MUNI
PHARM

Electrochemistry I

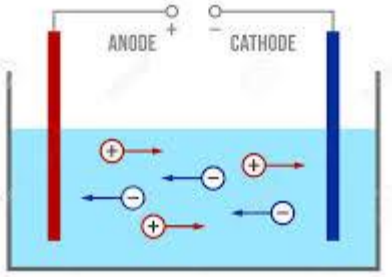
Physical chemistry

Basic concepts

Electrochemistry – studies the relationship between electric and chemical phenomena. Electrochemistry deals with the interaction between **electrical energy and chemical change**.

Ions – positively or negatively charged particles which move in the solution by applying electrical fields.

Electrolyte – allow passage of electrical current by movement of ions in solution (conductors classe II). **Strong electrolytes**: solution completely dissociated into ions. **Weak electrolytes**: solution dissociated only partially (pK_a).

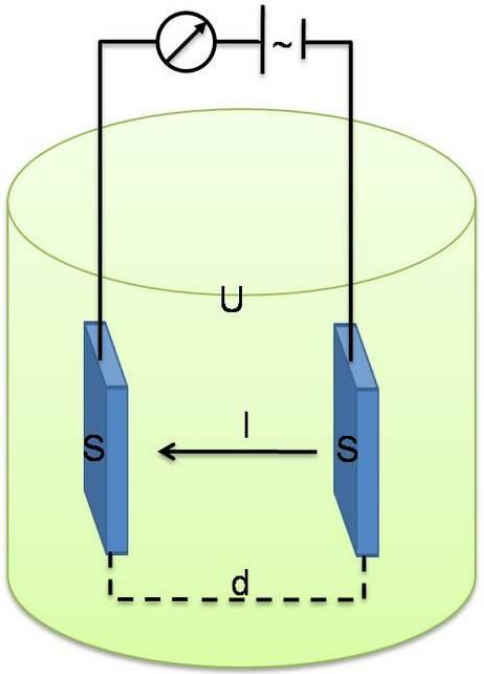


Conductivity in liquids

Conductivity is related with **transfer of ions due to electric field**.

When the voltage is inserted on electrodes, the ions start to move toward the electrodes.

Ability of conductor transfer electric current is characterized by its **resistance R** (Ohm's law R = U/I).



Electric conductance:

G = 1/R [Ω^{-1}, Siemens S]

Specific conductance (conductivity):

κ= (d/S) * G [$\Omega^{-1}m^{-1}$, Sm^{-1}]

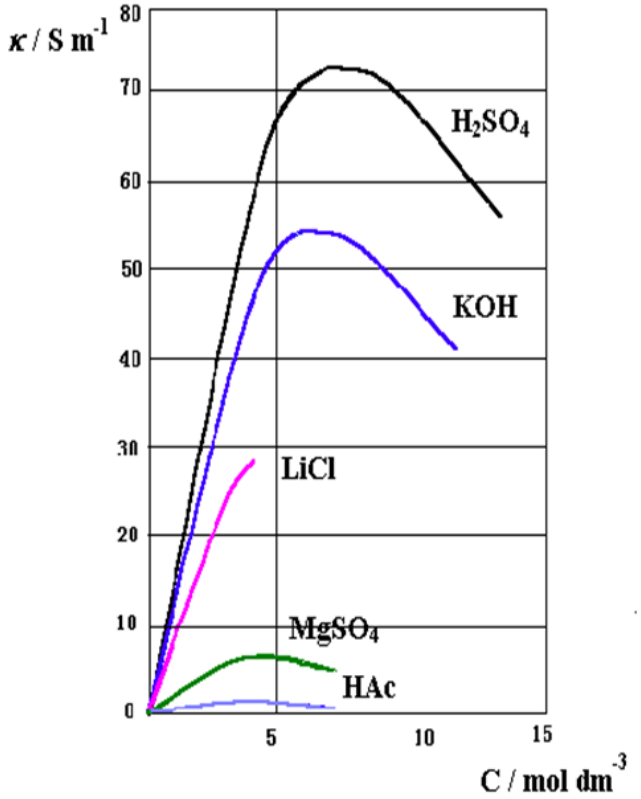
S – surface of electrode; d – distance between electrodes

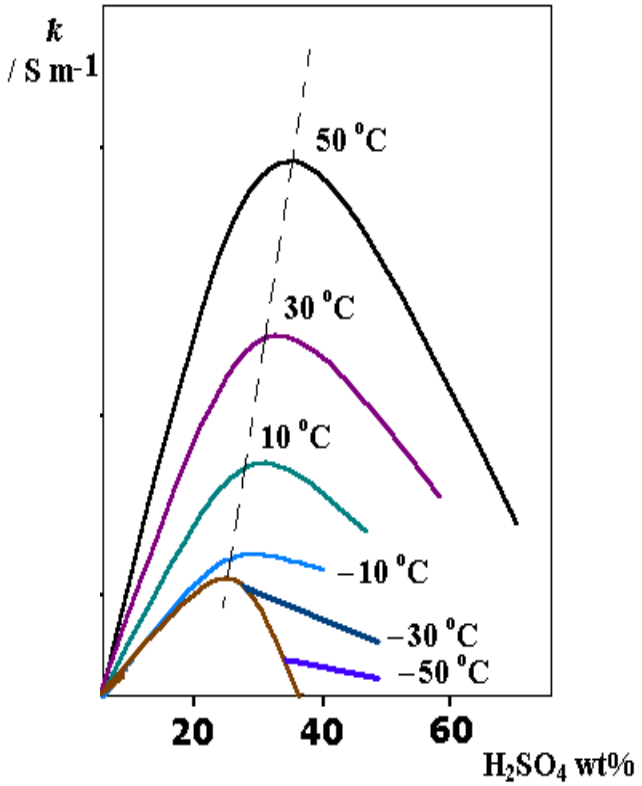
d/S – instrument constant

Factors influencing the conductivity

1. Concentration of ions
2. Type of the electrolyte
3. Measurement conditions

   (e.g. temperature, viscosity of the solvent)



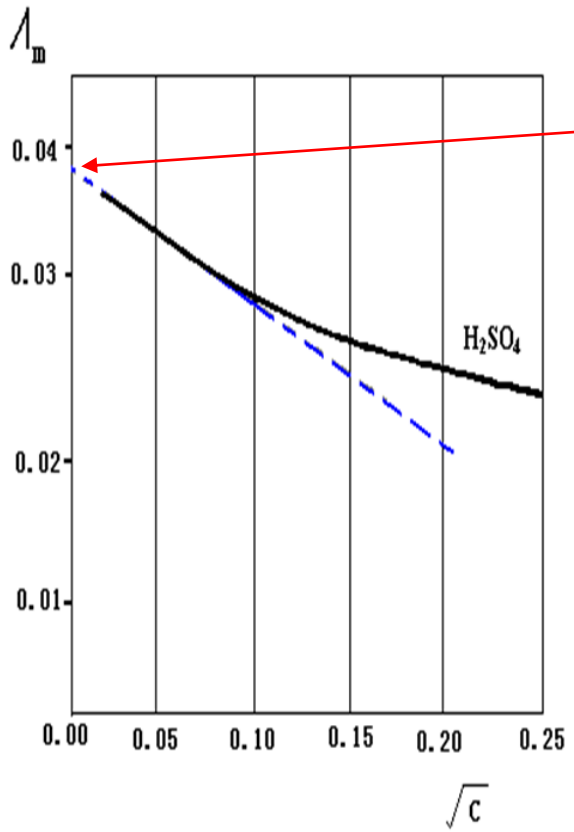


Molar conductivity

- The conductivity of a solution is approximately proportional to the concentration:

$$\Lambda_m = \frac{\kappa}{C} \qquad [\Omega^{-1}\,m^2\,mol^{-1}]$$

The molar conductivity depends on the concentration (decreases with increasing concentration).



Limit molar conductivity λ_m^0
- constant for a given electrolyte
(molar conductivity at 25 °C and c → 0).

Kohlrausch relationship:

$$\Lambda_m = \Lambda_m^0 - A\sqrt{c}$$

A – empirical constant

Limit molar conductivity

Kohlrausch law of independent migration of ions

Limit molar conductivity of the electrolyte is the sum of limit molar conductivities of ions.

$$\Lambda_m^0 = \lambda_{m+}^0 + \lambda_{m-}^0$$

The difference between values of limit molar conductivity of solutions of different salts which have **the same cation or anion don't dependent on the nature of this common ion**.

λ_m^0	K^+	Na^+	Tl^+
Cl^-	130.1	109.0	131.5
NO_3^-	126.5	105.3	127.5
F^-	111.3	90.1	112.5

difference ca 3.8

difference ca 15

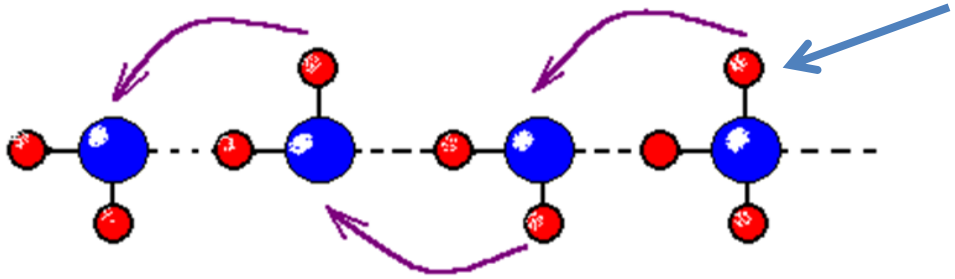
difference ca 21

difference ca 22.5

Limit molar conductivity

Factors influencing λ_m^0 :

1. The nature of the ion
   a) charge
   b) radius
   c) transport mechanism



The proton from H_3O^+ is taken by a water molecule and new H_3O^+ is formed. Transferring of the proton will much faster than the transport of whole large ion H_3O^+.

2. Measurement conditions (e.g. temperature, viscosity of the solvent)

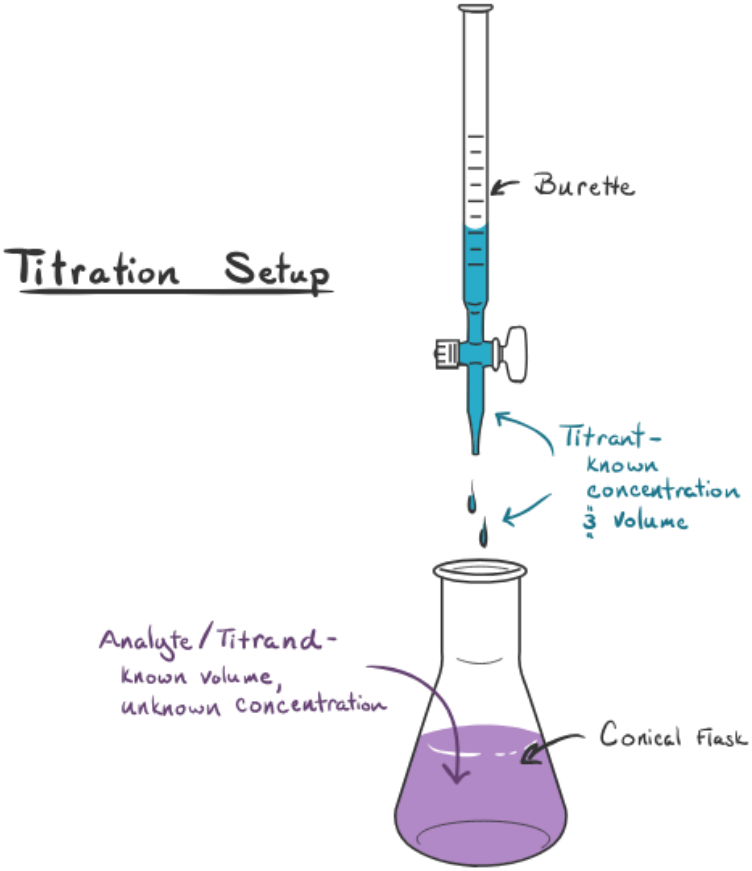
Application

1. **Conductometric titration**

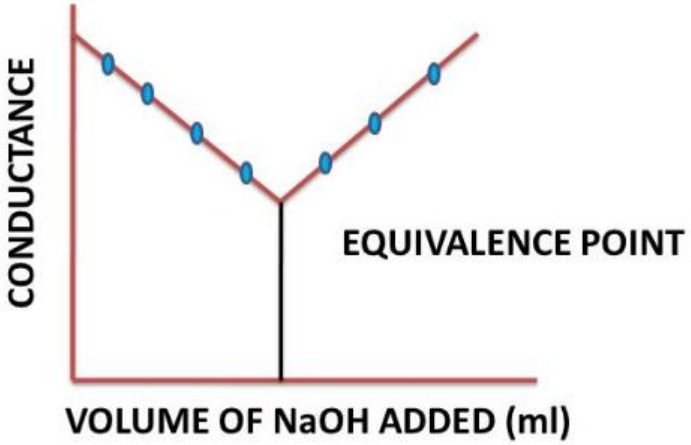
- can be used for indication of equivalence point:

a) in the formation of non-conductive particles from ions (neutralization, precipitation)

b) where there is an exchange of particles with different molar conductivity (complexation r.).



$(H^+ + Cl^-) + (Na^+ + OH^-) \longrightarrow Na^+ + Cl^- + H2O$



Note: According to the Pharmacopoeia, there are several methods of indicating the equivalence point, e.g. conductometry, potentiometry or visual indication based on colour change of the indicator.

Application

2. **Direct conductometry** - Determining the concentration of the electrolyte. Conductivity is not specific to individual ions. Used mainly for determination of trace concentrations of ions in solution (control water purity according to Ph. Eur. - purified and highly purified water).

3. **Determining the solubility** of slightly soluble salts

4. **Determining the degree of dissociation** (α): with increasing concentration of weak electrolyte conductivity decreases (decrease dissociation), $\lambda = \lambda^0 \alpha$

Basic concepts

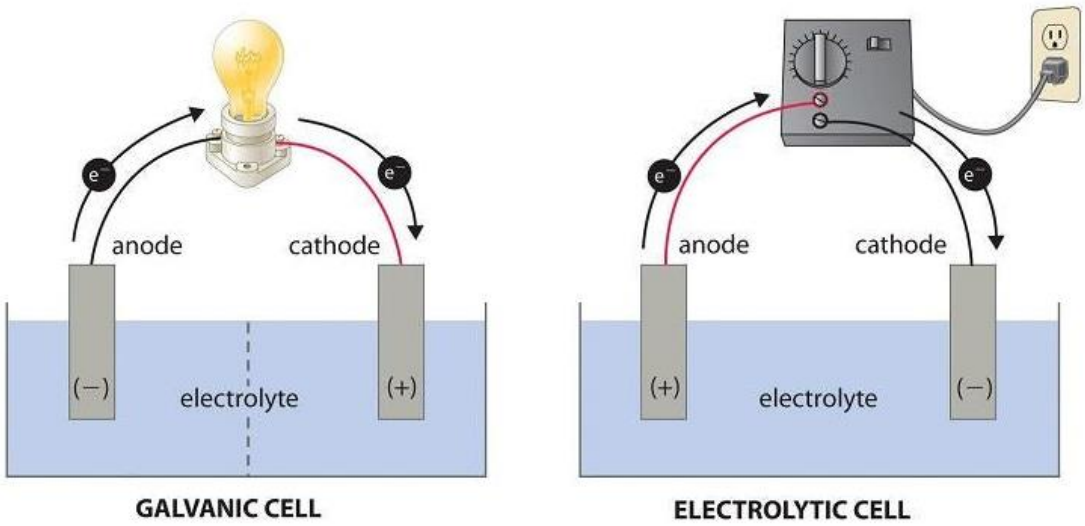
Redox reactions – (oxidation-reduction) are chemical reactions in which the oxidation state of atoms is changing. Each redox reaction is composed of two half-reactions (oxidation and reduction) which occur simultaneously. In the **oxidation**, the oxidation number of an atom increases, thus **atom loses electrons**, in the **reduction** the oxidation number decreases, thus **atom accepts electrons**.

Electrode - an electrical conductor in contact with the non-metallic parts of the electrical circuit (e.g. electrolyte). In electrochemistry, the **cathode** is defined as the electrode at which **reduction** takes place, and the **anode** is the electrode at which **oxidation** occurs. Each of the two electrodes may have a different charge (+ or -), depending on whether it is an electrolytic cell (electrolysis – we put the voltage on the electrodes), or galvanic cell (spontaneous process).

Basic concepts

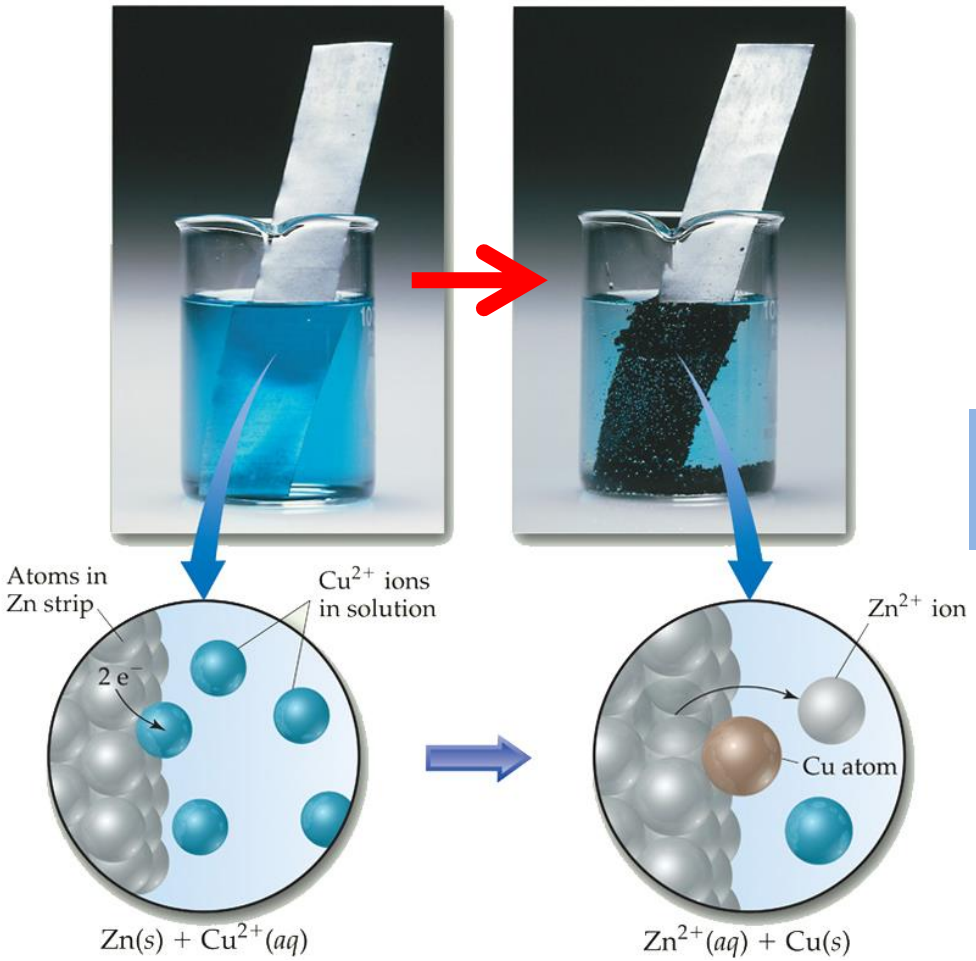
Galvanic cell – **Transform the chemical energy to the electrical energy**. After connecting the galvanic cell in the electrical circuit, the reactions take place inside the cell, which gradually reduces the electrical energy stored in a galvanic cell - the cell is discharging. These reactions may be irreversible (primary cells) or reversible - cell can be recharged (battery).

Electrolytic cell – **Transform the electrical energy to the chemical energy.** Is caused by passage of electric current in liquid in which chemical changes occurs on the electrodes. The electrochemical reaction takes place in the opposite direction than in galvanic cell.



Electrode potential

The formation of the electorde potential is based on reaction occurring on the surface of the electrode.



There is a potential difference between the two phases (metal and solution).

$$Zn(s) = Zn^{2+}(aq) + 2e$$

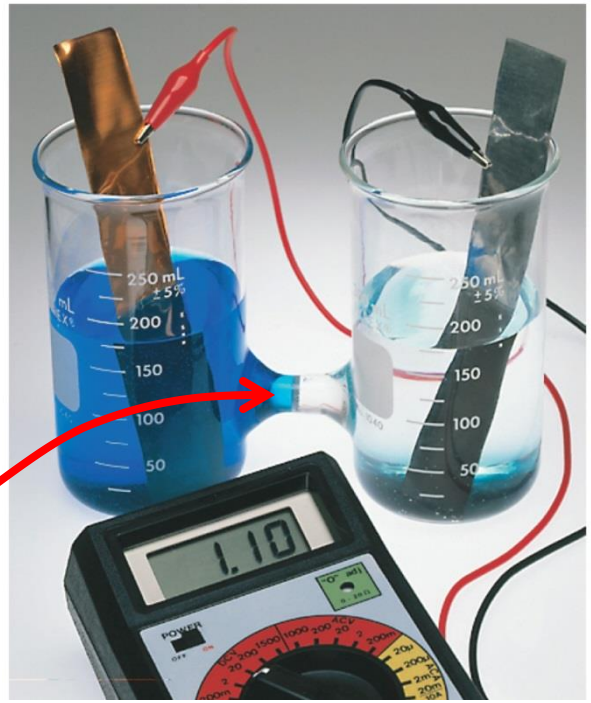
$$Cu^{2+}(aq) + 2e = Cu(s)$$

This redox reaction occurs due to the potential difference between the metal and the solution.

Galvanic cell

- in an electrolyte solution are immersed two different electrodes (two electrodes are need to connect the electrical circuit), which are charged against the solution to different charge (+/-), the system may produce a electrical work (voltage).

The electrodes may have a common electrolyte solution or the solutions can be different. If the electrolyte solutions are different, must be electrically connected (salt bridge or diaphragm).

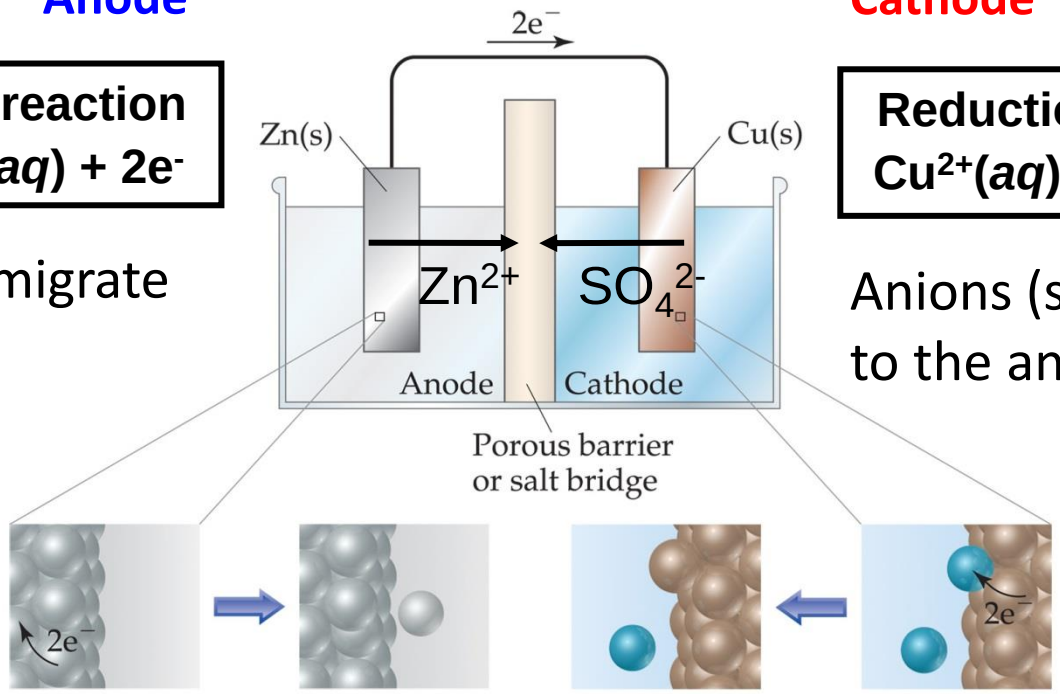


Galvanic cell

Anode

Oxidation half-reaction
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Cations (Zn^{2+}) migrate to the cathode



Cathode

Reduction half-reaction
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Anions (sulfate) migrate to the anode

Overall (cell) reaction
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Galvanic cell

Schematic writing of the cell (Daniell cell):

The **anode** reaction is written on the **left**.

The **cathode** reaction is written on the **right**.

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

The single line shows a phase boundary between the components of a half-cell.

The double line shows that the half-cells are physically separated (diaphragm).

If needed, concentrations of dissolved components are given in parentheses. (If not stated, it is assumed that they are 1 M.)

Electrode potential

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

The spontaneous reaction occurs as a result of the different abilities of metals to give up their electrons.

Zn is a stronger reducing agent than Cu.

Zn has a higher potential energy than Cu. When the electrodes are connected, the flow of e^- from Zn to Cu equalize the difference in electrical potential.

$$Zn(s) = Zn^{2+}(aq) + 2e$$

$$Cu^{2+}(aq) + 2e = Cu(s)$$

The electrode potential *E* depends upon:

a) **the nature of the metal and its ions**,

b) the concentration of the ions in the electrolyte,

c) the temperature

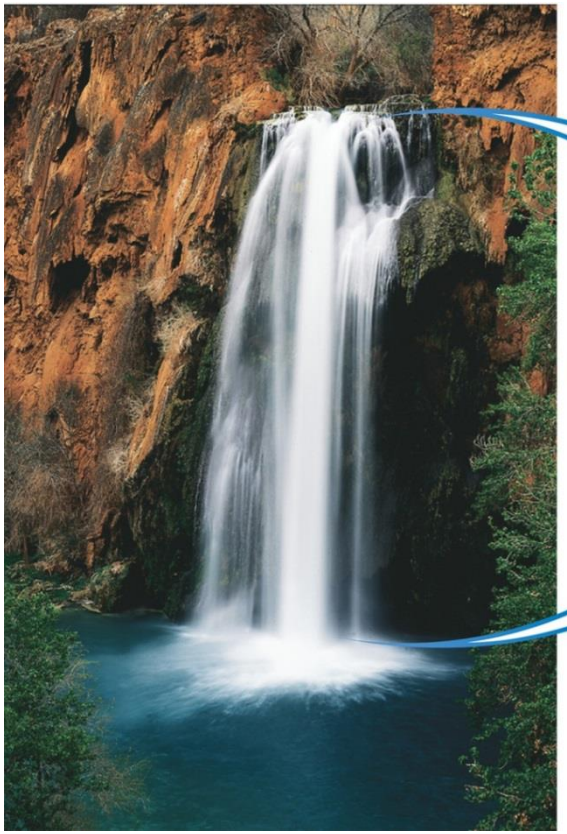
The difference in electrode potential between the two electrodes is called electromotive force (EMF).

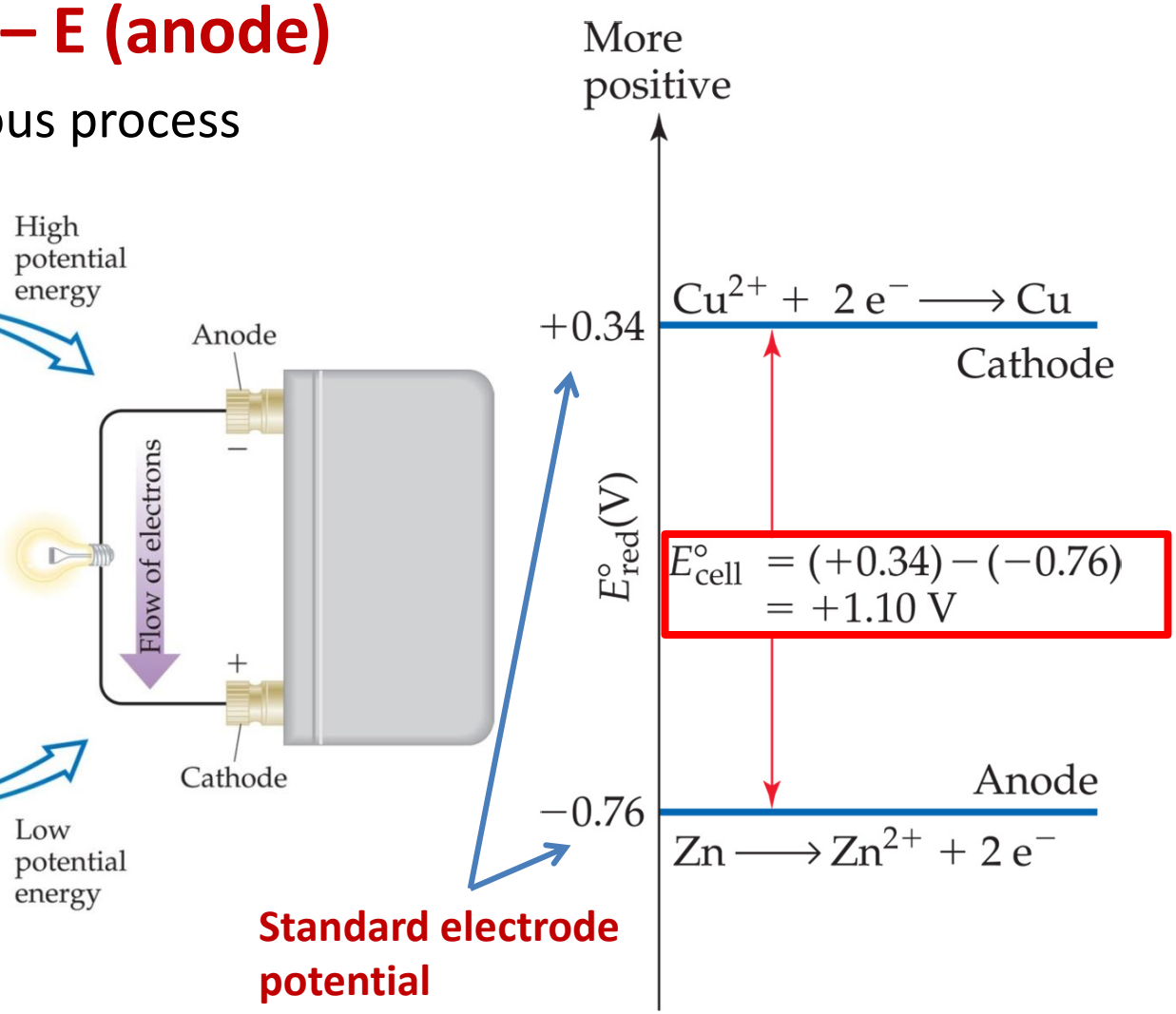
Electromotive forces EMF

The electromotive forces is the maximum voltage of the galvanic cell (so called cell potential).

EMF = E (cathode) – E (anode)

EMF > 0 for a spontaneous process





Standard Electrode Potentials E^0

The standard electrode potential ($E°_{\text{half-cell}}$) is the potential of a given half-reaction when all components are in their standard states (unit activity of all components, temperature 273.15 K = 0 °C).

Since a half cell in an electrochemical cell can work only in combination with the other half cell and does not work independently, **it is not possible to determine the absolute electrode potential** of an electrode. We can, therefore, find only the relative electrode potential.

This difficulty can be solved by selecting one of the electrodes as a **reference electrode** and arbitrarily fixing the potential of this electrode as zero. For this purpose, reversible hydrogen electrode has been universally accepted as a reference electrode (**standard hydrogen electrode** , S.H.E).

$$E°_{\text{cell}} = E°_{\text{cathode (reduction)}} - E°_{\text{anode (oxidation)}}$$

E° is the electromotive force of an electrochemical cell consisting of an electrode in the standard state and the standard hydrogen electrode.

Standard Reduction Potentials

Ox. agent strength increases

Reduction Half-Reaction	E°(V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	1.50
$Cl_2(g) + 2\ e^- \rightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$	1.23
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.23
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.37
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

Red. agent strength increases

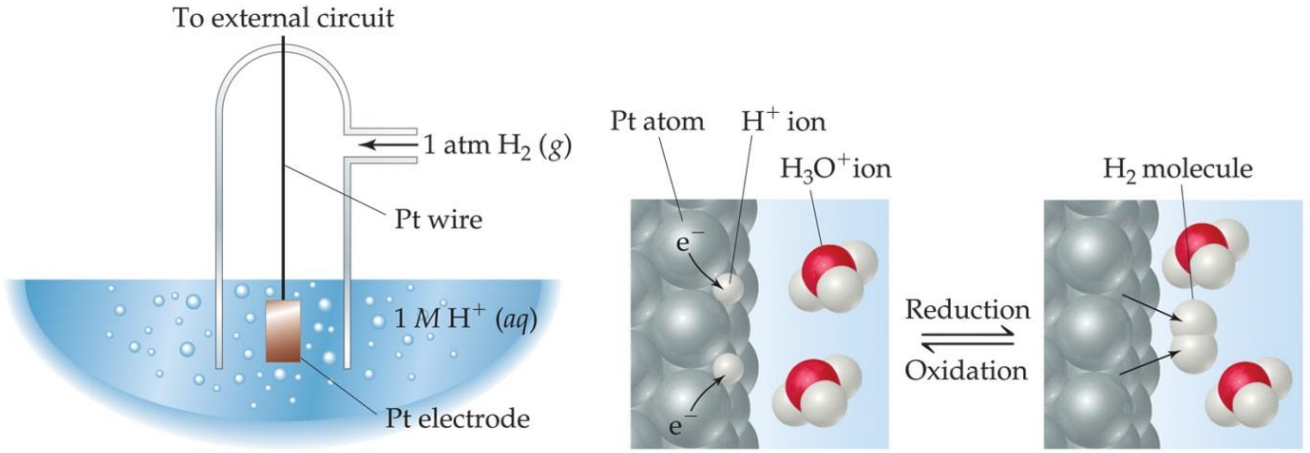
Standard Hydrogen Electrode

By definition, the reduction potential for S.H.E is 0.0 V:

$2\ H^+\ (aq, 1M) + 2\ e^- \longrightarrow H_2\ (g, 1\ atm)$

$E^0\ (H_3O^+/H_2) = 0$

SHE electrode is formed of platinum coated with platinum black, aerated with hydrogen gas under pressure of 101 325 Pa at a temperature of 273.15 K, immersed in a solution with a unit activity of hydrogen ions (H^+) = 1

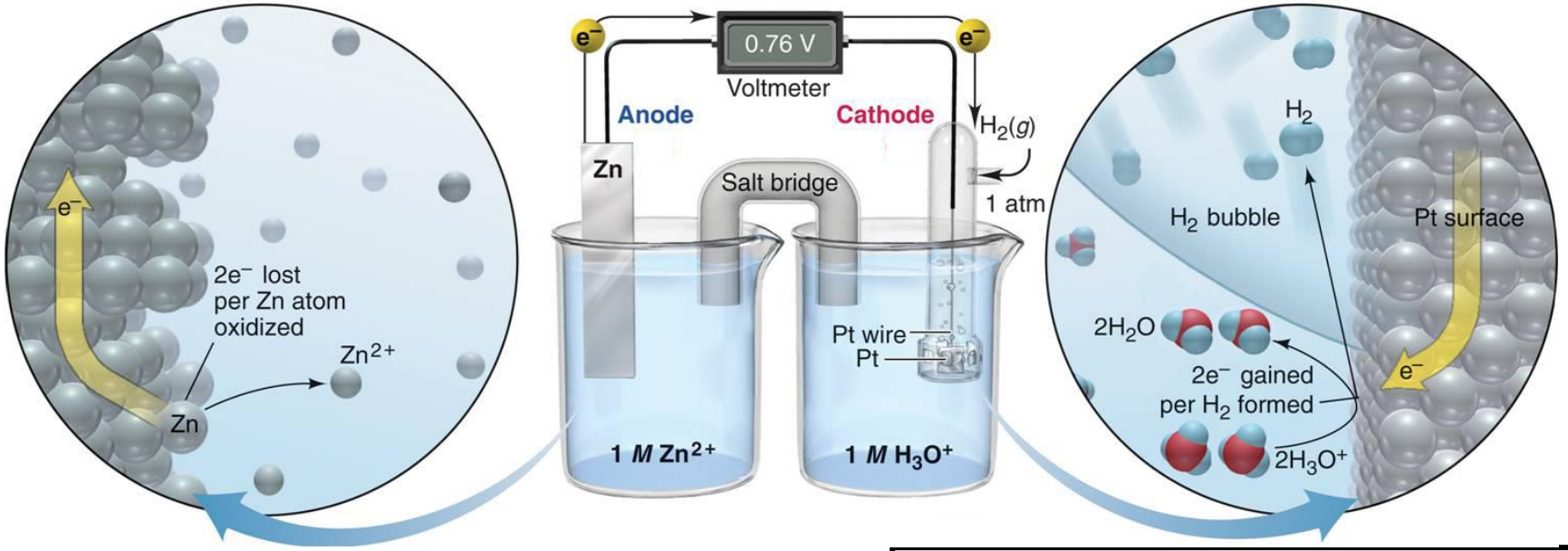


Standard Hydrogen Electrode

Oxidation half-reaction
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

EMF = E (cathode) – E (anode)

$$E^0 = E^0_{cathode}\ (0\ V) - E^0_{anode}\ (0.76\ V) = -0.76\ V$$

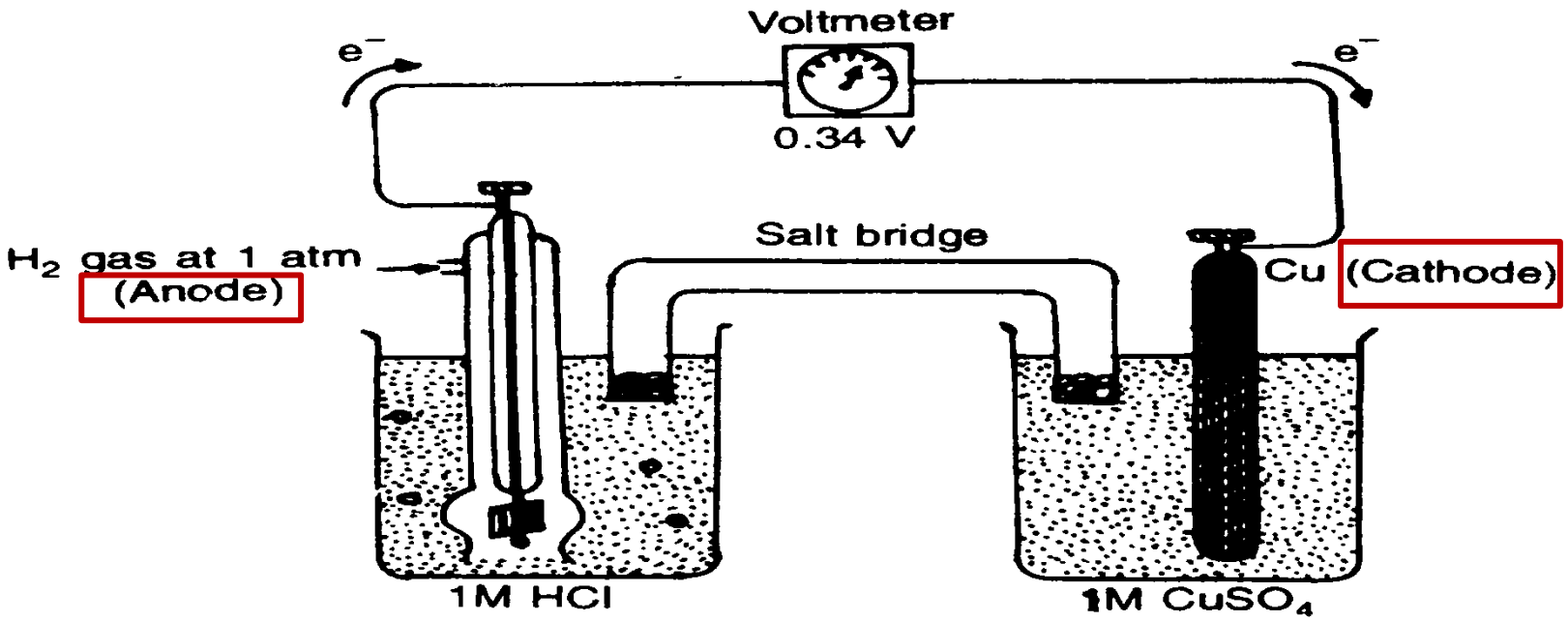


Reduction half-reaction
$2H_3O^+(aq) + 2e^- \rightarrow H_2(g) + 2H_2O(l)$

Overall (cell) reaction
$Zn(s) + 2H_3O^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) + 2H_2O(l)$

Standard Hydrogen Electrode

$Pt , H_2 (1\ atm) | H^+ (1M) || Cu^{2+} (1M) | Cu$



The cell potential has been measured to be 0.34 V.

EMF = E (cathode) – E (anode)

$E^0 = E^0_{cathode}$ (0.34 V) – E^0_{anode} (0 V) = 0.34 V

Electrodes at which reduction occurs in connection with SHE have positive reduction potentials.

Sample Problem 1: Calculate an unknown $E°_{\text{half-cell}}$ from $E°_{\text{cell}}$

The galvanic cell reaction takes place:

$Br_2(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Br^-(aq)$ $\quad E°_{cell} = 1.83$ V

Calculate $E°_{bromine}$, $E°_{Zn} = -0.76$ V

$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$ [reduction; cathode]

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ [oxidation; anode] $\quad E°_{Zn} = -0.76$ V

$E°_{cell} = E°_{cathode} - E°_{anode}$

$1.83 = E°_{bromine} - (-0.76)$

$1.83 - 0.76 = E°_{bromine}$

$$\boxed{E°_{bromine} = 1.07 \text{ V}}$$

Sample Problem 2: Using half-reactions to write a spontaneous redox reaction and calculating $E°_{cell}$

$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \quad E°_{Sn} = -0.14\ V$$
$$Ag^+(aq) + e^- \rightarrow Ag(s) \quad E°_{Ag} = 0.80\ V$$

Here the Ag^+/Ag half-reaction has **the more positive E° value** => reduction reaction (cathode).

We reverse the Sn^{2+}/Sn half-reaction, but we do not reverse the sign:

$$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^- \quad E°_{Sn} = -0.14\ V$$

The number of electrons in both half-reaction must be the same (E^0 is unchanged):

$$\mathbf{2}Ag^+(aq) + \mathbf{2}e^- \rightarrow \mathbf{2}Ag(s) \qquad E°_{Ag} = 0.80\ V$$

$$\mathbf{Sn(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Sn^{2+}(aq)}$$

$E°_{cell} = E°_{cathode\ (reduction)} - E°_{anode\ (oxidation)}$

$E°_{cell} = E°_{Ag} - E°_{Sn} = 0.80 - (-0.14) = \mathbf{0.94\ V}$

Nernst equation

The electrode potential depends on the temperature and electrolyte concentration.

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{red}}{a_{ox}}$$

In the case of solid phase (metal) the concentration is unit:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

or

$$2.3\frac{RT}{F} = 0.059 \text{ (at 298.15 K)}$$

$$E = E^\circ + \frac{0.059}{n} \log [M^{n+}]$$

Sample Problem 3: Determine the electrode potential of the zinc electrode; electrolyte concentration is 0.5 mol/l at 0 ° C.

$E = E^\circ + RT / (zF) * \ln c$ = -0.76 + [8.314 * 273.15 / (2 * 9.65*10^4)]* ln0.5 = -0.763 + (-1574.17)/193000 = -0.77 (V)

Sample Problem 4: What voltage will produce an electrochemical cell consisting of beryllium electrode immersed in the electrolyte Be^{2+} (c=0.01 mol/l) and a silver electrode immersed in the electrolyte Ag^+ (c=0.05 mol/l) at 10 ° C?

Be: $E_1 = E^\circ + RT / (z F) * \ln c$ = -1.85 + [8.314 * 283.15 / (2 * 9.65*10^4)] * ln 0.01 = -1.90 V

Ag: $E_2 = E^\circ + RT / (zF) * \ln c$ = 0.80 + [8.314 * 283.15 / (1 * 9.65*10^4)] * ln 0.05 = 0.73 V (greater potential than Be => reduction => cathode)

U = $E_{cathode}$ - E_{anode} = 0.73 – (-1.90) = **2.63 V**

Nernst equation and equilibrium constant

The equilibrium constant specifies the range of the electrochemical reaction (if the *K* value is large, the reaction takes place extensively). The EMF of the cell may be used to calculate the equilibrium constant for the cell reaction. Consider the following redox reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

$$K = \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$$

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

$$([Zn(s)] = 1, [Cu(s)] = 1)$$

$$E = E° - \frac{RT}{nF} \ln \frac{a_{red}}{a_{ox}} \Rightarrow E = E° - \frac{RT}{nF} \ln \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$$

At equilibrium, the electrode potentials of the two electrodes become equal so that EMF of the cell is zero (E = 0).

$$E° = \frac{RT}{nF} \ln K$$

Gibbs Free Energy and Electrical Work

The Gibbs free energy is the amount of "free" or "useful" energy available to do work (this maximum can be attained only in a completely reversible process).

For a spontaneous redox reaction $\Delta G < 0$ and $E_{cell} > 0$.

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

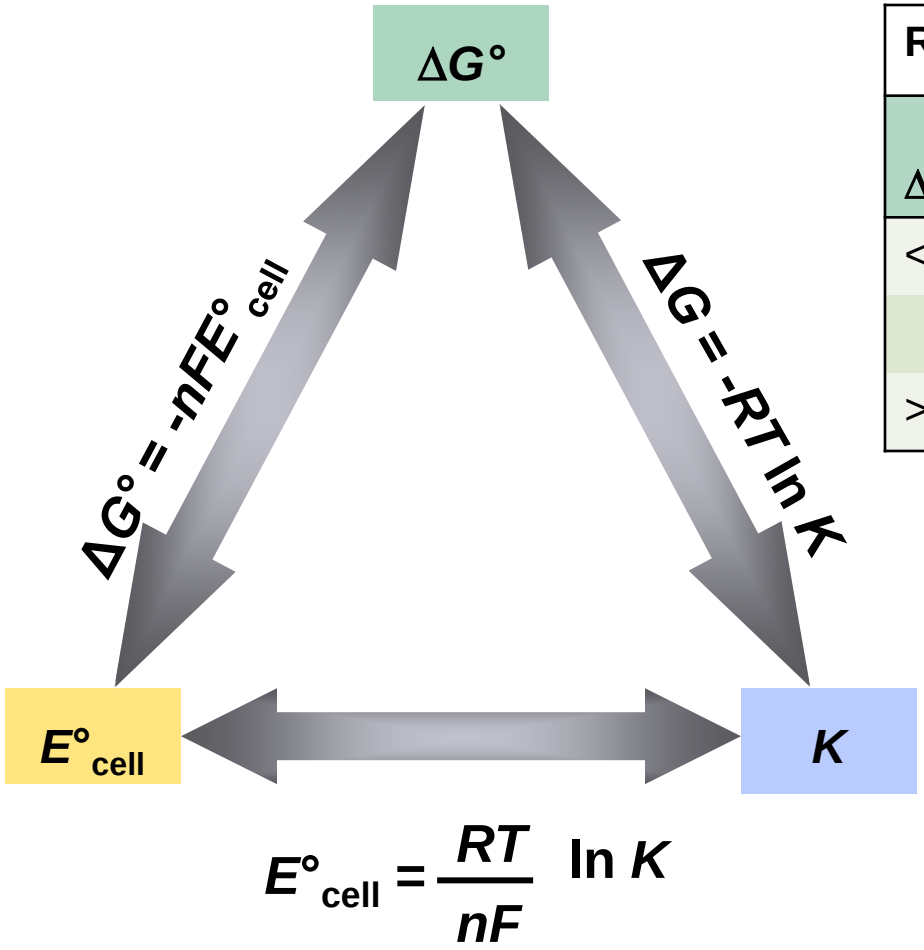
Under standard conditions $\Delta G^\circ = -nFE^\circ$

$$\boxed{E^\circ = \frac{RT}{nF} \ln K}$$

$$\Delta G^\circ = -nF \frac{RT}{nF} \ln K$$

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

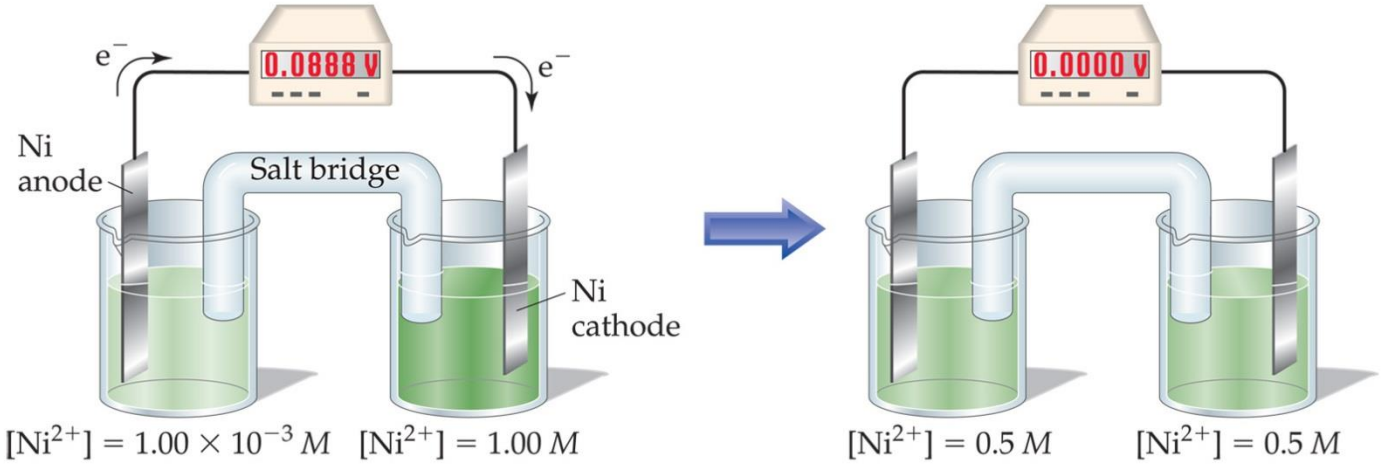
The interrelationship of $\Delta G°$, $E°_{cell}$, and K.



Reaction Parameters at the Standard State			
$\Delta G°$	K	$E°_{cell}$	Reaction at standard-state conditions
< 0	> 1	> 0	spontaneous
0	1	0	at equilibrium
> 0	< 1	< 0	nonspontaneous

Concentration Cells

- Concentration cell uses the same electrodes and electrolytes but the concentration of electrolytes is different.
- Therefore, as long as the concentrations of electrolytes are different, E will not be 0 and the cell can do work.



oxidation

$Ni(s) \rightarrow Ni^{2+}(aq, 0{,}001\ M) + 2e^-$

reduction

$Ni^{2+}(aq, 1{,}0\ M) + 2e^- \rightarrow Ni(s)$

overall cell reaction

$Ni^{2+}(aq, 1{,}0\ M) \rightarrow Ni^{2+}(aq, 0{,}1\ M)$