

Chapter 20 Electrochemistry

Electrochemistry

- **Electrochemistry:** study of the relationship between chemical change and electrical energy
- Investigated through use of **electrochemical cells:** that incorporate oxidation-reduction (or redox reaction) to produce electrical energy

Electrochemistry

- Thermodynamic principles explain how cells work
- Whether an electrochemical process releases or absorbs energy, it always involves *movement of electrons from one chemical species to another in a redox reaction.*
- Let's review redox terminology!

Review

A redox reaction involves a change in oxidation numbers.

Oxidation: loss of electrons

Reduction: gain of electrons

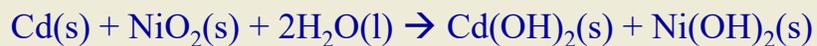
Oxidizing agent: causes oxidation of another by accepting e^- from it

Reducing agent: causes reduction by giving e^-

Reduction-oxidation always occurs in pairs and the number of electrons gained by the oxidizing agent always equals the number lost by the reducing agent.

Example

What is being *oxidized* and *reduced* in the following:



Overview of Electrochemical Cells

Two types of cells based on general thermodynamics:

1. **Voltaic cell** (or galvanic cell): uses a spontaneous reaction ($\Delta G < 0$) to generate electrical energy (flashlights, CD player, car)
2. **Electrolytic cell**: uses electrical energy to drive a nonspontaneous reaction ($\Delta G > 0$) (electroplating)

Overview of Electrochemical Cells

Two **electrodes** (conduct electricity between cell and surroundings) are dipped into **electrolyte** (mixture of ions, usually in aqueous solution) that are involved in the reaction or that carry the charge.

- Oxidation: **anode**
- Reduction: **cathode**



Voltaic or Galvanic Cells

- **Reaction of zinc metal with Cu^{2+} solution**
 - Electrons are transferred but system does not generate electrical energy (*oxidizing reagent and reducing agent are in physical contact*).
 - If half-reactions are physically separated and connected by external circuit, electrons are transferred by travelling through the circuit, producing an *electric current*.
 - *Separation* of half-reactions is key to a **voltaic cell**.

Microsoft Illustration

- Oxidation (anode):** Zn metal bar immersed in a Zn^{2+} electrolyte (ZnSO_4). Zn bar conducts released electrons *out* of its half-cell.
- Reduction (cathode):** Cu metal bar immersed in Cu^{2+} electrolyte (CuSO_4). Cu conducts electrons *into* its half-cell.
- Electrode charges are determined by *source of electrons and direction of electron flow*. (In any voltaic cell, the anode is - and the cathode +.)
- Uses a *spontaneous* reaction ($\Delta G < 0$) to generate electrical energy.



LHS

- oxidation
- anode
- -ve charge
- mass of Zn rod decreases
- $[\text{Zn}^{2+}]$ increases
- $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

RHS

- reduction
- cathode
- +ve charge
- mass of Cu rod increases
- $[\text{Cu}^{2+}]$ decreases
- $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$

Electrons flow from the zinc rod to the copper rod and the voltmeter registers +1.10 V when switch is first closed.

Voltaic or Galvanic Cells

- Two parts are connected by a **salt bridge**
 - Tube containing a concentrated solution of electrolyte (KNO_3 , KCl) which allows ions of electrolyte to migrate
- What would happen if no salt bridge? If only a wire, a few electrons pass, but then current stops
 - **Right-hand becomes – because of the transfer of e^- into it**
 - **Left-hand becomes + because e^- leave**
 - **This would prevent any further transfer of electrons.**
 - **Adding a salt bridge allows the two half-cells to lose their excess charge and permits more electrons to flow**

How Does a Voltaic Cell Work?

- By using a light bulb or voltmeter we can see that the Zn/Cu^{2+} cell generates electrical energy but *why*?
 - *Why do the electrons flow in the direction shown?*
 - *What is the driving force?*



How Does a Voltaic Cell Work?

- *Spontaneous reaction occurs due to different abilities of metals to give up their electrons and ability of electrons to flow through circuit.*
 - Electrons flow from anode to cathode because of a difference in *electrical potential energy*
 - Higher in anode than in cathode



Cell Potential

- Difference in potential energy per electrical charge between two electrodes is measured in *volts*
- $1 \text{ V} = 1 \text{ J C}^{-1}$
- Electrical energy can do work and is proportional to the *difference in electrical potential between the two electrodes.*
- Difference is measured with a *voltmeter*
 - Reading is known as **cell potential (E_{cell})** or electromotive force (emf) or voltage of the cell
 - The “pull” or driving force on the electrons.

Cell Potential

- A Galvanic cell has a *positive* voltage when the cell reaction is *spontaneous*.

$$E_{\text{cell}} > 0$$

- More positive E_{cell} is, more work cell can do and farther reaction proceeds to right as written.

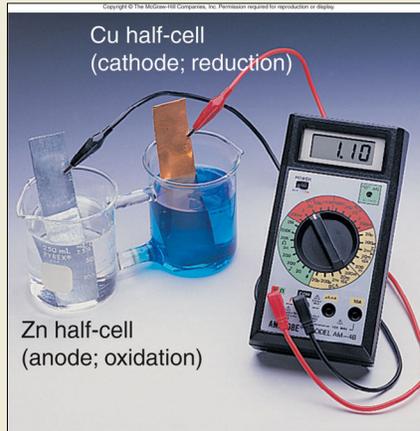


$$E_{\text{cell}} > 0 \text{ for a spontaneous process}$$

Standard Cell Potential

- A cell potential measured under standard state conditions is called the standard cell potential (E°_{cell})
 - 298 K, 1 atm for gases, 1 M solns, pure solids
- Sum of half-cell potential E°_{ox} of anode and half-cell potential E°_{red} of cathode is the cell potential, E°_{cell}

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{ox}} + E^{\circ}_{\text{red}}$$



Standard Hydrogen Electrode

- No way to measure actual potential of individual electrode
 - Only measure E_{cell} as every cell involves two half-cells
- If one electrode is *assigned* a standard potential (or reference), others can be reported by comparison

Standard hydrogen electrode (SHE)



- Assigned a potential of zero volts
- Potentials of all other electrodes are reported relative to it
- Pt electrode in 1 M strong $\text{H}^+(\text{aq})$ with $\text{H}_2(\text{g}, 1\text{atm})$ bubbles

Selected Standard Electrode Potentials (298 K)

Half-Reaction	E°/V
$\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$	+2.87
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{MnO}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+0.96
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{g}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$	+0.40
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{N}_2(\text{g}) + 5\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons \text{N}_2\text{H}_5^+(\text{aq})$	-0.23
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
$\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li}(\text{s})$	-3.05

More positive $E^\circ_{\text{half-cell}}$, more readily half-reaction occurs.

Calculation of standard cell emfs

For a **spontaneous** reaction $E_{\text{cell}} > 0$ and the half-cell with the **more positive** standard **reduction potential** is the **cathode**.

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Calculation of Cell Potentials

- E° values are for *reduction* half-reactions and the sign must be reversed when used for an oxidation half-reaction
- Changing stoichiometric coefficients does not change value of E° (*intensive potentials*)



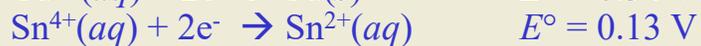
Example

Determine the cell reaction and the cell potential for a cell based on the following half-reactions.



Example

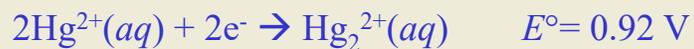
A cell can be prepared from copper and tin. What is the E°_{cell} for the cell that forms from the following half-reactions?



- A. 0.47 V
- B. 0.21 V
- C. -0.21 V
- D. -0.47 V
- E. 0.42 V

Example

What is the E°_{cell} for the cell represented by the combination of the following half-reactions?



- A. -0.18 V
- B. 0.18 V
- C. 1.28 V
- D. 1.66 V
- E. 2.12 V

Example

Select the strongest oxidizing agent among the following:



- A. $\text{Cr}^{2+}(\text{aq})$
- B. $\text{Fe}(\text{s})$
- C. $\text{Fe}^{2+}(\text{aq})$
- D. $\text{Sr}^{2+}(\text{aq})$
- E. $\text{Co}^{2+}(\text{aq})$

Example

A galvanic cell consists of an Fe electrode in a 1.0 M $\text{Fe}(\text{NO}_3)_2$ solution and a Ag electrode in a 1.0 M AgNO_3 solution. Calculate the standard emf of this cell at 25 °C.

Example

Is the following reaction spontaneous as written?



If not, write the equation for the spontaneous reaction and calculate E°_{cell} .

Example

A voltaic cell houses the reaction between aqueous bromine and zinc metal.



$$E^\circ_{\text{cell}} = 1.83 \text{ V}$$

Calculate E°_{bromine} , given $E^\circ_{\text{zinc}} = -0.76\text{V}$.

Notation for a Voltaic Cell

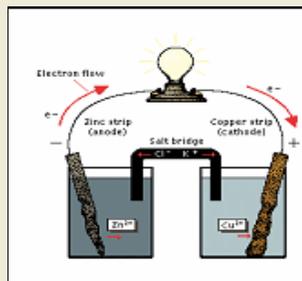
Line notation for Zn/Cu²⁺ cell



anode | anode electrolyte || cathode electrolyte | cathode

Key parts

1. Anode (oxidation) to the left
2. Vertical line: phase boundary (comma if same phase)
3. Double vertical line separates half-cell (salt bridge)



Example

A voltaic cell prepared using aluminum and nickel has the following cell notation.



Which of the following reactions occurs at the anode?

- A. $\text{Al}(s) \rightarrow \text{Al}^{3+}(aq) + 3e^{-}$
- B. $\text{Al}^{3+}(aq) + 3e^{-} \rightarrow \text{Al}(s)$
- C. $\text{Ni}(s) \rightarrow \text{Ni}^{2+}(aq) + 2e^{-}$
- D. $\text{Ni}^{2+}(aq) + 2e^{-} \rightarrow \text{Ni}(s)$

Example

A voltaic cell prepared using aluminum and nickel has the following cell notation.



Which of the following represents the correctly balanced spontaneous reaction equation for the cell?

- A. $\text{Ni}^{2+}(aq) + \text{Al}(s) \rightarrow \text{Al}^{3+}(aq) + \text{Ni}(s)$
- B. $3\text{Ni}^{2+}(aq) + 2\text{Al}(s) \rightarrow 2\text{Al}^{3+}(aq) + 3\text{Ni}(s)$
- C. $\text{Ni}(s) + \text{Al}^{3+}(aq) \rightarrow \text{Ni}^{2+}(aq) + \text{Al}(s)$
- D. $3\text{Ni}(s) + 2\text{Al}^{3+}(aq) \rightarrow 3\text{Ni}^{2+}(aq) + 2\text{Al}(s)$

Example

Write the notation for a voltaic cell that consists of one half-cell with a Cr bar in a $\text{Cr}(\text{NO}_3)_3$ solution, another half-cell with an Ag bar in an AgNO_3 solution, and KNO_3 salt bridge.

*Need to figure out which is the **anode** and which is the **cathode**!*

Gibbs Energy and Electrical Work

- Spontaneous reaction: $\Delta G < 0$
- Spontaneous electrochemical reaction:

$$E_{\text{cell}} > 0$$

$$\Delta G^\circ = -nFE^\circ$$

n = number of moles of electrons

F = Faraday = 96 485 C mol⁻¹ or 96 485 J V⁻¹ mol⁻¹

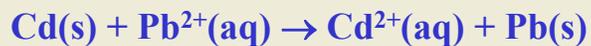
Example

Calculate ΔG° for the previous example
($E^\circ_{\text{cell}} = 1.54 \text{ V}$):

- A. -235 kJ
- B. -678 kJ
- C. -346 kJ
- D. -446 kJ
- E. -124 kJ

Example

Calculate the standard Gibbs energy change at
25 °C for the reaction



- A. -26.8 kJ
- B. -53.5 kJ
- C. -35.5 kJ
- D. -60.7 kJ
- E. -70.2 kJ

Calculation of Equilibrium Constants for Redox Reactions

- Electrochemical measurements provide data used to determine **thermodynamic parameters** and **equilibrium constants** for a wide variety of chemical changes.
- Direct method for determining K and ΔG° from E°_{cell}

$$\log(K) = \frac{nE^\circ}{0.0592} \text{ at } 25^\circ \text{C}$$

Example

When cadmium metal reduces Cu^{2+} in solution, Cd^{2+} forms in addition to copper metal. If $\Delta G^\circ = -143 \text{ kJ}$, calculate K at 25°C . What is E°_{cell} in a voltaic cell that uses this reaction?

$$F = \text{Faraday} = 96\,485 \text{ C mol}^{-1} \text{ or } 96\,485 \text{ J V}^{-1} \text{ mol}^{-1}$$

Relationship Between E°_{cell} , ΔG° , and K

E°_{cell}	ΔG°	K	Rxn Under Stand State Conditions
Positive	Negative	> 1	Spontaneous (favours products)
0	0	$= 1$	Favours reactants and products equally
Negative	Positive	< 1	Nonspontaneous (favours reactants)

Nernst Equation

- Cell need not operate at **standard state conditions**.
 - We can calculate potential of a cell in which some or all components are not in std states.
 - Need to understand how cell potential changes with concentration and/or temperature changes.

$$E = E^\circ - \frac{0.0592}{n} \log(Q)$$

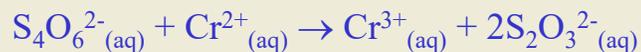
Example

Calculate the voltage produced by the cell at 25 °C:

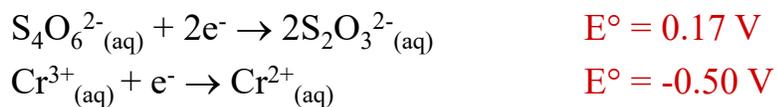


Example

For the oxidation-reduction reaction:



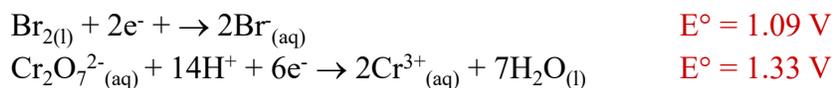
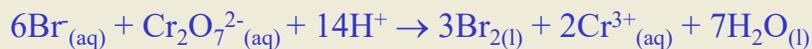
The appropriate half-reactions are



Balance redox reaction and calculate E°_{cell} & K at 25 °C.

Example

Use the standard reduction potentials below to calculate the equilibrium constant at 25 °C for the reaction:



- A. 1.1×10^{10}
- B. 3.4×10^{12}
- C. 5.6×10^8
- D. 2.1×10^{24}
- E. 5.6×10^{-10}

Electrolytic Cells

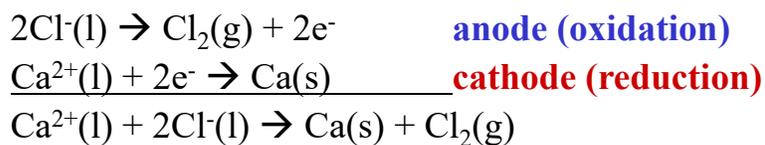
- Electrical energy from an external source drives a non-spontaneous reaction.



- This is *non-spontaneous* but we can make this process happen by supplying from an **external source** an electrical potential greater than E°_{cell} .

Electrolysis

- Non-spontaneous reaction is caused by the passage of an electric current through a solution
 - Used to decompose a compound into its elements
- Used to isolate metal or nonmetal from molten salt



Also used to prepare Na, Mg, Br₂, etc.

Table 17.2 The Price of Aluminum, 1855–1990

Date	Price of Aluminum (\$/lb)*
1855	\$100,000
1885	100
1890	2
1895	0.50
1970	0.30
1980	0.80
1990	0.74

- Al is the metal produced in greatest quantities by electrolysis.
 - Found in nature as *bauxite*
- Uses:** cans, foil, construction (windows, doors, mobile homes, gutters) and alloys

Quantitative Aspects of Electrolysis

- **Electroplating:** Uses electrolysis to deposit a thin layer of one metal on another metal in order to improve beauty or resistance to corrosion.
 - Chrome plating, bronzing, refining of copper
- **Faraday's Law of electrolysis:** *the amount of a substance produced at each electrode is directly proportional to the quantity of charge flowing through the cell (and molar mass)*

Faraday's Law of Electrolysis

“How much material will form as a result of a given quantity of current?” or “How much charge is needed to produce a given amount of material?”

Using Faraday's Law:

1. Balance the half-reaction to find the number of moles of electrons needed per mole of product.
2. Use Faraday constant ($F = 9.65 \times 10^4 \text{ C mol}^{-1} \text{ e}^-$) to find the charge.
3. Use the molar mass to find the charge needed for a given mass of product.

Stoichiometry of electrolysis

- To supply the correct amount of electricity, we need some means of finding the charge flowing through the cell.
- Cannot measure charge directly but *can* measure current (charge flowing per unit of time) in ampere (A)

$$1 \text{ ampere} = 1 \text{ coulomb/second or } A = C/s$$

- **Example:** How long does it take to produce 3.0 g of $\text{Cl}_2(\text{g})$ from the electrolysis of NaCl using a power supply with a current of 12 A?

Example

Calculate the number of grams of Al produced in 1.00 hr by the electrolysis of molten AlCl_3 if the electrical current is 10.0 A.

(1 hr = 3600 s and MM of Al = 27.0 g mol⁻¹)

- A. 1.27 g
- B. 2.56 g
- C. 3.00 g
- D. 3.36 g
- E. 4.78 g

Example

Calculate the mass of magnesium formed upon passage of a current of 60.0 A through $\text{MgCl}_{2(l)}$ for a period of 4.00×10^3 s. ($MM \text{ Mg} = 24.3 \text{ g mol}^{-1}$)

- A. 10.2 g
- B. 14.5 g
- C. 24.5 g
- D. 29.8 g
- E. 30.2 g

Example

How many seconds would be required to produce 50.0 g of Mg from $\text{MgCl}_{2(l)}$ if the current is 100.0 A?

- A. 1200 s
- B. 2300 s
- C. 3970 s
- D. 4090 s
- E. 6080 s