

Chapter 17: Electrochemistry

1.1 The scope of electrochemistry

Electrochemistry involves chemical phenomena associated with charge separation. Often this charge separation leads to charge transfer, which can occur homogeneously in solution, or heterogeneously on electrode surfaces. In reality, to assure electroneutrality, two or more charge transfer half-reactions take place, in opposing directions. Except in the case of homogeneous redox reactions, these are separated in space, usually occurring at different electrodes immersed in solution in a cell. These electrodes are linked by conducting paths both in solution (via ionic transport) and externally (via electric wires etc.) so that charge can be transported. If the cell configuration permits, the products of the two electrode reactions can be separated. When the sum of the free energy changes at both electrodes is negative the electrical energy released can be harnessed (batteries). If it is positive, external electrical energy can be supplied to oblige electrode reactions to take place and convert chemical substances (electrolysis).

1

17.1 Electrochemistry

Deals with chemical reactions that produce electricity and the changes associated with the passage of charge through matter.

Reactions involve electron transfer – oxidation/reduction (redox)

Common Electrical Terms

Quantity	Definition	Measure or Unit
Electric charge	Charge on a proton	$1.602 \times 10^{-19} \text{ C}$
Electric current	The movement of charge	ampere = $A = 1 \text{ C/s}$
Electric potential	The force trying to move the charge	volt = $V = \text{J/C}$
Electric field	The force acting upon other charges in the vicinity	

Table 17.1

Example: A typical AA alkaline battery is rated at 1.5 V. This means the electrical potential difference between the +/– terminals is 1.5 V. It is the chemical reactions in the battery that give rise to this difference.

2

Redox Recap

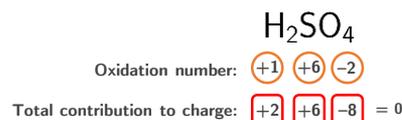
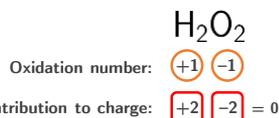
Oxidation number rules:

- 1.) Ox. # = 0 for an atom in pure, elemental state
- 2.) Ox. # = <charge> for monatomic ion: Ox. # = 2 for Ca^{2+}
- 3.) Sum of all Ox. #'s for atoms in polyatomic ion = charge on polyatomic ion
- 4.) Sum of all Ox. #'s = charge on species: H_2O Ox.(H) = 1, Ox(O) = -2

Element	Oxidation number	Exceptions
Fluorine	-1	
Group 1A or 2A metal	+1 or +2, respectively	
Hydrogen	+1	Any combination with a Group 1A or 2A metal to form a metal hydride. Examples: LiH and CaH_2 —the oxidation number of H is -1 in both examples.
Oxygen	-2	Any combination with something higher on the list that necessitates its having a different oxidation number (see rule 2 for assigning oxidation numbers). Examples: H_2O_2 and KO_2 —the oxidation number of O for H_2O_2 is -1 and for KO_2 is $-\frac{1}{2}$.
Group 7A (other than fluorine)	-1	Any combination with something higher on the list that necessitates its having a different oxidation number (see rule 2 for assigning oxidation numbers). Examples: ClF , BrO_2 , and IO_2 —the oxidation numbers of Cl, Br, and I are +1, +7, and +5, respectively. Remember that these exceptions do not apply to fluorine, which always has an oxidation state of -1 when it is part of a compound.

3

Assigning oxidation numbers



4

Redox terminology

Oxidation – the **loss** of electrons
 Reduction – the **gain** of electrons

OIL RIG – “oxidation is losing,
 reduction is gaining”

“Substance X undergoes oxidation.” – X lost electrons

“Substance Y was reduced.” – Y gained electrons

Oxidizing agent – the species that undergoes **reduction**

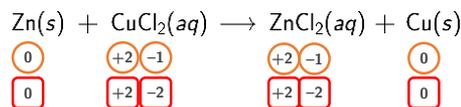
Reducing agent – the species that undergoes **oxidation**

“Substance Z is the oxidizing agent.” – Z gains electrons

(Think: Travel agent – allows someone *else* to travel)

5

5

Redox terminology applied

What was oxidized? Zn Oxidizing agent = CuCl₂

What was reduced? Cu²⁺ Reducing agent = Zn

What is the spectator ion? Cl⁻

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17.1 Balancing redox reactions

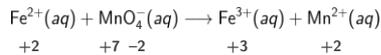
- 1.) Assign oxidation states to all atoms. Identify what is being oxidized and reduced.
- 2.) Separate overall reaction into two half-reactions
- 3.) Balance all atoms except H & O
- 4.) Balance O (by adding H₂O)
- 5.) Balance H (by adding H⁺)
- 6.) Balance charges (by adding e⁻)
- 7.) Make the number of e⁻ in both half reactions equal
- 8.) Combine both half-reactions canceling out terms
- 9.) If solution is basic, add enough OH⁻ to combine with all H⁺ (on left hand side) to make H₂O. Add same number of OH⁻ to right hand side.

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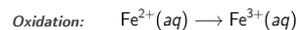
Example: Balancing redox reaction in acidic solution

- 1.) Assign oxidation states to all atoms. Identify what is being oxidized and reduced.



Fe is oxidized. Mn is reduced.

- 2.) Separate overall reaction into two half-reactions



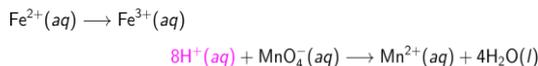
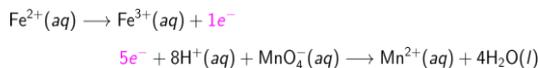
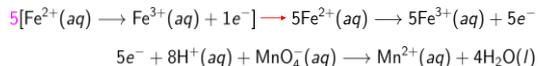
- 3.) Balance all atoms except H & O



Already balanced. Move to step 4.

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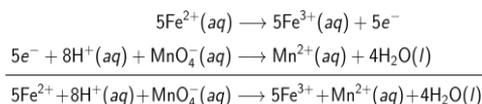
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Example: Balancing redox reaction in acidic solution4.) Balance O (by adding H₂O)5.) Balance H (by adding H⁺)6.) Balance charges (by adding e⁻)7.) Make the number of e⁻ in both half reactions equal

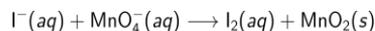
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Example: Balancing redox reaction in acidic solution

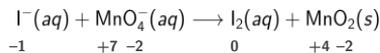
8.) Combine both half-reactions canceling out terms

9.) If solution is basic, add enough OH⁻ to combine with all H⁺ (on left hand side) to make H₂O. Add same number of OH⁻ to right hand side.Acidic solution
so skip step 9.

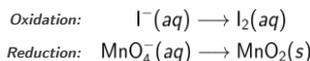
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Example: Balancing redox reaction in basic solution

1.) Assign oxidation states to all atoms. Identify what is being oxidized and reduced.

I⁻ is oxidized. Mn is reduced.

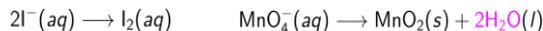
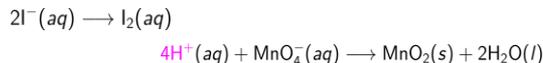
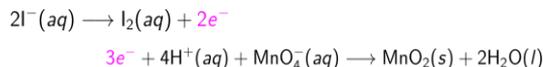
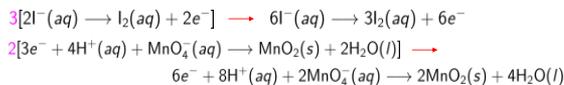
2.) Separate overall reaction into two half-reactions



3.) Balance all atoms except H & O



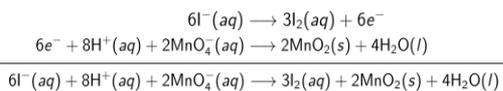
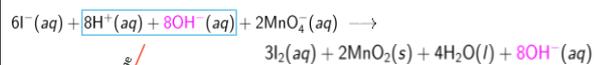
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Example: Balancing redox reaction in basic solution4.) Balance O (by adding H₂O)5.) Balance H (by adding H⁺)6.) Balance charges (by adding e⁻)7.) Make the number of e⁻ in both half reactions equal

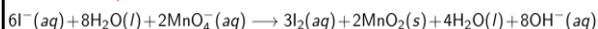
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Example: Balancing redox reaction in basic solution

8.) Combine both half-reactions canceling out terms

9.) If solution is basic, add enough OH^- to combine with all H^+ (on left hand side) to make H_2O . Add same number of OH^- to right hand side.

Combine

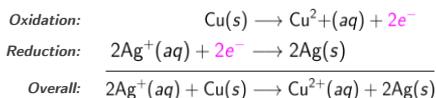


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17.2 Galvanic cell

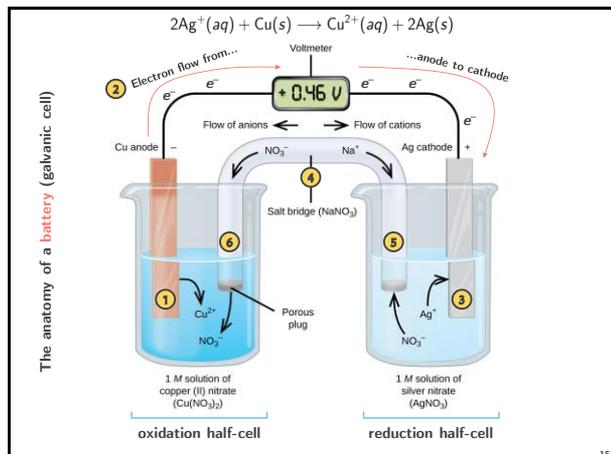
- Produces electricity (**electrical energy**) from spontaneous redox reactions (**chemical energy**)
- Also called "voltaic" cell



Electrons flow from copper solid to silver solution **spontaneously**.
Separate oxidation/reduction reactions; channel electrons through wires/circuits

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15

Galvanic cell anatomy

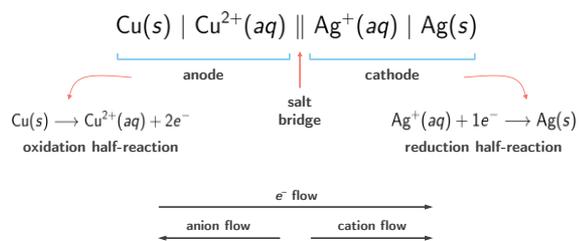
- 1 Oxidation takes place at the **anode (-)**. $\text{Cu} (\text{s})$ dissolves into $\text{Cu}(\text{NO}_3)_2$ solution. Anode **loses mass**.
 $\text{Cu} (\text{s}) \longrightarrow \text{Cu}^{2+} (\text{aq}) + 2\text{e}^-$
- 2 Electrons produced by oxidation reaction flows through wire (at particular voltage) to cathode. Electrons flow from **low to high** potential.
- 3 Reduction takes place at the **cathode (+)**. $\text{Ag}^+ (\text{aq})$ precipitates out of AgNO_3 solution and deposits on cathode. Cathode **gains mass**.
 $2\text{Ag}^+ (\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Ag} (\text{s})$
- 4 The NaNO_3 salt bridge contains a soluble salt. Necessary for **charge balance**.
- 5 Cathode half-cell experiences build-up of **negative charge** as it receives e^- . Salt bridge provides Na^+ to keep charge neutral at cathode.
- 6 Anode half-cell experiences build-up of **positive charge** as it loses e^- . Salt bridge provides NO_3^- to keep charge neutral at anode.

16

16

17.2 Cell Diagram

Shorthand notation is used to describe a galvanic cell.



Solution concentrations may also be written.



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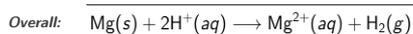
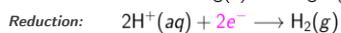
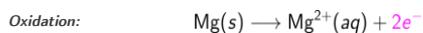
Electrodes

Active electrodes are directly involved in the redox reactions. They undergo either oxidation or reduction (they gain or lose mass).

Inert electrodes (such as Pt, Au, graphite, etc.) are chemically inactive. They only serve to allow current to flow, especially when species involved in reaction is poor conductor of electricity.

Example: $\text{H}_2(g)$ generation from solution

1. $\text{H}_2(g)$ generated from acidic aqueous solution (poor conductor).
2. Electrons are provided by an oxidation reaction (sacrificial e^{-} source).
3. The electrode at the cathode is not involved in the reduction reaction (inert).

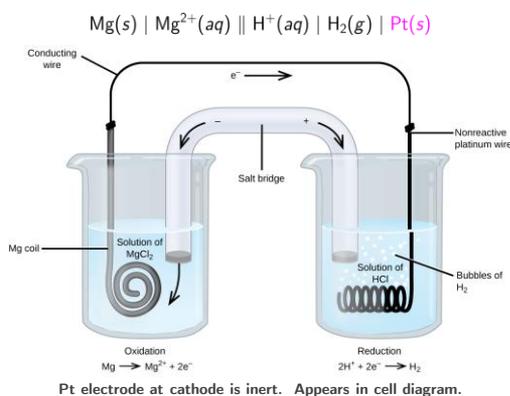


(see next slide)

18

18

Electrolysis of water



19

19

Example

Identify the cathode and anode in: $\text{Ni}(s) \mid \text{Ni}^{2+}(aq) \parallel \text{Ag}^{+}(aq) \mid \text{Ag}(s)$

Which electrode gains mass? Which one loses mass?

Cathode: Ag (s)

Anode: Ni (s)

Gains mass: Ag (s)

Loses mass: Ni (s)

20

20

Cell potential

- Electrons spontaneously flows from anode (low potential) to cathode (high potential)
- The difference in potentials is called the **cell potential** (E_{cell})

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

\uparrow \uparrow \uparrow
 cell potential reduction reduction
 (V) potential at potential at
 cathode (V) anode (V)

Standard cell potentials (E_{cell}°) are based on standard reduction potentials (E°) defined by the following conditions:

- solution concentration = 1 M
- gas pressure = 1 atm
- solids that are pure

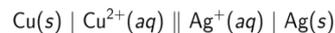
$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

21

21

Cell potential

As previously seen, electrons flow from Cu (low potential) to Ag (high potential) and gives a voltage of 0.46 V.



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

$$0.80 \text{ V} - 0.34 \text{ V} = 0.46 \text{ V}$$

How are *standard reduction potentials* defined?

Reduction potentials are *relative values*. Here, Cu has a reduction potential that is 0.46 V larger than Ag.

What if both half-cells were *identical* (in all aspects – pressure, concentration, temperature, etc.)? Cell potential = 0 V

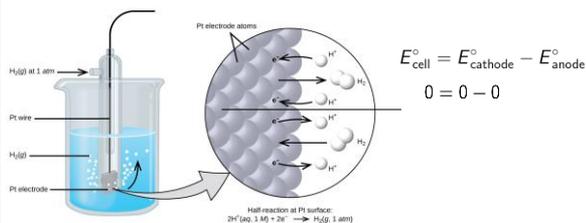
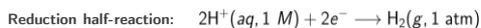
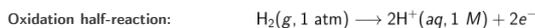
Standard hydrogen electrode (SHE) is the standard reference.

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22

Standard hydrogen electrode

Reduction potentials are referenced to the **standard hydrogen electrode** (SHE) which has a standard reduction of 0.00 V.



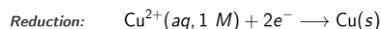
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23

Standard reduction potentials

Hook up a *different* half-cell to SHE to get standard reduction potential.

Example: What is the standard reduction potential of Cu^{2+} ? Note that electrons flow to Cu^{2+} meaning Cu^{2+} undergoes reduction.



Example: What is the standard reduction potential of Cu?

$$E_{\text{cell}}^{\circ} = E_{\text{cathode, Cu}}^{\circ} - E_{\text{anode, SHE}}^{\circ}$$

$$0.34 \text{ V} = E_{\text{cathode, Cu}}^{\circ} - 0$$

$$0.34 \text{ V} = E_{\text{cathode, Cu}}^{\circ}$$

24

24

Standard reduction potentials

Many standard reductions have been tabulated. Stronger oxidizing agents (those that more **easily gain** electrons) at top.

For a **spontaneous** galvanic cell...
Larger potentials (E°) occur at **cathode**.
Smaller potentials at **anode** (electrons flow from low \rightarrow high potential).

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}}$$

$$E^\circ_{\text{cell}} \begin{cases} + \text{ for spontaneous} \\ - \text{ for non-spontaneous} \end{cases}$$

Standard Reductions	E° (V)
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	+2.87
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	+1.50
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.09
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	+0.54
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.26
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.45
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{l})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.93
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04

See Table 17.2 for full list of reduction potentials

↑ Stronger oxidizing agents

25

25

E°_{cell} and ΔG°

Recall that for a spontaneous process: $E^\circ_{\text{cell}} > 0$
 $\Delta G^\circ < 0$
 $K > 1$

Related by:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

n = moles e^- transferred in redox reaction

$$F \text{ (Faraday's constant)} = \text{charge/mol of } \text{e}^- \\ = (\text{e}^- \text{ charge}) \times (\text{Avogadro's number}) \\ = (1.60 \times 10^{-19} \text{ C})(6.02 \times 10^{23} \text{ mol}^{-1}) \\ = 96,500 \text{ C/mol } \text{e}^- \\ = 96,500 \text{ J mol}^{-1} \text{ V}^{-1}$$

E°_{cell} = cell potential (in V)

ΔG° = free energy (in kJ mol⁻¹)

26

26

E°_{cell} and K

Recall that for a spontaneous process: $E^\circ_{\text{cell}} > 0$
 $\Delta G^\circ < 0$
 $K > 1$

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF} \right) \ln K \xrightarrow[\text{(std. temp.)}]{@25^\circ\text{C}} E^\circ_{\text{cell}} = \frac{0.0257 \text{ V}}{n} \ln K$$

R = gas constant (8.315 J mol⁻¹ K⁻¹)

T = temperature in K

n = moles e^- transferred (from balanced half-reactions reactions)

F = 96,500 J mol⁻¹ V⁻¹

K = equilibrium constant

E°_{cell} = cell potential (in V)

$$\text{In log form...} \\ E^\circ_{\text{cell}} = \frac{0.0592 \text{ V}}{n} \log K$$

27

27

ΔG° and K

Recall that for a spontaneous process: $E^\circ_{\text{cell}} > 0$
 $\Delta G^\circ < 0$
 $K > 1$

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

R = gas constant (8.315 J mol⁻¹ K⁻¹)

T = temperature in K

K = equilibrium constant

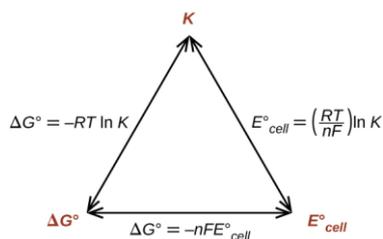
ΔG° = free energy (in kJ mol⁻¹)

28

28

E°_{cell} , ΔG° , and K

If any one of the values (E°_{cell} , ΔG° , and K) is known, either of the other two values can be determined.



29

29

 E°_{cell} and E_{cell}

Nernst Equation – relates E°_{cell} to E_{cell}

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

n = moles e^- transferred in redox reaction

$$F \text{ (Faraday's constant)} = 96,500 \text{ C/mol } e^- \\ = 96,500 \text{ J mol}^{-1} \text{ V}^{-1}$$

R = gas constant (in $\text{J mol}^{-1} \text{ K}^{-1}$)

T = in K

E_{cell} = cell potential (in V)

ΔG° = free energy (in kJ mol^{-1})

30

30

Concentration cell

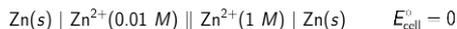
Galvanic cell under non-standard conditions – both half-cells have *different concentrations*

Example: Galvanic cell with half-cells with *identical electrodes* under standard conditions



$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V} \quad E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ = -0.76 - (-0.76) = 0$$

Example: Galvanic cell with half-cells with *identical electrodes and different concentrations* (at 25°C)



$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q = 0 - \frac{(8.314)(298.15)}{(2)(96500)} \ln \frac{[0.01]}{[1.0]} \\ = 0 - (-0.059) \\ = 0.059$$

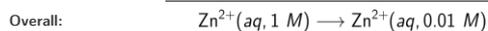
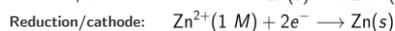
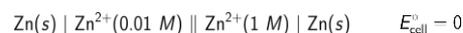
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Concentration cell

Note: Concentration at anode is products; concentration at cathode is reactants

Example: Galvanic cell with half-cells with *identical electrodes and different concentrations* (at 25°C)



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32

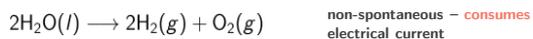
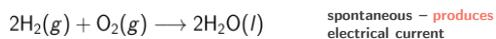
Electrolytic cell

Galvanic cells produce electric current via spontaneous redox reactions.

Electrolytic cells drive non-spontaneous redox reactions using supplied electric current through a process called **electrolysis**.

Cell type	Chemical reaction	Energy	Anode	Cathode
Galvanic	spontaneous	produced	-	+
Electrolytic	non-spontaneous	consumed	+	-

Example:

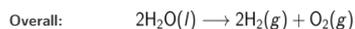
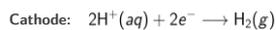
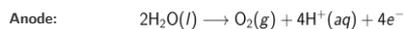


33

33

Electrolysis

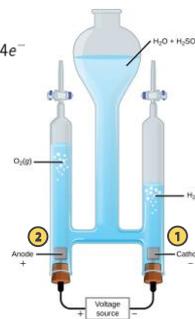
The splitting of water to produce H_2



$$E_{\text{cell}}^{\circ} = -1.24 \text{ V}$$

Non-spontaneous under standard conditions

- Water splits when losing electrons; O_2 produced
- Protons gain electrons; H_2 produced



Reaction driven by providing more than 1.24 V of electric current.

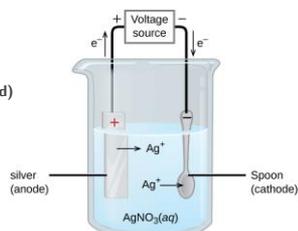
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34

Electrolysis

Used to plate metals to other metals

- Silver anode dissolves (oxidized)
- Silver ions plate to cathode (reduced)



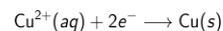
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35

Quantitative electrochemistry

- Method used to determine the **amount of substance** oxidized or reduced in an electrochemical reaction
- Based on stoichiometry

Stoichiometrically, 1 mole of Cu^{2+} is reduced when 2 moles e^- are transferred.



One can determine the number of moles of e^- for a reaction by knowing the total charge (C) that flowed into the electrolysis cell which depends on the magnitude of the current (A) and the amount of time (in s) the current was applied.

$$1 \text{ A} = 1 \frac{\text{C}}{\text{s}}$$

$$\text{Current} \left(\frac{\text{C}}{\text{s}} \right) \times \text{time (s)} = \text{charge (C)}$$

36

36

Quantitative electrochemistry

$$\text{Current} \left(\frac{\text{C}}{\text{s}} \right) \times \text{time (s)} = \text{charge (C)}$$

Charge can be converted to moles of e^- using Faraday's constant.

$$F = \frac{96,500 \text{ C}}{\text{mol } e^-}$$

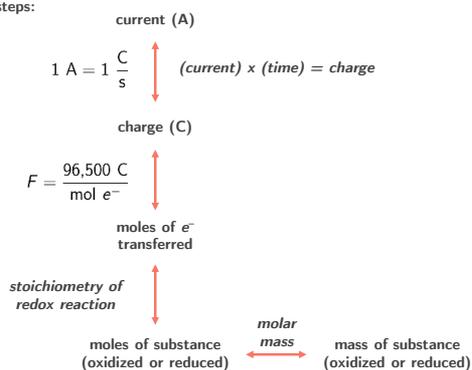
Moles of e^- can be used to determine **amount of substance** oxidized or reduced in an electrochemical reaction based on stoichiometry.

37

37

Quantitative electrochemistry

Summary of steps:

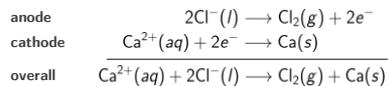


38

38

Example

What is the mass of Cl_2 (in g) produced by passing a 0.452 A current through molten CaCl_2 for 1.50 h?

A: 0.897 g Cl_2

current (A) \rightarrow charge (C) $0.452 \text{ A} \rightarrow 0.452 \text{ C s}^{-1} \times 5400 \text{ s} = 2440.8 \text{ C}$

charge (C) \rightarrow moles e^- $2440.8 \text{ C} \times \frac{1 \text{ mol } e^-}{96500 \text{ C}} = 0.0253 \text{ mol } e^-$

moles $e^- \rightarrow$ moles substance oxidized $0.0253 \text{ mol } e^- \times \frac{1 \text{ mol } \text{Cl}_2}{2 \text{ mol } e^-} = 0.01265 \text{ mol } \text{Cl}_2$

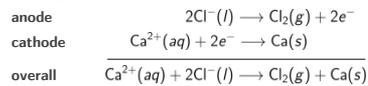
moles \rightarrow mass $0.01265 \text{ mol } \text{Cl}_2 \times \frac{70.90 \text{ g } \text{Cl}_2}{1 \text{ mol } \text{Cl}_2} = 0.897 \text{ g } \text{Cl}_2$

39

39

Practice

An electrolysis cell operates with a current of 0.452 A to generate 0.897 g of Cl_2 . How long (in h) did the cell operate to produce this?



A: 1.50 h

40

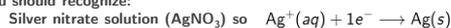
40

Practice

A current of 10.23 A was passed through an electrolytic cell containing silver nitrate for exactly 1 hour to electroplate silver. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

A: 0.3817 mol e^- ; 41.19 g Ag

You should recognize:



1 mol of Ag^+ for every 1 mol e^-

Silver cation is *reduced* to silver solid

41

41

17 Practice

What is E_{cell}° (in V) for the following galvanic cell composed of an Au electrode in a 1.0 M $\text{Au}(\text{NO}_3)_3$ solution and Ni electrode in a 1.0 M $\text{Ni}(\text{NO}_3)_2$ solution? (refer to standard reduction potential table)

A: +1.76 V

What is E_{cell}° (in V) for the following galvanic cell? Is it spontaneous?



A: +1.10 V

Would the following galvanic cell undergo a spontaneous redox reaction?



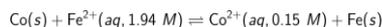
A: -2.46 V

What is the equilibrium constant and standard free energy change (in kJ mol^{-1}) for the following reaction (at 25 °C)?



A: 1.8×10^{42} ; -241 kJ mol^{-1}

What is E_{cell}° (in V) for the following reaction (at 25 °C)? Is it spontaneous?



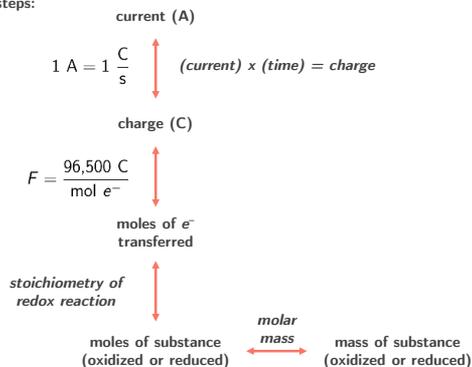
A: -0.14 V; no

42

42

Quantitative electrochemistry

Summary of steps:

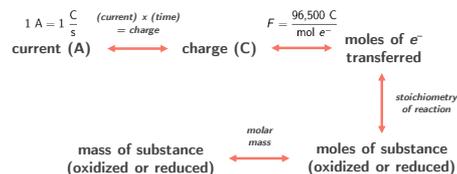


43

43

Quantitative electrochemistry

Summary of steps:



44

44