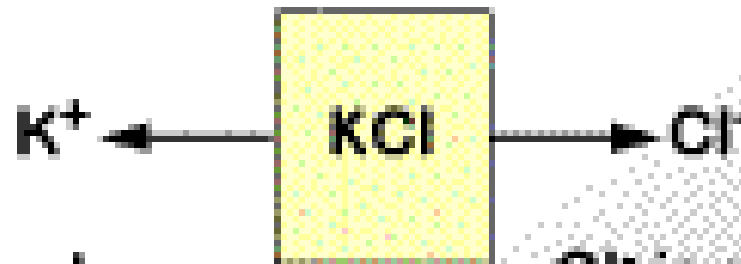


Salt bridge = completes the electrical circuit.
= allows ion movement but doesn't allow solutions to mix

Salt bridge

Allows ion migration in solution but prevents extensive mixing of electrolytes.

It can be a simple porous disk or a gel saturated with a non-interfering salt like KCl.

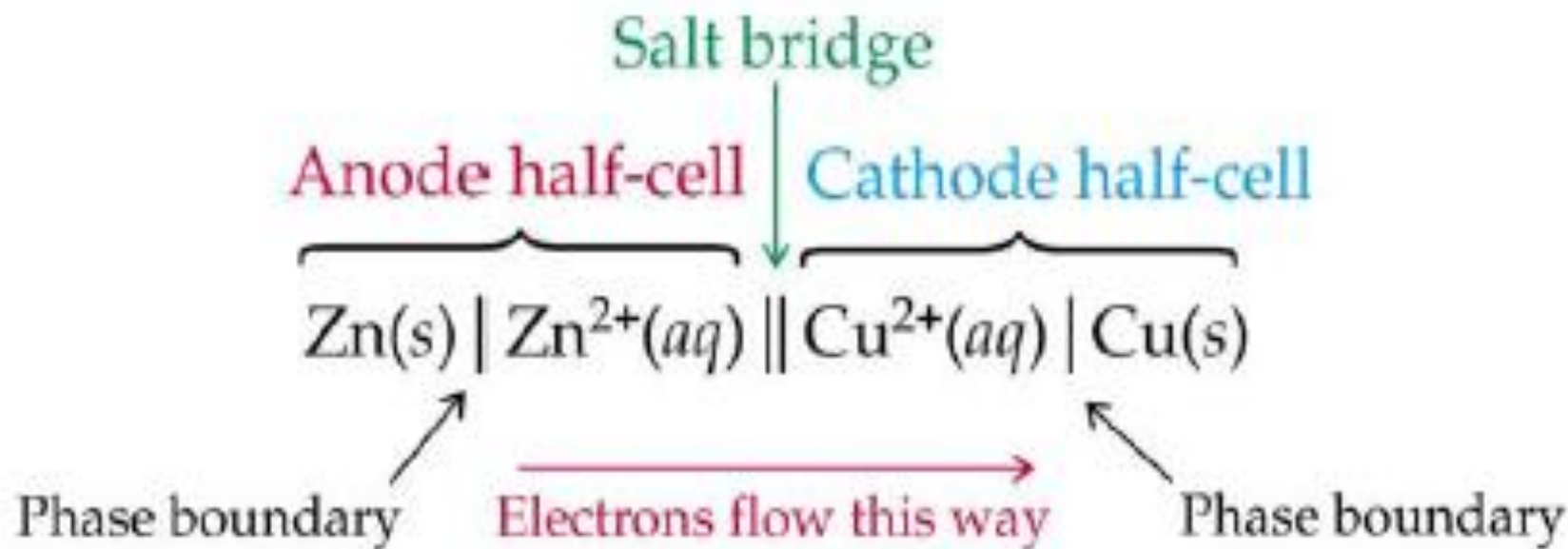


K^+ is released
to Zn side as Zn^{2+}
is converted to Zn^0

Cl^- is released
as Cu is
converted to Cu^{2+}

Electrochemical Cells – Shorthand Notation

- The shorthand notation for describing the cell:



- Electrons flow from anode to cathode.
- Anode is placed on left by convention.

Standard Reduction Potentials

- The standard cell potential of any galvanic cell is the sum of the standard half-reaction potentials for the oxidation and reduction half-cells.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation}} + E^{\circ}_{\text{reduction}}$$

- Standard half-cell potentials are always quoted as a reduction process (See Table 18.1).
- If your half-reaction is an oxidation, the numerical value is the same as in the Table but the sign must be changed.

Table 5.3. Standard reduction electrode potentials at 298 K.

Electrode	Electrode reaction (reduction)	E° (volts)
Li	$\text{Li}^+(aq) + e^- \longrightarrow \text{Li}(s)$	-3.05
K	$\text{K}^+(aq) + e^- \longrightarrow \text{K}(s)$	-2.93
Ba	$\text{Ba}^{2+}(aq) + 2e^- \longrightarrow \text{Ba}(s)$	-2.90
Ca	$\text{Ca}^{2+}(aq) + 2e^- \longrightarrow \text{Ca}(s)$	-2.87
Na	$\text{Na}^+(aq) + e^- \longrightarrow \text{Na}(s)$	-2.71
Mg	$\text{Mg}^{2+}(aq) + 2e^- \longrightarrow \text{Mg}(s)$	-2.37
Al	$\text{Al}^{3+}(aq) + 3e^- \longrightarrow \text{Al}(s)$	-1.66
Zn	$\text{Zn}^{2+}(aq) + 2e^- \longrightarrow \text{Zn}(s)$	-0.76
Cr	$\text{Cr}^{3+}(aq) + 3e^- \longrightarrow \text{Cr}(s)$	-0.74
Fe	$\text{Fe}^{2+}(aq) + 2e^- \longrightarrow \text{Fe}(s)$	-0.44
Cd	$\text{Cd}^{2+}(aq) + 2e^- \longrightarrow \text{Cd}(s)$	-0.40
Co	$\text{Co}^{2+}(aq) + 2e^- \longrightarrow \text{Co}(s)$	-0.28
Ni	$\text{Ni}^{2+}(aq) + 2e^- \longrightarrow \text{Ni}(s)$	-0.25
Sn	$\text{Sn}^{2+}(aq) + 2e^- \longrightarrow \text{Sn}(s)$	-0.14
Pb	$\text{Pb}^{2+}(aq) + 2e^- \longrightarrow \text{Pb}(s)$	-0.13
Pt	$2\text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2(g)$	0.00
Cu	$\text{Cu}^{2+}(aq) + 2e^- \longrightarrow \text{Cu}(s)$	+0.34
I ₂	$\text{I}_2(s) + 2e^- \longrightarrow 2\text{I}^-(aq)$	+0.54
Fe	$\text{Fe}^{3+}(aq) + e^- \longrightarrow \text{Fe}^{2+}(aq)$	+0.77
Hg	$\text{Hg}_2^{2+}(aq) + 2e^- \longrightarrow \text{Hg}(l)$	+0.79
Ag	$\text{Ag}^+(aq) + e^- \longrightarrow \text{Ag}(s)$	+0.80
Br ₂	$\text{Br}_2(l) + 2e^- \longrightarrow 2\text{Br}^-(aq)$	+1.08
Cl	$\text{Cl}_2(g) + 2e^- \longrightarrow 2\text{Cl}^-(aq)$	+1.36
Au	$\text{Au}^{3+}(aq) + 3e^- \longrightarrow \text{Au}(s)$	+1.42
Mn	$\text{MnO}_4^-(aq) + 8\text{H}_3\text{O}^+(aq) + 5e^- \longrightarrow \text{Mn}^{2+}(aq) + 12\text{H}_2\text{O}(l)$	+1.51
F ₂	$\text{F}_2(g) + 2e^- \longrightarrow 2\text{F}^-(aq)$	+2.87

↑
INCREASING
(a) tendency for oxidation to occur
(b) power as reducing agent

↓
INCREASING
(a) tendency for reduction to occur
(b) power as oxidising agent



using E^0 data from Table , $E_{\text{cathode, Red}} = + 0.337$, Cu^{2+}

$$E_{\text{oxid, Zn}} = -0.763 \longrightarrow 0.763$$

$$E_{\text{cell}} = \text{Oxid} + \text{Red}$$

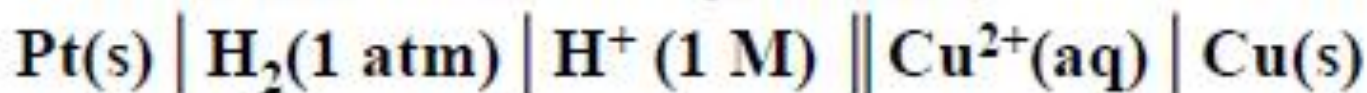
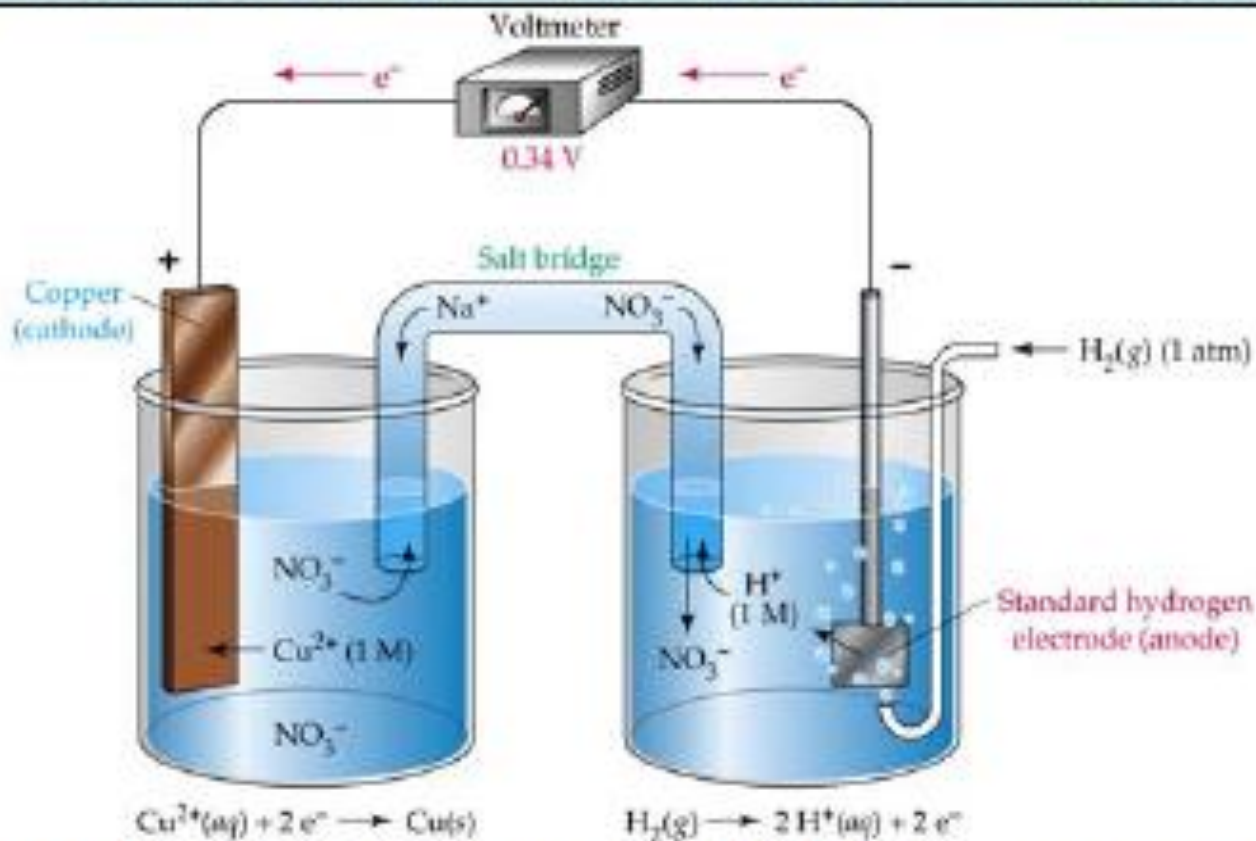
$$E_{\text{cell}} = 0.763 + 0.337 = +1.100 \text{ V}$$

OR

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

$$= + 0.337 - (-0.763) = +1.100 \text{ V}$$

Standard Reduction Potentials



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{H}_2 \rightarrow \text{H}^{+}} + E^{\circ}_{\text{Cu}^{2+} \rightarrow \text{Cu}}$$

$$0.34 \text{ V} = 0 \text{ V} + E^{\circ}_{\text{Cu}^{2+} \rightarrow \text{Cu}}$$

Mass transfer

❖ **Mass transfer**, is the movement of material from one location in solution to another.

➤ The modes of mass transfer are:

1. **Migration:** Movement of a charged body under the influence of an electric field (a gradient of electrical potential).

➤ The migrational component can be reduced to negligible levels by addition of an inert electrolyte (*a supporting electrolyte*) at a concentration much larger than that of the electroactive species .

2. **Diffusion:** Movement of a species under the influence of a gradient of chemical potential (i.e., a concentration gradient).

✓ Diffusional transport also occurs in the vicinity of the electrodes.

Cont.,,,

3. **Convection:** **Stirring** or hydrodynamic(moved by liquid) transport.

- Generally, fluid flow occurs because of *natural convection* (**convection caused by density gradients**) and *forced convection*, and may be characterized by stagnant(slugish) regions, laminar flow, and **turbulent(unstable) flow**.
- Convection can be avoided by **preventing stirring** and **vibrations** in the electrochemical cell.

1.3 Main Branches of Electroanalytical Chemistry

- **Potentiometry**: measure the **potential of electrochemical** cells without drawing substantial current
 - **Examples**: **pH** measurements, ion-selective electrodes, titrations (e.g. KF endpoint determination)
- **Coulometry**: measures the **electricity** required to drive an electrolytic oxidation/reduction to completion
 - **Examples**: titrations (KF titrant generation), “chloridometers” (AgCl)
- **Voltammetry**: measures **current as a function of applied potential** under conditions that keep a working electrode polarized
 - **Examples**: cyclic voltammetry, many biosensors

Nernst equation

- If a system follows the Nernst equation or an equation derived from it, the electrode reaction is often said to be thermodynamically or electrochemically **reversible** (or *nernstian*).

$$E_{\text{cell}} := E_{\text{std_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left[\frac{(C_{\text{O}})^{\text{O}}}{(C_{\text{R}})^{\text{R}}} \right]$$

$$T := 298 \cdot \text{K}$$

$$F := 96484.6 \cdot \frac{\text{coul}}{\text{mole}}$$

$$\mathcal{E}_{\text{Cell}} = \mathcal{E}_{\text{Cell}}^0 - \frac{0.0591}{n} \cdot \log Q$$

$$R := 8.31441 \cdot \text{joule} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$$

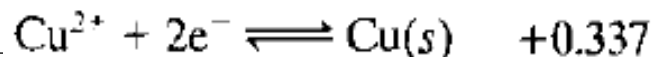
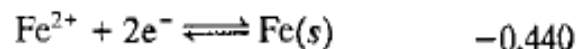
- It is now clear that the emf of any cell reaction, in terms of the electrode potentials of the two half-reactions, is

$$\boxed{E_{\text{rxn}} = E_{\text{right}} - E_{\text{left}}} \quad E_{\text{cell}} := E_{\text{cathode}} - E_{\text{anode}} \quad E_{\text{std_cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

- where E_{right} and E_{left} refer to the cell schematic and are given by the appropriate Nernst equation.

- Standard Electrode potential

Reaction	E° at 25°C, V
$\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-$	+1.359
$\text{O}_2(g) + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.229
$\text{Br}_2(aq) + 2e^- \rightleftharpoons 2\text{Br}^-$	+1.087
$\text{Br}_2(l) + 2e^- \rightleftharpoons 2\text{Br}^-$	+1.065
$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}(s)$	+0.799
$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$	+0.771
$\text{I}_3^- + 2e^- \rightleftharpoons 3\text{I}^-$	+0.536
$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}(s)$	+0.337
$\text{Hg}_2\text{Cl}_2(s) + 2e^- \rightleftharpoons 2\text{Hg}(l) + 2\text{Cl}^-$	+0.268
$\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^-$	+0.222
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + e^- \rightleftharpoons \text{Ag}(s) + 2\text{S}_2\text{O}_3^{2-}$	+0.010
$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(g)$	0.000
$\text{AgI}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{I}^-$	-0.151
$\text{PbSO}_4(s) + 2e^- \rightleftharpoons \text{Pb}(s) + \text{SO}_4^{2-}$	-0.350
$\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}(s)$	-0.403
$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}(s)$	-0.763



Calculation of cell potentials (E_{cell}) from electrode potentials

- An important use of standard electrode potentials is the calculation of the potential obtainable from a galvanic cell or the potential required to operate an electrolytic cell.
- The electromotive force(emf) of a cell is obtained by combining half-cell potentials as follows:

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

where, E_{anode} and E_{cathode} are the electrode potentials for the two half-rxns constituting the cell.

➤ Consider the hypothetical cell



using E^0 data from Table , $E_{\text{cathode}} = + 0.337$, Cu^{2+}

$$E_{\text{cell}} = +0.337 - (-0.763) = +1.100 \text{ V}$$

The positive sign for the cell potential indicates that the reaction occurs spontaneously and that this is a galvanic cell.



Cont.,,,

The foregoing cell, diagrammed as



implies that the copper electrode is now the anode. Thus,

$$E_{\text{cell}} = -0.763 - (+0.337) = -1.100 \text{ V}$$

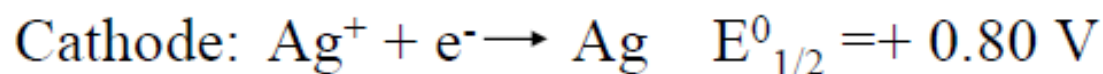
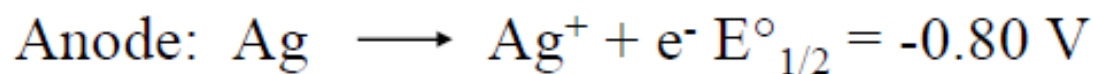
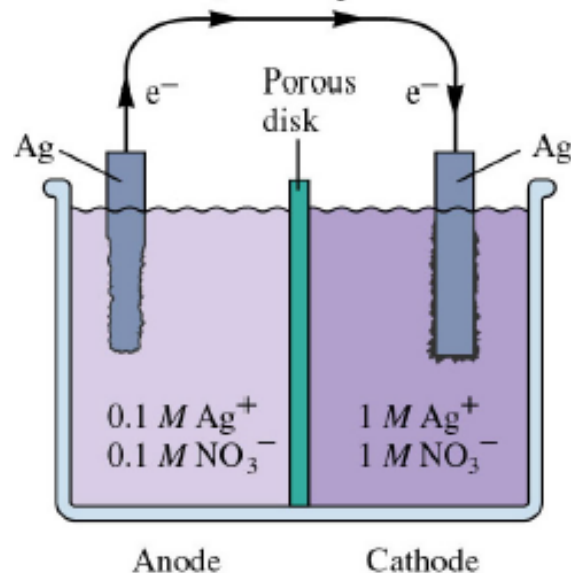
The -ve sign indicates the **nonspontaneity** of the reaction



The application of an external potential greater than 1.100 V is required to cause this rxn to occur.

Silver Concentration Cell

Driving force for the reaction: Get the concentration up on the left, so produce more ions there. Will stop when concentrations in both beakers are equal ($Q=1$ but not Std State)



$$Q = \frac{[\text{Ag}^+]_{\text{Anode}}}{[\text{Ag}^+]_{\text{Cathode}}} = \frac{(0.1)}{(1.0)} = 0.1$$

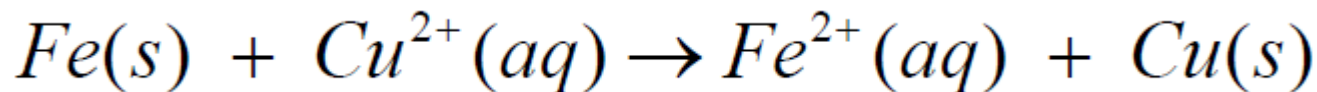
$$n = 1$$

$$E_{\text{cell}} = E_{\text{Cell}}^{\circ} - \frac{0.059}{n} \log_{10} Q$$

$$E_{\text{cell}} = 0.0 - \frac{0.059}{1} \log_{10} 0.1 = 0. + 0.059 = 0.06\text{ V}$$

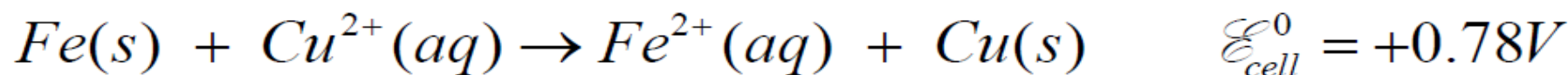
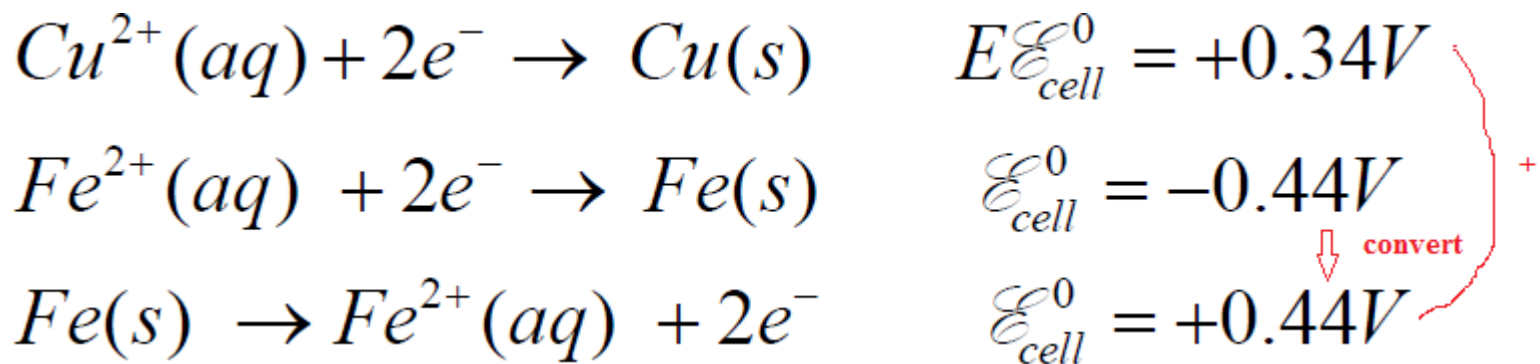
Example: Calculate the cell potential for the following:

When $[\text{Cu}^{2+}] = 0.3 \text{ M}$ and $[\text{Fe}^{2+}] = 0.1 \text{ M}$.



Solution:

- First, need to identify the 1/2 cells (table).
- Get the voltage under standard conditions



- Now, calculate Q and then E_{cell} .
- Notice, the concentrations are in separate containers.

$$Q = \frac{[Fe^{2+}]}{[Cu^{2+}]} = \frac{(0.1)}{(0.3)} = 0.33$$

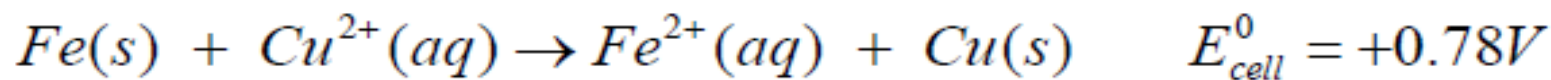
- $n=2$

$$E_{\text{Cell}} = E_{\text{Cell}}^o - \frac{0.06}{n} \log_{10} Q$$

$$E_{\text{Cell}} = 0.78 - \frac{0.06}{2} \log_{10} 0.33 = 0.78 + 0.014 = 0.80 \text{ V}$$

- **Example:**

If $[Cu^{2+}] = 0.3 \text{ M}$, what $[Fe^{2+}]$ is needed so that $E_{\text{cell}} = 0.76 \text{ V}$?



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log_{10} Q$$

$$0.76 = 0.78 - \frac{0.059}{2} \log_{10} Q$$

$$\log_{10} Q = \frac{2 \cdot 0.02}{0.059} = \frac{2}{3}$$

$$Q = 4.7 = \frac{[Fe^{2+}]}{[Cu^{2+}]} = \frac{[Fe^{2+}]}{0.3}$$

$$[Fe^{2+}] = 4.7 \cdot 0.3 = \underline{1.4M}$$

Example:

- What is the electrode potential for a **half-cell** consisting of a cadmium electrode immersed in a solution that is 0.0150 M in Cd^{2+} ?

Solution;



We will assume that $a_{\text{Cd}^{2+}} \approx [\text{Cd}^{2+}]$ and write

$$E_{\text{Cd}} = E_{\text{Cd}}^0 - \frac{0.0592}{2} \log \frac{1}{[\text{Cd}^{2+}]}$$

Substituting the Cd^{2+} concentration into this equation gives

$$E_{\text{Cd}} = -0.403 - \frac{0.0592}{2} \log \frac{1}{0.0150} = -0.457 \text{ V}$$