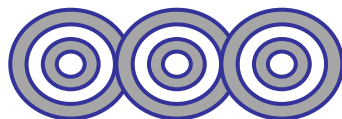




Instrumental Methods of Analysis



Electrode Potentials

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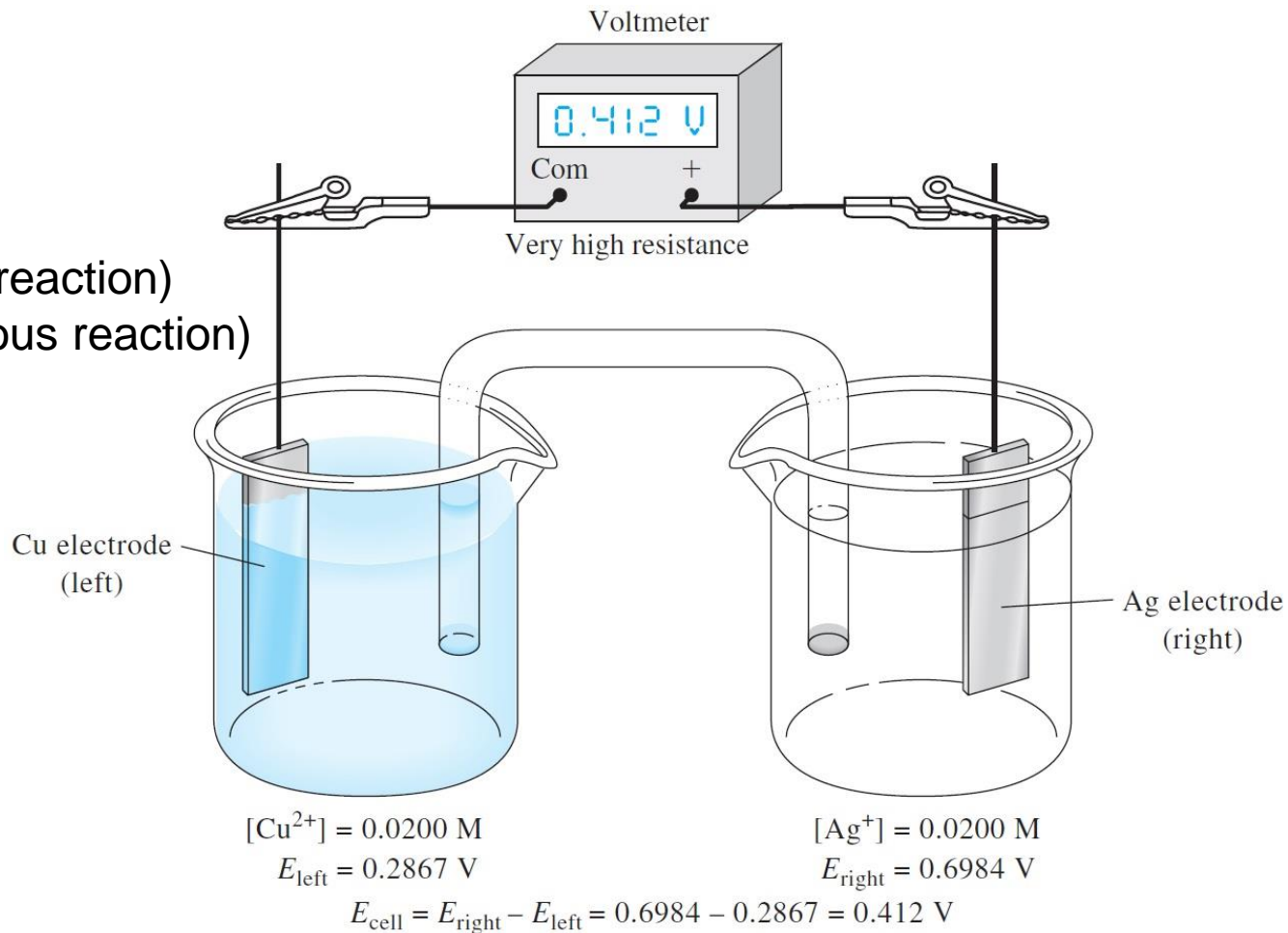
Electrode Potentials

The cell potential E_{cell} is related to the free energy of the reaction ΔG by:

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

ΔG -ve (spontaneous reaction)

ΔG +ve (nonspontaneous reaction)



If the reactants and products are in their **standard states**, the resulting cell potential is called the **standard cell potential**. This latter quantity is related to the standard free energy change for the reaction and thus to the equilibrium constant K_{eq} by

$$\Delta G^{\circ} = -nFE^{\circ}_{cell} = -RT \ln K_{eq}$$

$$E^{\circ}_{cell} = \frac{RT}{nF} \ln K_{eq}$$

where R is the gas constant and T is the absolute temperature.

By convention, a cell is written

anode/solution/cathode

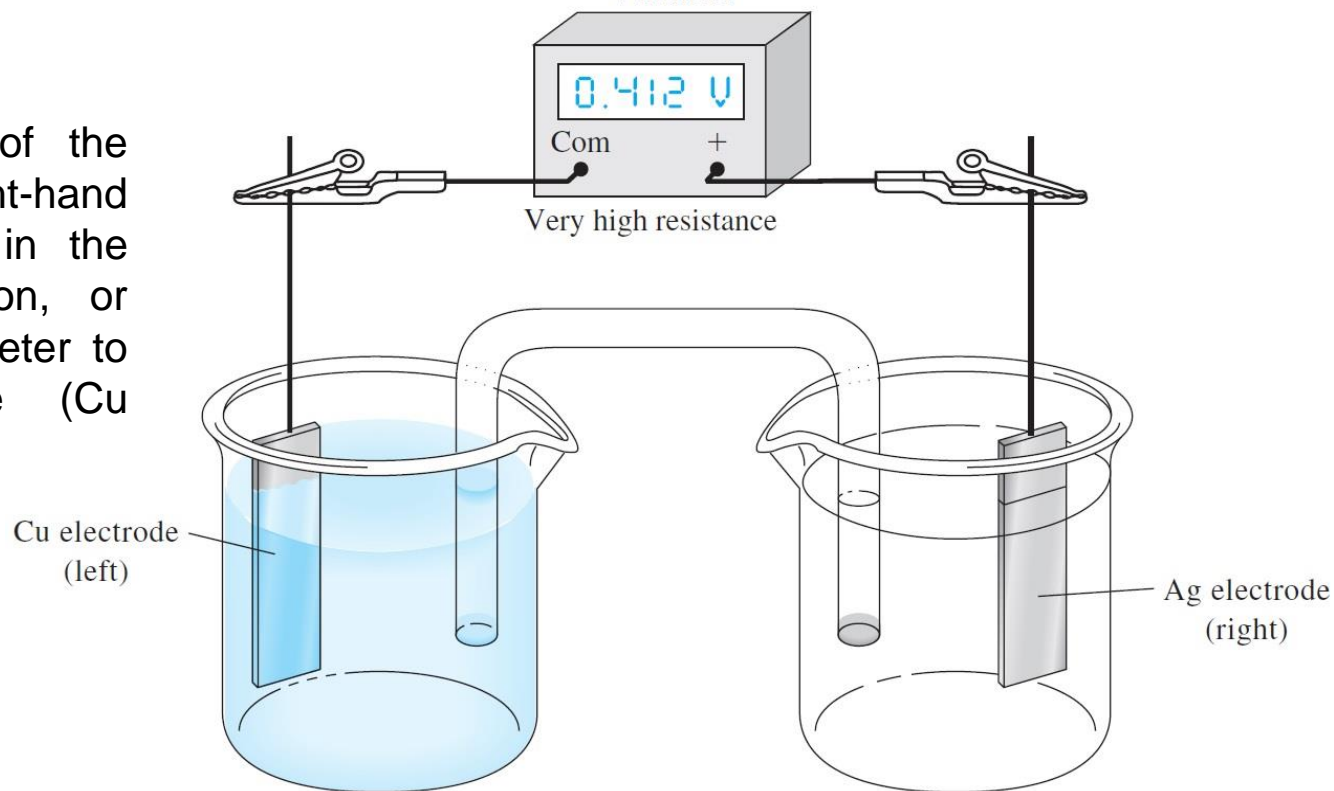
When we consider a normal chemical reaction, we speak of the reaction occurring from reactants on the left side of the arrow to products on the right side.

By the IUPAC sign convention, when we consider an electrochemical cell and its resulting potential, we consider the cell reaction to occur in a certain direction as well. The convention for cells is called the

plus right rule

plus right rule

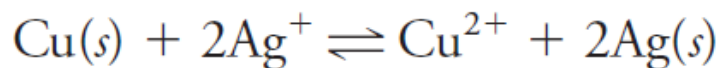
Connect the +ve lead of the voltmeter to the right-hand electrode (Ag electrode in the Figure) and the common, or ground, lead of the voltmeter to the left-hand electrode (Cu electrode in the Figure).



If we always follow this convention, the value of E_{cell} is a measure of the tendency of the cell reaction to occur spontaneously in the direction written below from left to right.



In other words, the reaction being considered is



- If E_{cell} is +ve, the reaction in the direction being considered would occur spontaneously.
- If E_{cell} is -ve, the reaction in the direction considered is *not* the spontaneous cell reaction.

Half-Cell Potentials

The potential of a cell is the difference between two half-cell or single-electrode potentials, one associated with the half-reaction at the right-hand electrode (E_{right}) and the other associated with the half-reaction at the left-hand electrode (E_{left}).

According to the IUPAC sign convention, we may write the cell potential E_{cell} as

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

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

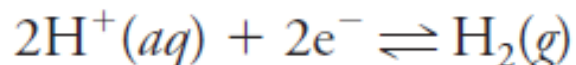
Although we cannot determine absolute potentials of electrodes, we can easily determine relative electrode potentials.

Substituting other electrodes while keeping one of the electrodes unchanged allows us to construct a table of relative electrode potentials.

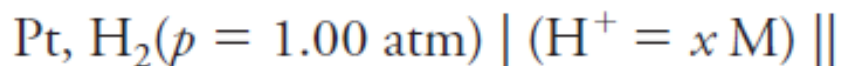
The Standard Hydrogen Reference Electrode

For relative electrode potential data to be widely applicable and useful, we must have a generally agreed-upon reference half-cell against which all others are compared.

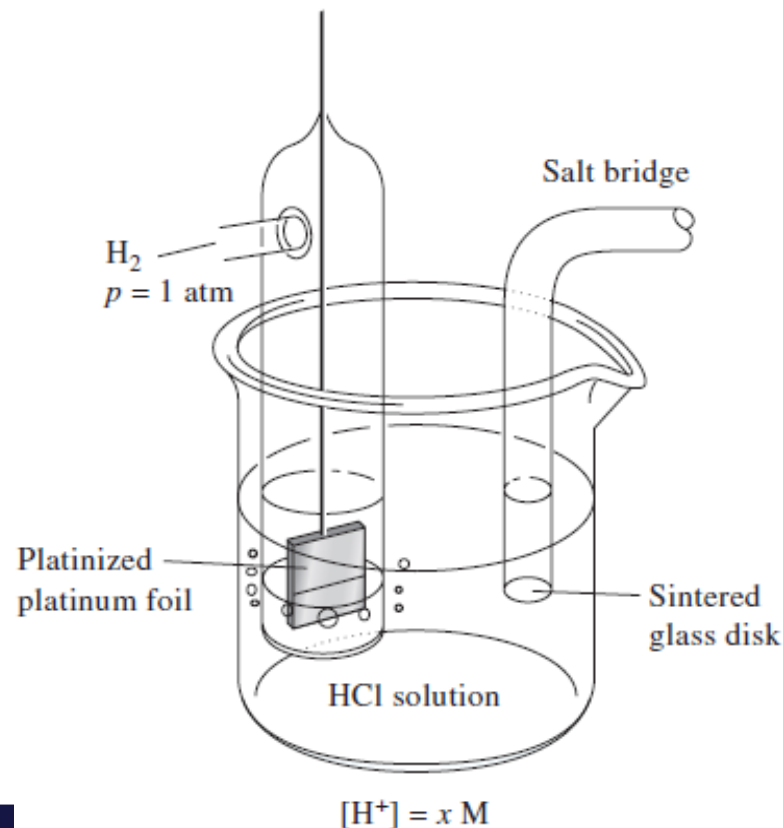
Such an electrode must be easy to construct, reversible, and highly reproducible in its behavior. The **standard hydrogen electrode (SHE)** meets these specifications and has been used as a universal reference electrode. It is a typical **gas electrode**.



The hydrogen electrode can be represented schematically as:



By convention, the potential of the standard hydrogen electrode is assigned a value of 0.000 V at all temperatures.



Electrode Potential and Standard Electrode Potential

An **electrode potential** is defined as the potential of a cell in which the electrode in question is the right-hand electrode and the standard hydrogen electrode is the left-hand electrode.

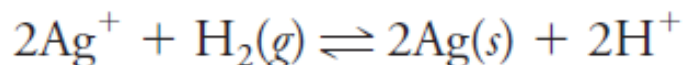
$$\begin{aligned}E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} \\&= E_X - E_{\text{SHE}} \\&= E_X - 0.000 \\&= E_X\end{aligned}$$

any potential developed in a galvanic cell consisting of a standard hydrogen electrode and some other electrode is attributed entirely to the other electrode.

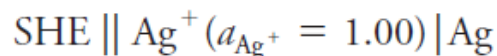
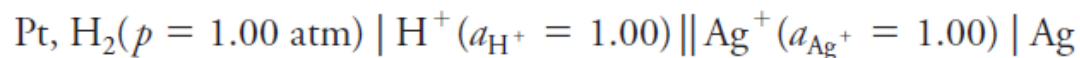
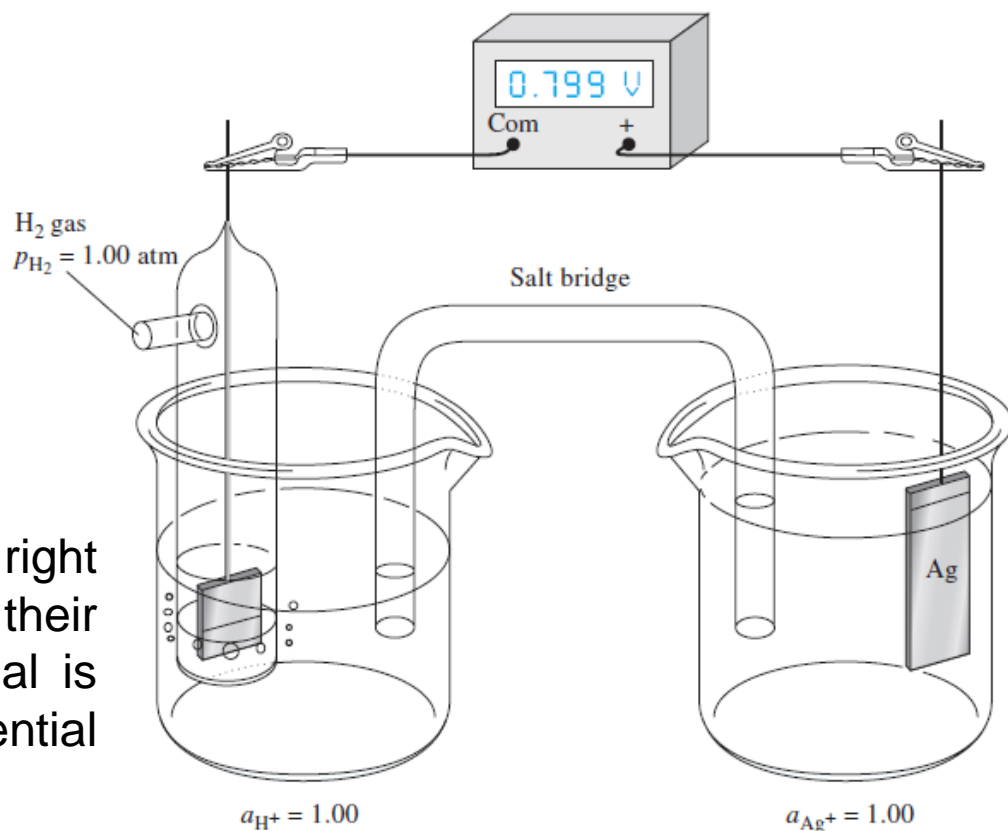
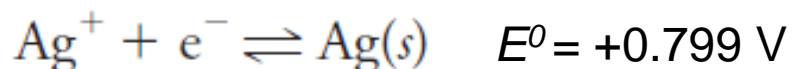
The **standard electrode potential**, E° , of a half-reaction is defined as its electrode potential when the activities of the reactants and products are all unity.

Measurement of the electrode potential for an Ag electrode

This galvanic cell develops a potential of +0.799 V with the silver electrode on the right, that is, the spontaneous cell reaction is oxidation in the left-hand compartment and reduction in the right-hand compartment:

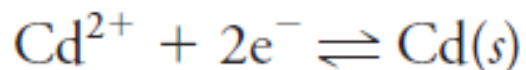


Because the silver electrode is on the right and the reactants and products are in their standard states, the measured potential is by definition the standard electrode potential for the silver half-reaction.



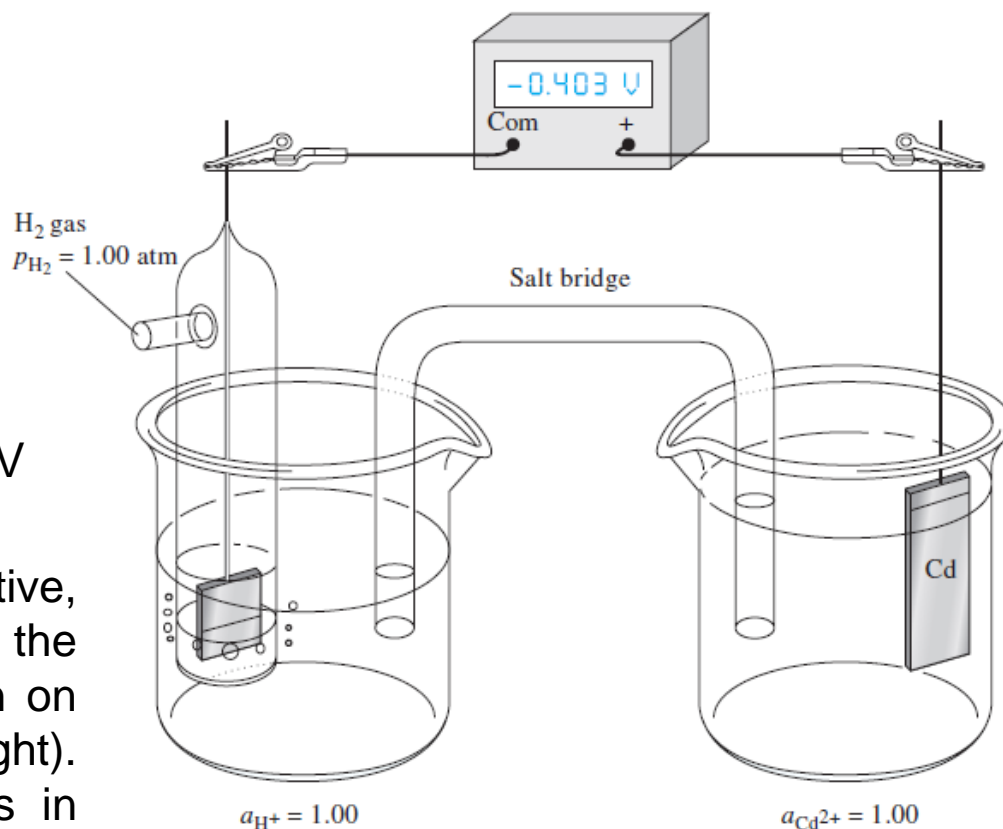
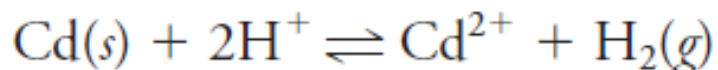
Measurement of the electrode potential for an Cd electrode

The cadmium electrode is -ve with respect to the standard hydrogen electrode. Therefore, the standard electrode potential of the Cd/Cd²⁺ couple is *by convention* given a -ve sign, and $E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.403 \text{ V}$.



$$E^\circ = -0.403 \text{ V}$$

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.



| Half-Reaction | Standard Electrode Potential, V |
|--|---------------------------------|
| $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}(s)$ | +0.799 |
| $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(g)$ | 0.000 |
| $\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}(s)$ | -0.403 |
| $\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}(s)$ | -0.763 |

The magnitudes of these electrode potentials indicate the relative strength of the four ionic species as electron acceptors (oxidizing agents), that is, in decreasing strength,



Standard Electrode Potentials*

| Reaction | E^0 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 |
| $\text{UO}_2^{2+} + 4\text{H}^+ + 2e^- \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$ | +0.334 |
| $\text{Hg}_2\text{Cl}_2(s) + 2e^- \rightleftharpoons 2\text{Hg}(l) + 2\text{Cl}^-$ | +0.268 |
| $\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^-$ | +0.222 |
| $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + e^- \rightleftharpoons \text{Ag}(s) + 2\text{S}_2\text{O}_3^{2-}$ | +0.017 |
| $2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(g)$ | 0.000 |
| $\text{AgI}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{I}^-$ | -0.151 |
| $\text{PbSO}_4 + 2e^- \rightleftharpoons \text{Pb}(s) + \text{SO}_4^{2-}$ | -0.350 |
| $\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}(s)$ | -0.403 |
| $\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}(s)$ | -0.763 |

Potential and Concentration

The Nernst Equation

The potential of a potentiometric electrochemical cell is given as

$$E_{\text{cell}} = E_{\text{c}} - E_{\text{a}}$$

where E_{c} and E_{a} are reduction potentials for the reactions occurring at the cathode and anode.

These reduction potentials are a function of the concentrations of those species responsible for the electrode potentials, as given by the **Nernst equation**

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

where

E° : the standard electrode potential (standard-state reduction potential)

R : the ideal gas constant, $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

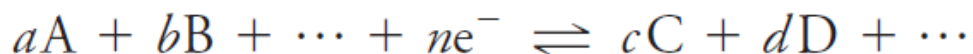
T : temperature, K

n : number of moles of electrons involved in the reduction reaction

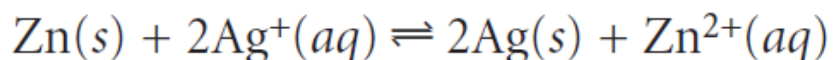
F : the faraday = $96,485 \text{ C (coulombs) per mole of electrons}$

\ln : natural logarithm = $2.303 \log$

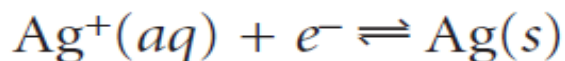
Q : is the reaction quotient



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$



$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

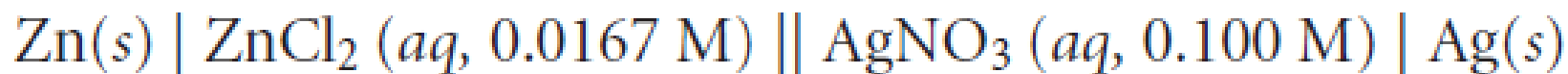
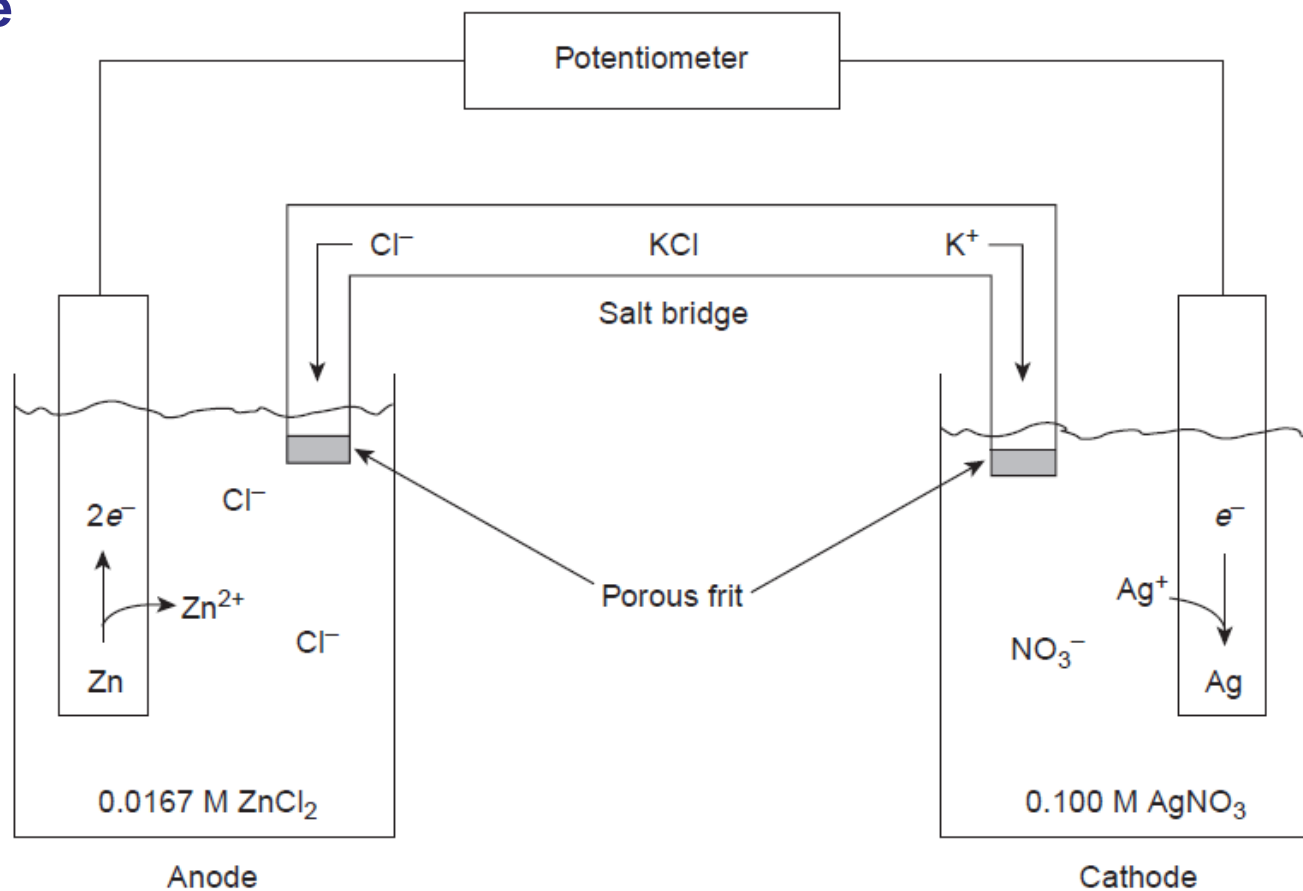


$$Q = \frac{1}{[\text{Ag}^+]}$$

Under typical laboratory conditions (temperature of 25 °C or 298 K) the Nernst equation becomes

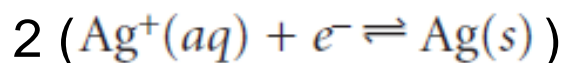
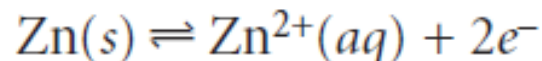
$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.05916}{n} \log Q$$

Example



What is the potential for this electrochemical cell?

| Half-Reaction | Standard Electrode Potential, V |
|--|---------------------------------|
| $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}(s)$ | +0.799 |
| $\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}(s)$ | -0.763 |



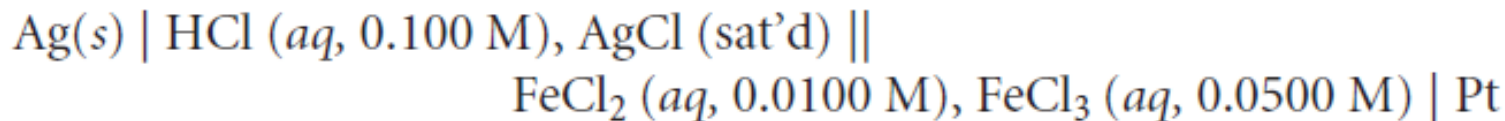
$$E_a = E_{\text{Zn}^{2+}/\text{Zn}}^\circ - \frac{0.05916}{2} \log \frac{1}{[\text{Zn}^{2+}]} = -0.7618 - \frac{0.05916}{2} \log \frac{1}{0.0167}$$

$$E_c = E_{\text{Ag}^+/\text{Ag}}^\circ - 0.05916 \log \frac{1}{[\text{Ag}^+]} = +0.7996 - 0.05916 \log \frac{1}{0.100}$$

$$E_{\text{cell}} = E_c - E_a$$

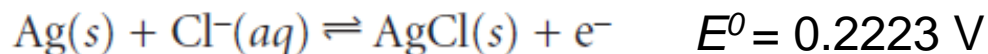
$$= 0.74044 - (-0.81437) = + 1.555 \text{ V}$$

Example

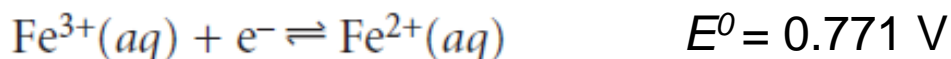


What is the potential for this electrochemical cell?

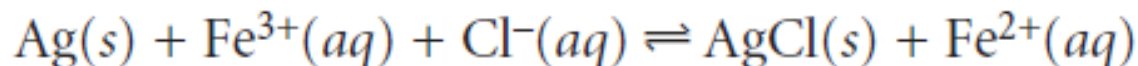
The oxidation of Ag to Ag⁺ occurs at the anode (the left-hand cell). Since the solution contains a source of Cl⁻, the anodic reaction is:



The cathodic reaction (the right-hand cell) is the reduction of Fe³⁺ to Fe²⁺



The overall cell reaction, therefore, is



$$\begin{aligned} E_{\text{cell}} &= \left(E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) - (E_{\text{AgCl}/\text{Ag}}^{\circ} - 0.05916 \log [\text{Cl}^-]) \\ &= \left(+0.771 - 0.05916 \log \frac{0.0100}{0.0500} \right) - [+0.2223 - 0.05916 \log (0.100)] \\ &= +0.531 \text{ V} \end{aligned}$$

