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CHEMISTRY II

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ELECTROCHEMISTRY I: BASIC CONCEPTS

Contents

Introduction
What is Electrochemistry?
Where can we find electrochemical processes?

Redox Equations
Half-Reactions
Rules for Assigning Oxidation numbers
Balancing redox equations
Examples

Electrochemical cells
How does an electrochemical cell work?
Galvanic and Electrolytic cells
Cell Notation
Standard Reduction Potentials
Examples

Spontaneity of redox reactions and equilibrium constants
Spontaneity of Redox Reactions
Relationships among E^0, DG^0, and K

The Nernst Equation
The effect of concentration on cell emf: The Nernst Equation
Concentration Cells
Examples

What is Electrochemistry?

Electrochemistry *is the branch of chemistry that deals with the interconversion of electrical energy and chemical energy*

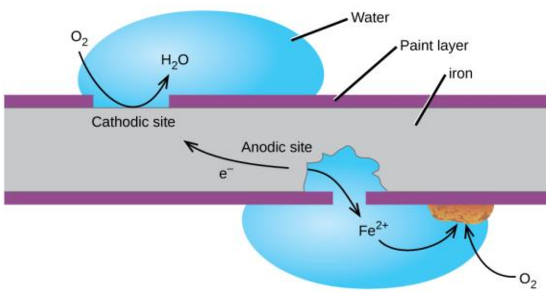
↓

Electrochemical processes are redox (oxidation-reduction) reactions in which the energy released by a spontaneous reaction is converted to electricity or in which electrical energy is used to cause a nonspontaneous reaction to occur.

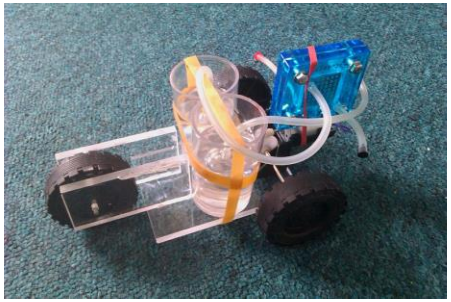
Chemical Energy

Electrical Energy

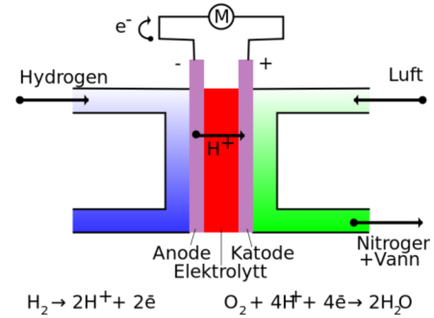
Where can we find electrochemical processes?



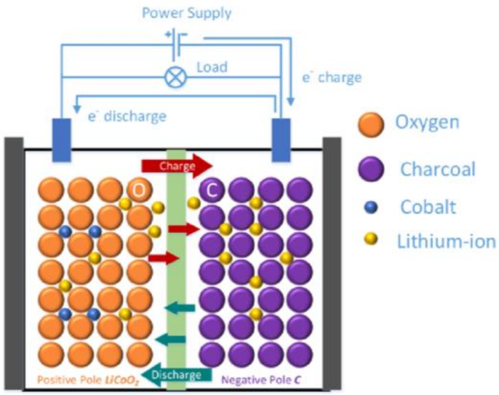
Metal ***Corrosion***



Generation of Energy: ***Fuel cells***



Storage of Energy: ***Batteries***



Half-Reactions

Electrochemical reaction: *involves electron transfer*

$$Zn\ (s) + 2Ag^{+}\ (aq) \longrightarrow Zn^{2+}\ (aq) + 2Ag\ (s)$$

Half-reactions

Oxidation reaction

It takes place when an element **donates electrons** and the oxidation number increases

$$\underset{\textbf{Reductant}}{\boxed{Zn\ (s)}} \longrightarrow Zn^{2+}\ (aq) + 2e^-$$

Reduction reaction

I takes place when an element **accepts electrons** and the oxidation number decreases

$$\underset{\textbf{Oxidant}}{\boxed{Ag^{+}\ (aq)}} + 1e^- \longrightarrow Ag\ (s)$$

Rules for Assigning Oxidation numbers

1. The oxidation state of any **neutral element** in its *naturally occurring state* is **zero.** Examples: He, Na, Cl_2, O_2

2. The oxidation number of a **monoatomic ion** is that ion's actual charge. Examples: K^+ is +1

3. The oxidation number of **F** is always -1.

4. The oxidation number of **oxygen** is **usually –2**. In peroxides H_2O_2 and O_2^{2-} is **–1**.

5. The oxidation number of **hydrogen** is **+1** *except* when it is **bonded to metals** (compounds called *hydrides*) in binary compounds. In these cases, its oxidation number is **–1**.

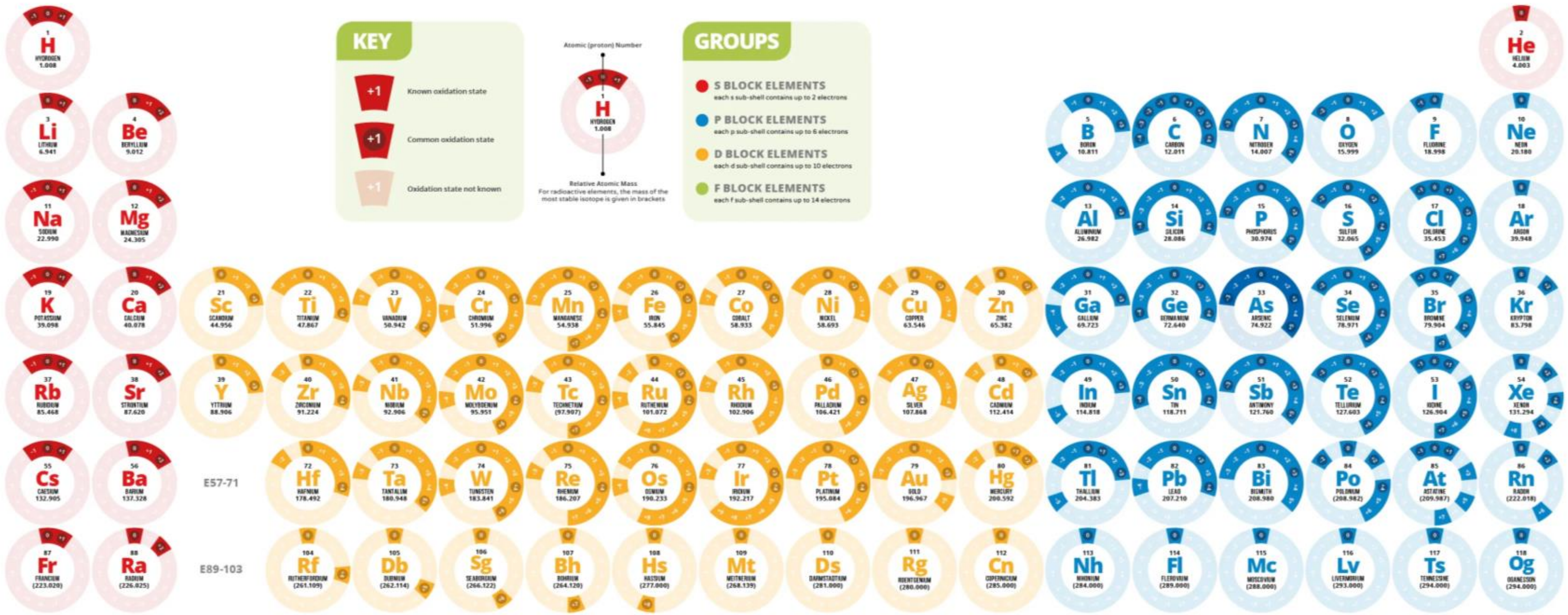
6. Oxidation numbers do not have to be integers. Example: Oxidation number of O in the superoxide ion, O_2^-, is **-½**.

7. The sum of the oxidation numbers of all of the atoms in a neutral compound is 0.

8. The sum of the oxidation numbers in a polyatomic ion is equal to the charge of the ion. Example: in the sulfate ion, SO_4^{2-}, the oxidation numbers of the sulfur and the oxygens add up to 2-. The oxygens are -2 each, and the sulfur is +6.

Oxidation numbers: Periodic Table

Noble Gases



Alkaline Metals

Alkaline Earth Metals

Boron family

Carbon family

Nitrogen family

Chalcogens

Halogens

Balancing Redox Equations

The **ion-electron method** to balance reactions in **acidic** medium:

Step 1. Write the unbalanced equation for the reaction in ionic form.

Step 2. Separate the equation into two half-reactions.

Step 3. Balance the atoms other than O and H in each half-reaction separately.

Step 4. Add H_2O to balance the O atoms and H^+ to balance H atoms.

Step 5. Add electrons to one side of each half-reaction to balance the charges. If necessary, equalize the number of electrons in the two half-reactions by multiplying one or both half-reactions by appropiate coefficients.

Step 6. Add the two-half reactions together and balance the final equation by inspection. The electrons on both sides must cancel.

Step 7. Verify that the equation contains the same types and numbers of atoms and the same charges on both sides of the equation.

The **ion-electron method** to balance reactions in **basic** medium:

Step 4-5. For every H^+ ion we would add an equal number of OH^- ions to both sides of the equation. Where H+ and OH- appeared on the same side of the equation, we would combine the ions to give H_2O.

How does an electrochemical cell work?

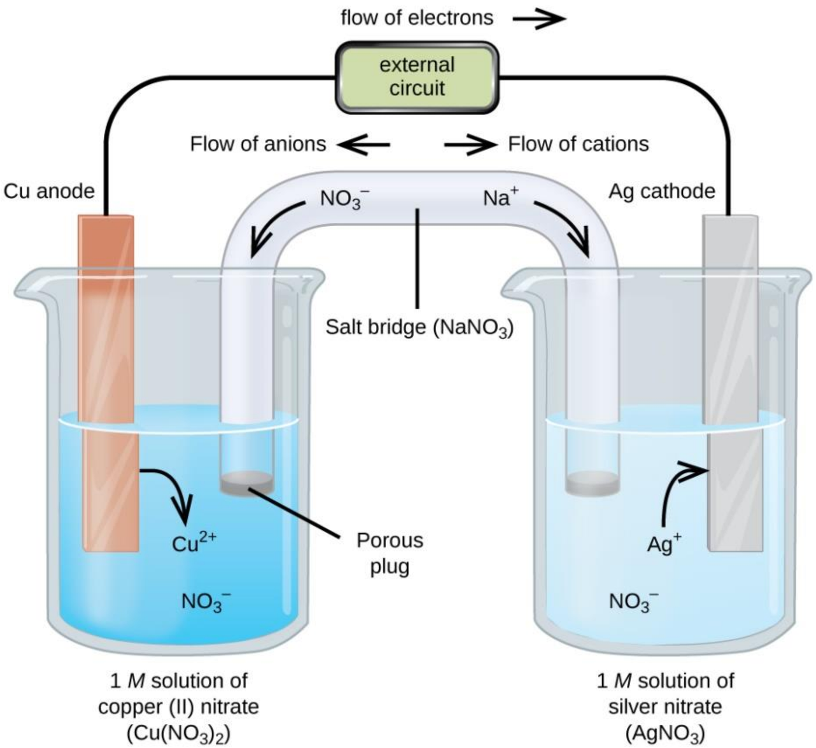
An electrochemical cell *is the experimental aparatus for generating electricity through the use of an spontaneous redox reaction:* ***Galvanic cell*** *or* ***Voltaic cell***

Components of a cell

Electrolyte: solution containing ions

Electrodes:
- **ANODE**: Oxidation process
- **CATHODE**: Reduction process

Salt bridge



Galvanic cell

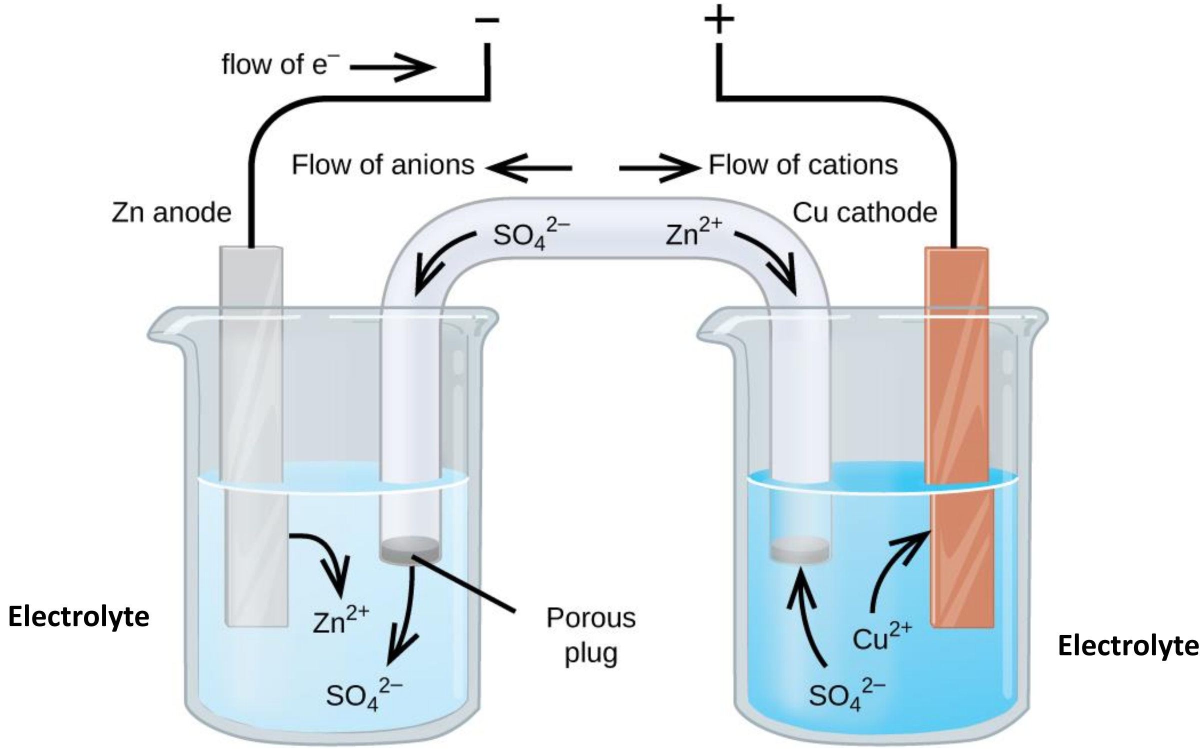
Spontaneous redox reaction ⇒ <u>produces</u> electric current
Cathode: + Pole
Anode: - Pole

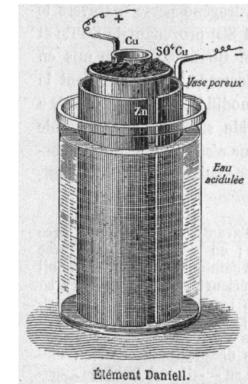
Electrolytic cell

Non-Spontaneous redox reaction ⇒ <u>consumes</u> electric current
Cathode: - Pole
Anode: + Pole

Galvanic cell

DANIELL CELL





ANODE

$$Zn \rightarrow Zn^{2+} + 2e^-$$

Oxidation

$$E_{Zn^{2+}/Zn} = -0.763\ V$$

Redox Reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

$\Delta G < 0$ ⟶ **Spontaneous**

CATHODE

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Reduction

$$E_{Cu^{2+}/Cu} = +0.34\ V$$

Cell Notation

1. The **anode** is represented to the **left** side of the diagram.
2. The **cathode** is represented to the **right** side of the cell diagram.
3. El **boundary between two cell compartments** (salt bridge) is represented by a **double vertical line (‖).**
4. The species in **water solution** are placed on **both sides of the double vertical line.**
5. The **boundary between two phases** within the same half-cell is represented by a **single vertical line (|).**
6. The different **species** in the **same solution** are separated by a **coma.**

e^- Flow $\longrightarrow$

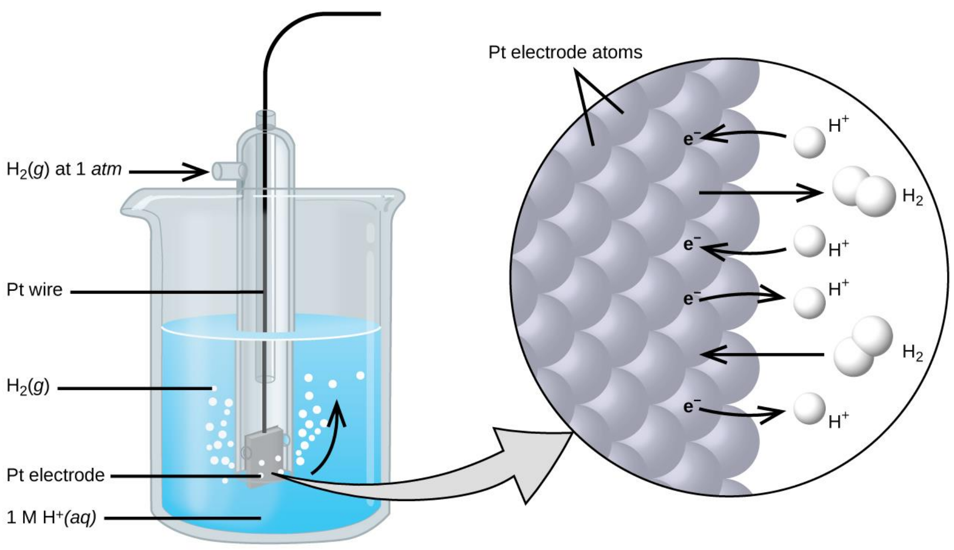
Anode $Zn\,(s) \mid Zn^{2+}(ac) \parallel Cu^{2+}(ac) \mid Cu\,(s)$ Cathode

Half-cell oxidation — Salt Bridge — Half-cell reduction

Standard Reduction Potentials

Standard Hydrogen Electrode (SHE):

The standard hydrogen electrode is used as **reference electrode to measure and tabulate the potentials** of the redox half-reactions.



Reduction reaction

$$2H^+(1M) + 2e^- \rightarrow H_2(1\ \ atm)$$

$$E^0_{2H^+/H_2} = 0\ \ V$$

Standard conditions: C = 1 M
P = 1 atm

Standard Reduction Potentials

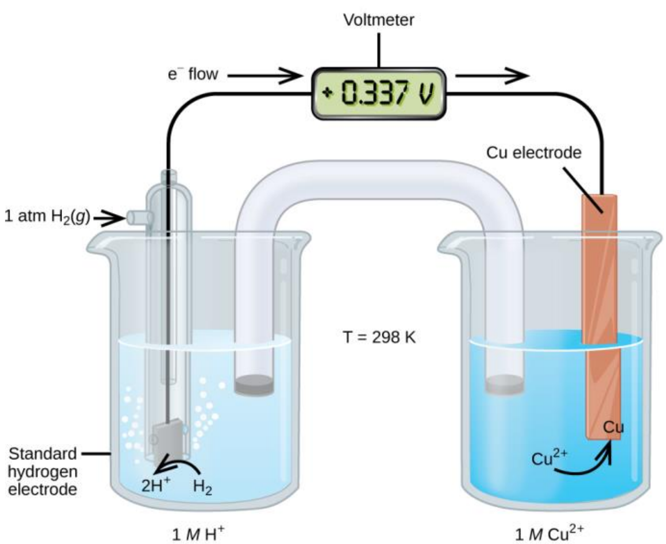
Measurement of the Standard Electrode Potentials

- Measured in concentrations of 1M.
- Expressed as reduction potentials.
- The difference in electrical potential between the anode and the cathode is called standard cell potential E°.

$$\boxed{E^0_{cell} = E^0_{cathode} - E^0_{anode}}$$

Standard cell potential

Example:



$$Anode \quad Cu \rightarrow Cu^{2+}(1\,M) + 2\,e^- \quad -E^0_{Cu^{2+}/Cu} = ?$$

$$Cathode \quad 2\,H^+\,(1\,M) + 2\,e^- \rightarrow H_2 \quad +E^0_{H^+/H_2} = 0\text{ V}$$

$$Overall\ reaction \quad Cu + 2\,H^+\,(1\,M) \rightarrow Zn^{2+}(1\,M) + H_2$$

$$E^0 = -0.34\,V$$

$$E^0 = E^0_{H^+/H_2} - E^0_{Cu^{2+}/Cu} \quad (sum\ of\ the\ half-cell\ reactions)$$

$$-0.34 = 0 - E^0_{Cu^{2+}/Cu}$$

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

Standard potential of the Cu electrode

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Standard Reduction Potentials

The strongest oxidizing agent

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathscr{E}°$ (V)	Half-Reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

The strongest reducing agent

Standard Reduction Potentials: Considerations

- The reactions are **reversible** (oxidation half-reactions)
- The **sign of E^0** for the oxidation reactions (i.e. for the reversed reactions).
- Variations in the **stoichiometric coefficients do not affect the value of E^0**.
- The **more positive (E^0)** the greater the tendency for the substance **to be reduced (more cathodic character**).
- The **more negative (E^0)** the greater the tendency for the substance **to be oxidized** (**more anodic character**).

Spontaneity of Redox Reactions

Relationship among E⁰, DG⁰, and K

The measured emf is the maximum voltage that the cell can achieve.

$$w_{\max} = w_{ele} = -nFE_{cell}$$

Specifically, the change in free energy (DG) represents the maximum amount of useful work that can be obtained from a reaction.

$$\Delta G = w_{\max}$$

So we can write:

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

Faraday constant:

$$F = 96500\ C/mol$$

For reactions in which reactants and products are in their standard states:

$$\boxed{\Delta G^0 = -nFE^0_{cell}}$$

The free energy change for a reaction is related to its equilibrium constant as follows:

$$\Delta G^0 = -RT\ln K$$

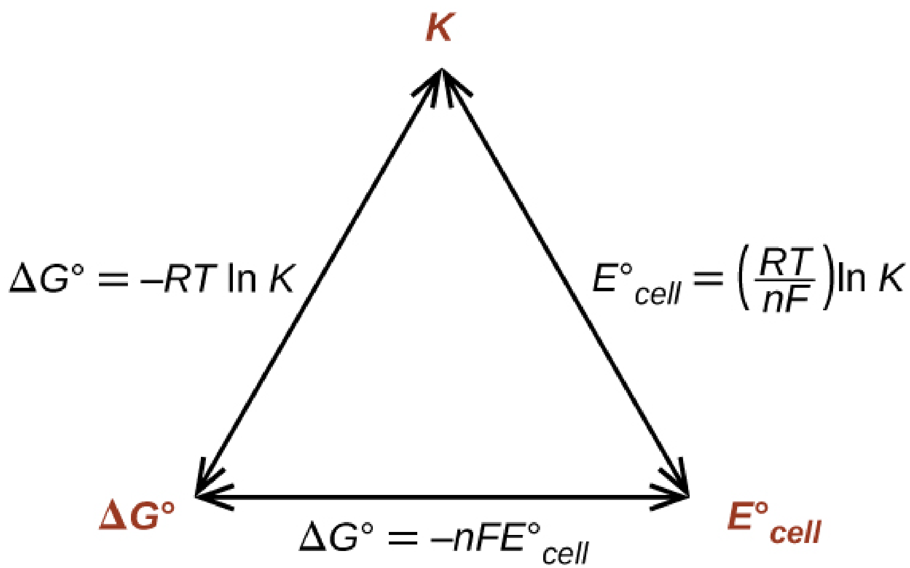
Therefore, if we combine equations we obtain:

$$-nFE^0_{cell} = -RT\ln K$$

Solving for the potential:

$$\boxed{E^0_{cel} = \frac{RT}{nF}\ln K}$$

Relationships among E^0, ΔG^0, and K



ΔG^0	K	E_{cell}^0	Spontaneity
< 0	> 1	> 0	Spontaneous
0	1	0	At equilibrium
> 0	< 1	< 0	Non-spontaneous

The Effect of Concentration on Cell emf: The Nernst Equation

Redox reaction:

$$aA + bB \rightarrow cC + dD$$

Under conditions that are not standard sate:

$$\Delta G = \Delta G^0 + RT \ln Q$$

Considering:

$$\Delta G = -nFE \quad and \quad \Delta G^0 = -nFE^0$$

The equation can be expressed as:

$$-nFE = -nFE^0 + RT \ln Q$$

Dividing the equation through by –nF we get:

$$\boxed{E = E^0 - \frac{RT}{nF} \ln Q}$$

Nernst Equation

At 298 K and using the base-10 logarithm of Q:

At equilibrium, there is no net transfer of electrons, so E = 0 and Q = K

$$E = E^0 - \frac{0,0592}{n} \log Q$$

Concentration cells

*In a **concentration cell**, the two electrodes are identical except for their concentration.*

Anode $Zn\,(s)\,|\,Zn^{2+}\,(0.1\ M)\,\|\,Zn^{2+}\,(1\ M)\,|\,Zn\,(s)$ Cathode

Anode (Oxidation)

$Zn\,(s) \longrightarrow Zn^{2+}\,(0.1\ M) + 2e^-$

Cathode (Reduction)

$Zn^{2+}\,(1.0\ M) + 2e^- \longrightarrow Zn\,(s)$

Overall reaction

$$\boxed{Zn^{2+}\,(1.0\ M) \longrightarrow Zn^{2+}\,(0.1\ M)}$$

The Nernst equation at 25 °C

$$\boxed{E = E^\circ - 0.0257\ V/2\ \ln [Zn^{2+}]_{diluted}/[Zn^{2+}]_{concentrated}}$$

$$E = 0 - 0.0257\ V/2\ \ln 0.10/1.0 = 0.0296\ V$$

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Slide 3:

- Chemical Energy image: Free Nature Stock in Seasonal, CC0 1.0, https://negativespace.co/camp-fire-flames-background/.
- Electrical Energy image: Royalty free photo, CC0 1.0, https://www.pickpik.com/ball-shaped-blur-bright-bulb-close-up-dark-100509.

Slide 4:

- Metal corrosion (chains): PxHere, CC0 1.0, https://pxhere.com/es/photo/678867.
- Fuel cell reaction: Bitjungle, CC BY-SA 3.0, https://commons.wikimedia.org/wiki/File:Fuel_cell_NO.svg.
- Fuel cell model car: matthew venn from london, uk, CC BY-SA 2.0, https://commons.wikimedia.org/wiki/File:Fuel_Cell_Model_Car.jpg.
- Battery: Martin Brown, PDM 1.0, https://nara.getarchive.net/media/electric-motor-electric-vehicle-controller-battery-charger-transmission-cutaway-212f6c.
- Battery reaction: Dewang Chen, Xiaoyu Zheng, Ciyang Chen, and Wendi Zhao, CC BY 4.0, https://www.researchgate.net/figure/The-lithium-ion-battery-working-principle-diagram_fig2_365377442.

Slides 4 (metal corrosion reaction), 9, 10, 12, 13, 17:

- Chemistry 2e. Paul Flowers, University of North Carolina at Pembroke, Klaus Theopold, University of Delaware, Richard Langley, Stephen F. Austin State University, William R. Robinson, Purdue University. 2019, Rice University, https://openstax.org/details/books/chemistry-2e.

Slide 7:

- Periodic table: Compound Interest, CC BY 4.0, https://commons.wikimedia.org/wiki/File:The-Periodic-Table-Of-Oxidation-States-2016.webp.

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