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USNCO Coaching Session Local Exam Preparation Tutorial Notes: Oxidation and Reduction

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Review
Electrons are transferred

LEO SAYS GER

Oxidation
Is
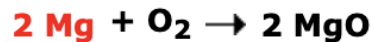**L**oss

Reduction
Is
Gain

Agents

An agent causes something to happen.

Metals tend to be oxidizing agents - give away electrons

An **oxidizing agent** allows something to be oxidized (lose electrons):

$$2\ Mg + O_2 \rightarrow 2\ MgO$$

reducing

agent

Nonmetals tend to be reducing agents - desire for electrons

A **reducing agent** allows something to be reduced (gain electrons):

$$2\ Mg + O_2 \rightarrow 2\ MgO$$

oxidizing

agent

Oxidation Numbers - Rules

Rule	Example
1. The oxidation number of any uncombined element is 0.	The oxidation number of Na(s) is 0.
2. The oxidation number of a monatomic ion equals the charge on the ion.	The oxidation number of Cl^- is −1.
3. The more-electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.	The oxidation number of O in NO is −2.
4. The oxidation number of fluorine in a compound is always −1.	The oxidation number of F in LiF is −1.
5. Oxygen has an oxidation number of −2 unless it is combined with F, in which it is +1 or +2, or it is in a peroxide, in which it is −1.	The oxidation number of O in NO_2 is −2.
6. Hydrogen's oxidation state in most of its compounds is +1 unless it is combined with a metal, in which case it is −1.	The oxidation number of H in LiH is −1.
7. In compounds, the elements of Groups 1 and 2 as well as aluminum have oxidation numbers of +1, +2, and +3, respectively.	The oxidation number of Ca in $CaCO_3$ is +2.
8. The sum of the oxidation numbers of all atoms in a neutral compound is 0.	The oxidation number of C in $CaCO_3$ is +4.
9. The sum of the oxidation numbers of all atoms in a polyatomic ion equals the charge of the ion.	The oxidation number of P in $H_2PO_4^-$ is +5.

Example Problem

37. What is the average oxidation state of tin in the mineral abhurite, $Sn_{21}Cl_{16}(OH)_{14}O_6$?

   (A) +1.71   **(B)** +2.00   **(C)** +2.76   **(D)** +3.43

2021

37.
$$\overset{-1}{Sn_{21}} \overset{-1}{Cl_{16}} (\overset{-1}{OH})_{14} \overset{-2}{O_6}$$

$$21x - 1(16) - 1(14) - 2(6) = 0$$

$$21x - 16 - 14 - 12 = 0$$

$$21x - 42 = 0$$

$$\frac{21x}{21} = \frac{42}{21}$$

$$\boxed{x = +2}$$

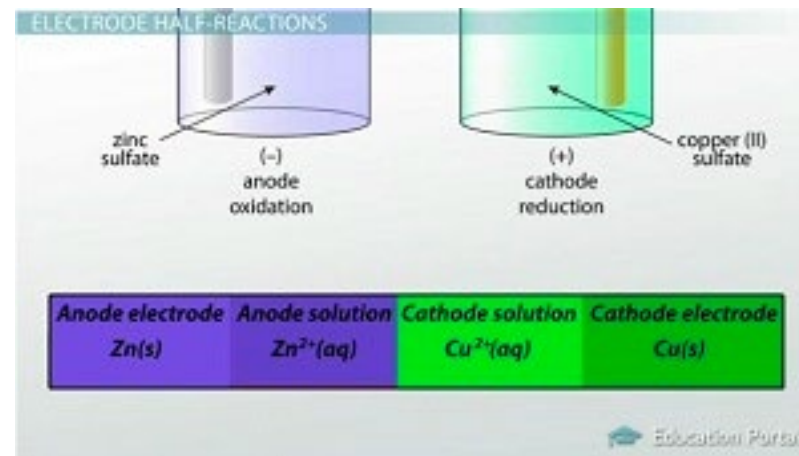# Electrochemical Cells - Terminology

Electrode: A conductor used to establish contact with a nonmetallic part of a circuit, such as an electrolyte

Half Cell: A metal electrode in contact with a solution of its own ions

Anode: The electrode where oxidation takes place. **Negative electrode**

Cathode: The electrode where reduction takes place. **Positive electrode**

Salt Bridge: A salt that will not precipitate with either ion. Balances charge

ELECTRODE HALF-REACTIONS

zinc sulfate | (–) anode oxidation | (+) cathode reduction | copper (II) sulfate

Anode electrode	Anode solution	Cathode solution	Cathode electrode
$Zn(s)$	$Zn^{2+}(aq)$	$Cu^{2+}(aq)$	$Cu(s)$

Education Portal

Cells

Cells generate electricity from chemical reactions

1. **Galvanic (Voltaic) cells** are spontaneous
   a. Voltage is positive
2. **Electrolytic cells** require external electricity to operate
   - electrolysis of water

Example Problem

Electrolysis - electrolytic cell

Electrolytic cell - anode is positive, cathode is negative

Electrons flow from **negative** to **positive**
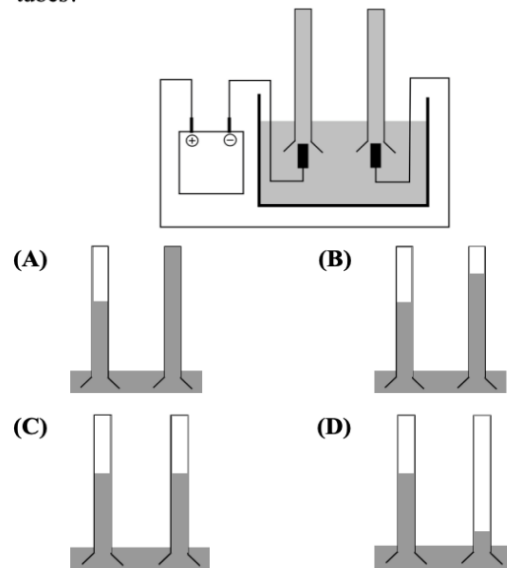
Water molecules attracted to ANODE (+).

Loses electrons, O_2 is formed

H^+ ions attracted to CATHODE (-).

Gains electrons.

Twice as much H_2 (left) than O_2 (right)

40. Electrolysis of water containing sulfuric acid as an electrolyte is carried out as shown and the gases produced at the electrodes collected in two identical tubes, both initially filled with the sulfuric acid solution. After electrolysis has been carried out for a certain time, which picture best represents the appearance of the tubes?
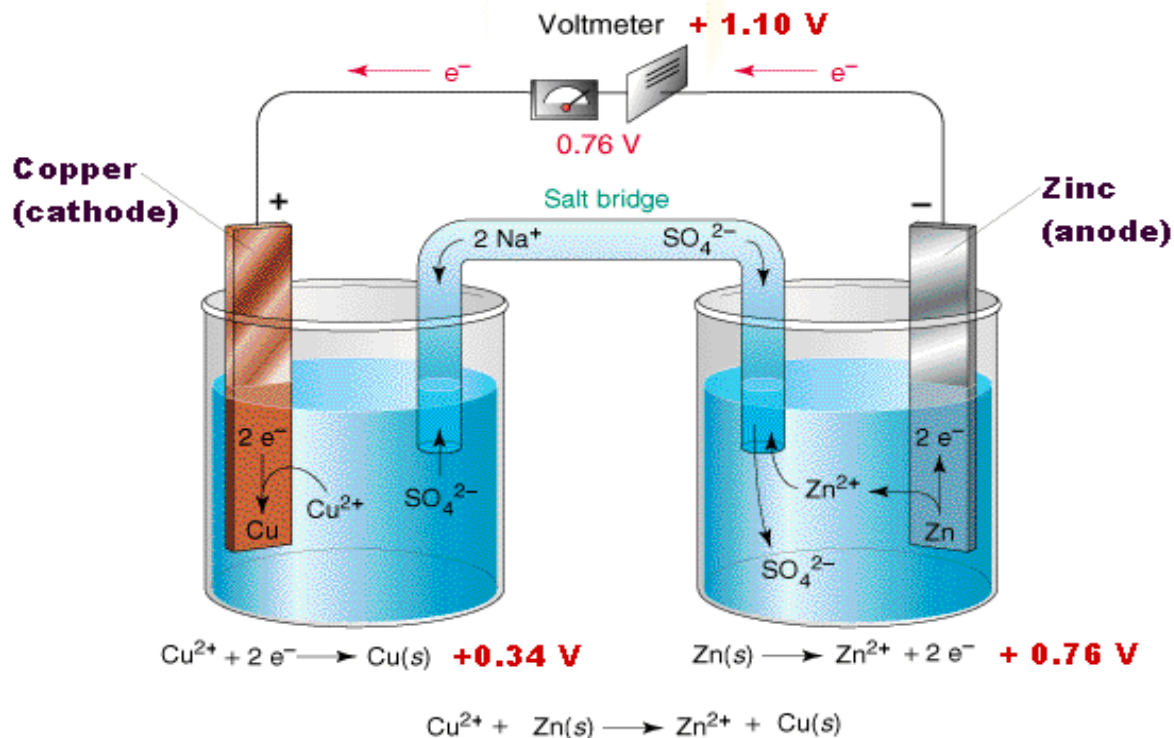
(A) (B) (C) (D)

Galvanic Cell - Example

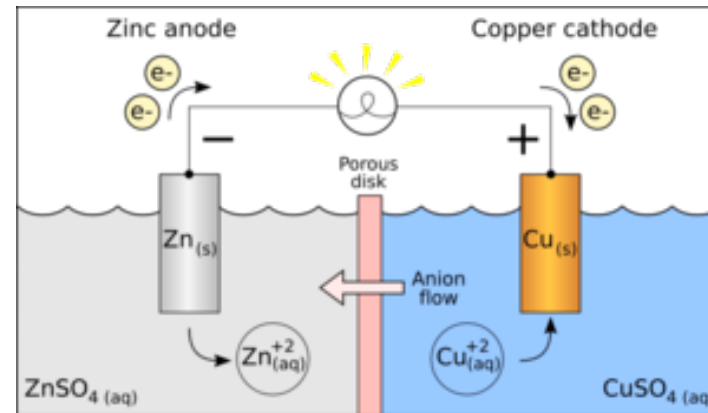Zn loses electrons

Cu gains electrons

Shorthand notation:

$Zn|Zn^{2+}||Cu^{2+}|Cu$

Voltmeter **+ 1.10 V**

0.76 V

Copper (cathode)

Salt bridge

Zinc (anode)

$2\,Na^+$ SO_4^{2-}

+

−

$2\,e^-$

Cu^{2+} SO_4^{2-}

Cu

Zn^{2+}

$2\,e^-$

Zn

SO_4^{2-}

$Cu^{2+} + 2\,e^- \longrightarrow Cu(s)$ **+0.34 V**

$Zn(s) \longrightarrow Zn^{2+} + 2\,e^-$ **+ 0.76 V**

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

Half Reactions

Anode:

Oxidation: $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e$

Cathode

Reduction: $Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)}$
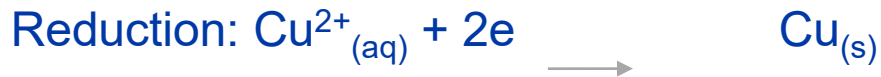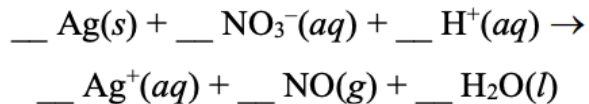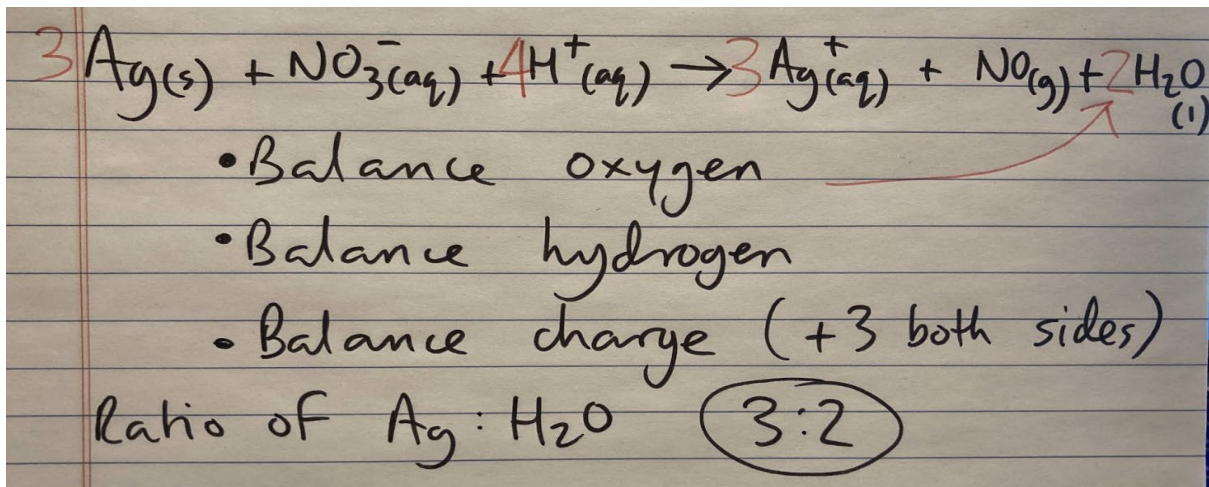
Balancing Redox Reactions

- Separate half reactions: oxidation and reduction
- Balance atoms - add in hydrogen or water as needed
- Balance charges - electrons
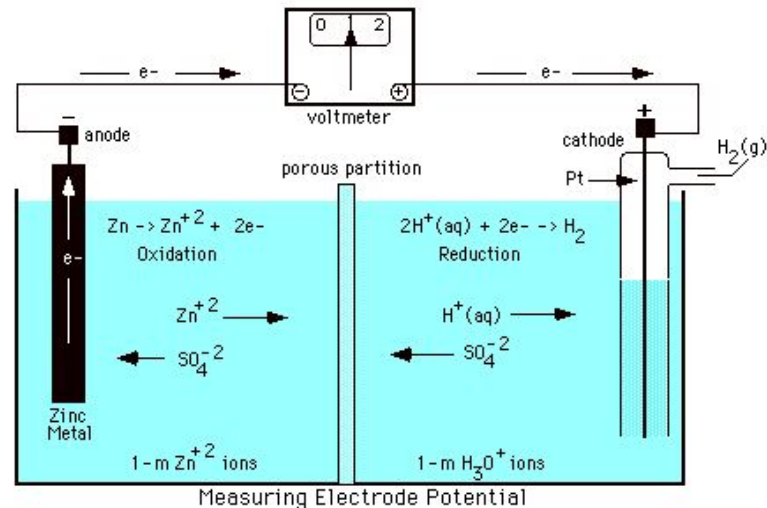- Add the 2 halves together again

Example Problem

37. When the chemical equation is balanced, what is the ratio of the coefficient of Ag(s) to the coefficient of $H_2O(l)$?

$$\_\_ Ag(s) + \_\_ NO_3^-(aq) + \_\_ H^+(aq) \rightarrow$$
$$\_\_ Ag^+(aq) + \_\_ NO(g) + \_\_ H_2O(l)$$

(A) 1 : 1   **(B)** 2 : 1   **(C)** 3 : 1   **(D)** 3 : 2

$$3Ag_{(s)} + NO_{3(aq)}^- + 4H^+_{(aq)} \rightarrow 3Ag^+_{(aq)} + NO_{(g)} + 2H_2O_{(l)}$$

- Balance oxygen
- Balance hydrogen
- Balance charge (+3 both sides)

Ratio of Ag : H_2O (3:2)

Standard Reduction Potential

Likelihood of something being reduced

Based on hydrogen - which is zero

Higher number = higher possibility of reduction

Activity series - more active metals replace less active ones

Reduction Half-Reaction	Standard Reduction Potential (V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$	+2.01
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.09
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$I_2(l) + 2e^- \rightarrow 2I^-(aq)$	+0.54
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$S(s) + 2H^+(aq) + 2e^- \rightarrow H_2S(g)$	+0.14
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	**0.00**
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(g)$	-0.14
$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$	-0.26
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	-1.18
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

Calculating Standard Cell Potentials

Use half-cell reactions

Half-cell with **higher SRP** will be reduced

Half-cell with **lower SRP** will be oxidized

Positive = spontaneous

Example Problem

$$E^0_{cell} = E^0_{red} - E^0_{ox}$$

Silver is reduced

(gains electrons)

Nickel is oxidized (loses electrons)

$$E^0_{cell} = +0.80 - (-0.23) = 1.03 \text{ V}$$

Half reactions would have to have equal amounts of electrons lost and gained. NOT voltages!!

40. What is the standard cell potential of the following electrochemical cell?

$$Ni(s) \mid Ni^{2+}(aq), 1.0 \text{ M} \parallel Ag^+(aq), 1.0 \text{ M} \mid Ag(s)$$

Half-Reaction	E^o, V
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.23
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80

(A) −1.83 V **(B)** 0.57 V **(C)** 1.03 V **(D)** 1.83 V

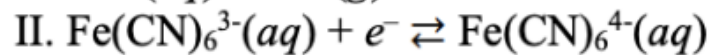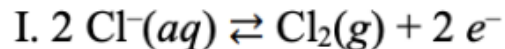# Inert Electrodes

Some materials are poor conductors

No solid conducting metal

A different material is used for the electrode - inert electrode

Platinum, gold are common choices.

Example Problem

38. If used in an electrochemical cell, which of the following half-reactions would require an inert electrode?

I. $2\ Cl^-(aq) \rightleftarrows Cl_2(g) + 2\ e^-$
II. $Fe(CN)_6{}^{3-}(aq) + e^- \rightleftarrows Fe(CN)_6{}^{4-}(aq)$

(A) I only

(B) II only

(C) Both I and II

(D) Neither I nor II

Answer: C

Iron is in aqueous phase on both sides of the equation.

Chlorine is not solid on either side of the equation

Relationship between ΔG and E⁰

ΔG = amount of energy available to do work

In galvanic cells, ΔG is negative. $E^0_{cell} > 0$

Formula: **$\Delta G = -nFE^0$**

n = moles of electrons

F = Faraday constant (amount of charge carried by 1 mole of electrons)

E^0 = Cell potential

Example Problem

40. What is the standard reduction potential of $Cr^{3+}(aq)$ to form metallic chromium?

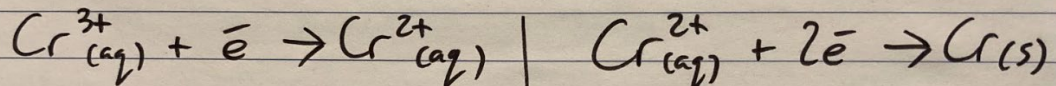| Half-reaction	$E°$, V
$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$	−0.41
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	−0.91
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	???

(A) −0.74 V
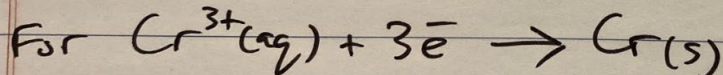
(B) −1.32 V

(C) −1.73 V

(D) −2.23 V

Solution to Problem 40

- Calculate ΔG for both ½ reactions
- Add together
- Convert back to E^0
- Total # of $\bar{e}$ = amount of energy to do work.

$$Cr^{3+}_{(aq)} + \bar{e} \rightarrow Cr^{2+}_{(aq)}$$

$$\Delta G = -nFE^0$$
$$= -1 \times 96500 \times -0.41$$
$$= 39565 \, J$$

$$Cr^{2+}_{(aq)} + 2\bar{e} \rightarrow Cr_{(s)}$$

$$\Delta G = -nFE^0$$
$$= -2 \times 96500 \times -0.91$$
$$= 175630 \, J$$

For $Cr^{3+}_{(aq)} + 3\bar{e} \rightarrow Cr_{(s)}$

$$\Delta G = -nFE^0$$
$$215195 = -3 \times 96500 \times E^0$$
$$E^0 = -0.743$$

(A)

Example Problem

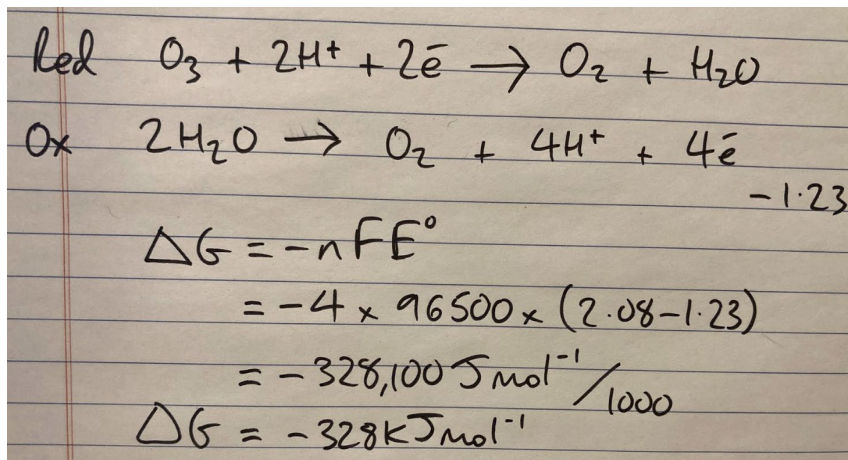Flip the half reactions to get highest

(most positive) cell potential!

Units!

41. What is the change in standard free energy at 298 K for the conversion of ozone to molecular oxygen as shown in the equation below?

$$2 O_3(g) \rightarrow 3 O_2(g) \qquad \Delta G° = ???$$

Half-Reaction	$E°$, V
$O_3(g) + 2 H^+(aq) + 2 e^- \rightarrow O_2(g) + H_2O(l)$	+2.08
$O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(l)$	+1.23

(A) -164 kJ mol^{-1} (B) -328 kJ mol^{-1}

(C) -401 kJ mol^{-1} (D) -492 kJ mol^{-1}

Red $O_3 + 2H^+ + 2\bar{e} \rightarrow O_2 + H_2O$

Ox $2H_2O \rightarrow O_2 + 4H^+ + 4\bar{e}$

-1.23

$\Delta G = -nFE°$

$= -4 \times 96500 \times (2.08 - 1.23)$

$= -328,100 \text{ J mol}^{-1} / 1000$

$\Delta G = -328 \text{ kJ mol}^{-1}$

Amps, Time and Mass

Electrolysis problems = Stoichiometry + Current

amps & time ⟷ Coulombs ⟷ Faradays ⟷ moles of electrons

1 Faraday = 96,500 C = 1 mole of electrons

Current (amperes or Amps or A) x time = Coulombs (electrical charge)

Example Problem

39. Chromium is electroplated industrially by the electrolysis of solutions of $K_2Cr_2O_7$. How much time would be required to deposit 1.00 kg of Cr using a current of 200.0 A?

(A) 2.58 h   **(B)** 7.74 h   **(C)** 15.5 h   **(D)** 31.0 h

- Mass → moles

$$1000g \times \frac{1 \text{ mole } Cr}{52.00g} =$$

$$= 19.23 \text{ moles}$$

- Oxidation state of Cr?

$$K_2Cr_2O_7 = 0$$
$$2(+1) + 2x + 7(-2) = 0$$
$$2 + 2x - 14 = 0$$
$$2x = 14 - 2$$
$$2x = 12$$
$$x = 6$$

- Half reaction: $Cr^{6+}_{(aq)} + 6\bar{e} \rightarrow Cr_{(s)}$

- Moles of $\bar{e}$:

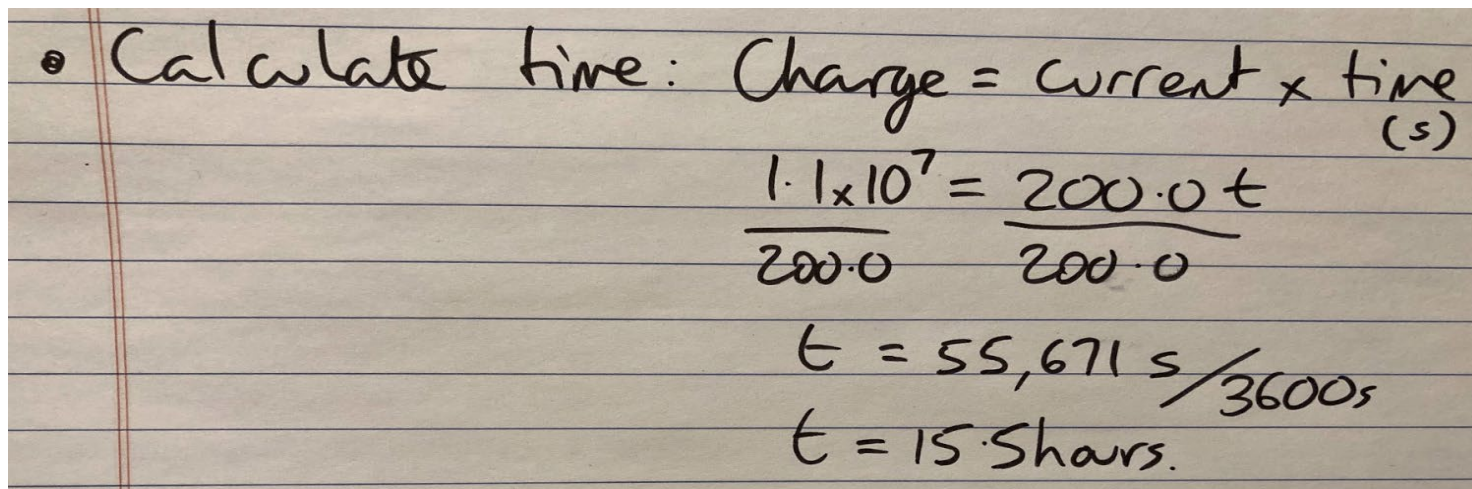$$19.23 \frac{\text{moles}}{Cr} \times \frac{6 \text{ moles } \bar{e}}{1 \text{ mole } Cr}$$

$$= 115.38 \text{ moles of } \bar{e}.$$

- Convert moles of $\bar{e} \rightarrow C$

$$115.38 \text{ moles of } \bar{e} \times \frac{96500 \, C}{1 \text{ mole of } \bar{e}} =$$

$$1.1 \times 10^7 \, C$$

Example Problem

39. Chromium is electroplated industrially by the electrolysis of solutions of $K_2Cr_2O_7$. How much time would be required to deposit 1.00 kg of Cr using a current of 200.0 A?

(A) 2.58 h   **(B)** 7.74 h   **(C)** 15.5 h   **(D)** 31.0 h

Calculate time: Charge = current × time (s)

$$\frac{1.1 \times 10^7}{200.0} = \frac{200.0 \, t}{200.0}$$

$$t = 55,671 \, s \, / \, 3600s$$

$$t = 15.5 \, hours.$$

Nernst Equation

Determine E^0 under nonstandard conditions

E = nonstandard E_{cell}

E^0 = cell potential standard conditions 298 Kelvin, 1M concentrations

R = Universal gas constant (8.314)

T = Temperature

n = number of moles

F = Faraday constant

Q = Reaction quotient - not at equilibrium

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

Reaction Quotient

For the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

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

Must be for aqueous ONLY! Use coefficients as exponents.

Using Nernst 1

If…	Then…
[REACTANTS] increases [PRODUCTS] decreases	equilibrium moves more to the right - more spontaneous E increases
[REACTANTS] decreases [PRODUCTS] increases	equilibrium moves more to the left - less spontaneous E = decreases

Using Nernst 2

Use "If…Then…" for help

Calculate Q

If reaction is at 298 K, use:

$$E = E^o - \frac{0.0592\ V}{n} \log_{10} Q$$

Balance half reactions to get moles of electrons

Determining Equilibrium Constant with the Nernst

When reactants and products reach equilibrium, $\Delta G = 0$.

Also, reaction quotient and equilibrium constant (K_c) are equal.

Since $\Delta G = -nFE^0$, cell potential = 0.

Substitute values of E and Q into Nernst

$0 = E^0 - (RT/nF) \ln K_c$

$E^0 = 0.0591/n \log Kc$

$\log Kc = nE^0/0.0591$