Chapter 19. Electrochemistry

What we will learn:

- Redox reactions
- Galvanic cells
- Standard reduction potentials
- Thermodynamics of redox reactions
- Effect of concentration on cell EMF
- Batteries
- Corrosion
- Electrolysis

Electrochemistry

Branch of chemistry that deals with the interconversion of electrical energy and chemical energy

Redox

(Oxidation-reduction) reactions where energy released by a spontaneous reaction is converted to electricity

Electronic background

Electrons are transferred from one substance to another

Oxidation numbers indicate which element loses and which gains electrons (for example Mg is oxidized, H_2 is reduced)

Balancing redox reactions

1. Write unbalanced ionic equations for the two half-reactions (Look at oxidation numbers in the "skeleton equation")

2. Balance atoms other than H and O

3. Balance O with H_2O

4. Balance H with H^+

5. Balance charge with appropriate number of electrons

6. If in acidic solution, then skip to step 7. If in basic solution, then add equal number of OH^- to both sides to cancel all of the H^+

7. Rewrite the balanced half reactions

8. Multiply balanced half-reactions by appropriate coefficients so that the number of electrons are equal

9. Add the half-reactions together

10. Cancel species that appear on both sides to get the balanced net ionic equation

11. If necessary, add spectator ions to get the balanced molecular equation

    Finally
    Check the final balance (atoms and charges)

Example

Balance the equation showing the oxidation of Fe^{2+} ions to Fe^{3+} ions by $Cr_2O_7^{2-}$ ions in an acetic medium

1. Write the unbalanced equation in ionic form

$$Fe^{2+} + Cr_2O_7^{2-} \rightarrow Fe^{3+} + Cr^{3+}$$

2. Separate the equation into two half-reactions

Oxidation: $Fe^{2+} \rightarrow Fe^{3+}$ (oxidation numbers 2 → 3)

Reduction: $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ (oxidation numbers 6 → 3)

3. Balance each half-reaction for number and type of atoms and charges. For reaction in an acetic medium, add H_2O to balance O atoms and H^+ to balance the H atoms

Oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

Reduction: $Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$

To balance the H atoms we add 14 H^+ ions on the left side

$$14\ H^+ + Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$$

There are 12 positive charges on the left side and six on the right side, therefore we add six electrons

$$14\ H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$$

4. Add two half-equations together and balance the final equation. The electrons of both sides must cancel. If the half-reactions contain different numbers of electrons, we need to multiply them to equlize the number of electrons

$$6\ (\ Fe^{2+} \rightarrow Fe^{3+} + e^-\ )$$

$$14\ H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$$

$$6\ Fe^{2+} + 14\ H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O + 6e^-$$

$$6\ Fe^{2+} + 14\ H^+ + Cr_2O_7^{2-} \rightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$$

Example

Balance the equation showing the oxidation of I^- ions to I_2 by MnO_4^- ions in an basic medium

1. Write the unbalanced equation in ionic form

$$MnO_4^- + I^- \rightarrow MnO_2 + I_2$$

2. Separate the equation into two half-reactions

Oxidation: $I^- \rightarrow I_2$ (oxidation numbers -1 → 0)

Reduction: $MnO_4^- \rightarrow MnO_2$ (oxidation numbers 7 → 4)

3. Balance each half-reactions for number and type of atoms and charges

$$2\ I^- \rightarrow I_2 + 2\ e^-$$

$$MnO_4^- \rightarrow MnO_2 + 2\,H_2O$$

$$MnO_4^- + 4\,H^+ \rightarrow MnO_2 + 2\,H_2O$$

$$MnO_4^- + 4\,H^+ + 3\,e^- \rightarrow MnO_2 + 2\,H_2O$$

4. Add two half-equations together and balance the final equation. The electrons of both sides must cancel. If the half-reactions contain different numbers of electrons, we need to multiply them to equlize the number of electrons

$$3\,(2\,I^- \rightarrow I_2 + 2\,e^-)$$

$$2\,(MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2\,H_2O\,)$$

$$6\,I^- + 2\,MnO_4^- + 8\,H^+ + 6\,e^- \rightarrow 3\,I_2 + 2\,MnO_2 + 4\,H_2O + 6\,e^-$$

Because the reaction is in a basic medium, every H^+ ion must be neutralized by OH^-

$$6\ I^- + 2\ MnO_4^- + 8\ H^+ + 8\ OH^- \rightarrow 3\ I_2 + 2\ MnO_2 + 4\ H_2O + 8OH^-$$

Finally

$$6\ I^- + 2\ MnO_4^- + 4\ H_2O \rightarrow 3\ I_2 + 2\ MnO_2 + 8\ OH^-$$

Example

Balance the following reaction that occurs in basic solution. Write complete, balanced equations for the oxidation and reduction half-reactions and the net ionic equation

$N_2H_4 + BrO_3^- \rightarrow NO + Br^-$

1 Check oxidation numbers to determine what is oxidized and what is reduced

- Bromine goes from +5 in BrO_3^- to -1 in Br^-. Thus, BrO_3^- is being reduced
- Nitrogen goes from -2 in N_2H_4 to +2 in NO. Thus, N_2H_4 is being oxidized

So, the two unbalanced half reactions are:

Reduction: $BrO_3^- \rightarrow Br^-$ (oxidation numbers 5 → -1)

Oxidation: $N_2H_4 \rightarrow NO$ (oxidation numbers -2 → 2)

2 Balance atoms other than H and O: $N_2H_4 \rightarrow 2\ NO$

3 Balance O with H_2O, and then

4 Balance H with H^+

$$2\ H_2O + N_2H_4 \rightarrow 2\ NO + 8\ H^+$$

$$6\ H^+ + BrO_3^- \rightarrow Br^- + 3\ H_2O$$

(Note: the atoms are balanced at this point but the charges are not)

5 Balance charge with electrons

$$2\ H_2O + N_2H_4 \rightarrow 2\ NO + 8\ H^+ + 8\ e^-$$

$$6\ e^- + 6\ H^+ + BrO_3^- \rightarrow Br^- + 3\ H_2O$$

6 Since the reaction is occurring in basic solution, the hydrogen ions (H^+) must be neutralized by adding equal numbers of OH^- ions to both sides of the equations

$8\ OH^- + 2\ H_2O + N_2H_4 \rightarrow 2\ NO + 8\ H^+ + 8\ e^- + 8\ OH^-$

$6\ OH^- + 6\ e^- + 6\ H^+ + BrO_3^- \rightarrow Br^- + 3\ H_2O + 6\ OH^-$

Now simplify by combining H^+ with OH^- and subtracting H_2O where possible

Reduction: $8\ OH^- + N_2H_4 \rightarrow 2\ NO + 8\ e^- + 6\ H_2O$

Oxidation: $3\ H_2O + 6\ e^- + BrO_3^- \rightarrow Br^- + 6\ OH^-$

7 You should now have the complete, balanced half-reactions. Rewrite them and check the balance of all atoms and charges

8 Multiply the balanced half-reactions by appropriate coefficients to make the number of electrons cancel. In this case, multiply the reduction by 3 and the oxidation by 4 for a total of 24 electrons on each side

$$3 \times (8\,OH^- + N_2H_4 \rightarrow 2\,NO + 8\,e^- + 6\,H_2O)$$

$$24\,OH^- + 3\,N_2H_4 \rightarrow 6\,NO + 24\,e^- + 18\,H_2O$$

$$4 \times (3\,H_2O + 6\,e^- + BrO_3^- \rightarrow Br^- + 6\,OH^-)$$

$$12\,H_2O + 24\,e^- + 4\,BrO_3^- \rightarrow 4\,Br^- + 24\,OH^-$$

9 Add the half-reactions together

$$24OH^- + 3N_2H_4 + 12H_2O + 24e^- + 4\,BrO_3^- \rightarrow 4Br^- + 24OH^- + 6NO + 24e^- + 18\,H_2O$$

10 Cancel species like H_2O, OH^-, or H^+ that may appear on both sides. In this case, subtract 24 e^-, 24 OH^- and 12 H_2O from each side

$$3\,N_2H_4 + 4\,BrO_3^- \rightarrow 4\,Br^- + 6\,NO + 6\,H_2O$$

11 If necessary add spectator ions to get the balanced molecular equation. That is not possible in this case because we started with an unbalanced ionic equation. Then, check the final balance, all atoms and total charges must be equal on both sides of the equations.

$$3\ N_2H_4 + 4\ BrO_3^- \rightarrow 4\ Br^- + 6\ NO + 6\ H_2O$$

Electrochemical cells

- Device that converts electrical energy into chemical energy or vice versa
- Generates electricity through the use of a spontaneous redox reaction

Conduction	
Metals	Solutions (or molten salts)
• Metallic (electronic) conduction	• Electrolytic (ionic) conduction
• Free movement of electrons	• Free movement of ions

Electrochemical cells	
Electrolytic cell	Galvanic (or voltaic) cell
• Converts electrical energy into chemical energy	• Converts chemical energy into electrical energy (a battery)
• Electricity is used to drive a non-spontaneous reaction	• Spontaneous reaction produces electricity

Electrodes	
Cathode	Anode
• Where reduction occurs	• Where oxidation occurs
Electrolytic cell	Galvanic (or voltaic) cell
• (+) anode → oxidation	• (+) cathode → reduction
• (-) cathode → reduction	• (-) anode → oxidation

Galvanic cells (batteries)

Produce electrical energy

A spontaneous reaction:

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

In a galvanic cell, the half reactions are occurring in separate compartments (half-cells)

Half-cell reactions

Anode (ox) $Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2\,e^-$ (electrons are formed)
Cathode (rd) $2\,e^- + Cu^{+2}\,(aq) \rightarrow Cu\,(s)$ (electrons are consumed)

Electrons move through wire from the anode → cathode
Ions (Cl^-, SO_4^{2-}, ...) move through salt bridge → anode

- Flow occurs because of difference in electrical potential between the anode and the cathode
- Measured as cell voltage, electromotive force (emf), or cell potential
- Dependent on nature of electrodes and ions, concentration, temperature

Cell Notation

summary of cell description (convention is anode on left)

$Zn(s)\ |\ Zn^{2+}(1\ M)\ \ ||\ \ Cu^{+2}(1\ M)\ |\ Cu(s)$

anode (ox) cathode (rd)

Cell potential

The difference in electrical potential between the anode and the cathode

- Cell Potential: E_{cell} (an electromotive force, emf)

  Units of E_{cell} are volts (1 volt = 1 joule/coulomb)

- E_{cell} is a measure of the relative spontaneity of a cell reaction

  Positive (+) value of E_{cell} indicates a spontaneous reaction

Standard reduction potentials

The voltage associated with a reduction reaction at an electrode when all solutes are at 1M and all gases are at 1 atm at 25 C

E^0 depends on:

- nature of reactants
- temperature -- superscript ^{0} means 25 C
- concentration -- superscript ^{0} means all are 1.00 M and all gases are 1.00 atm
- but, E^0 is independent of amounts of reactants

- The potential of a half-cell relative to a standard reference
- Usually hydrogen (set this one equal to zero)
- Standard hydrogen electrode: platinum electrode in HCl soln/25 C

$H_2 \rightarrow 2H^+ + 2e^-$

$2H^+ + 2e^- \rightarrow H_2$ $\quad E^0 = 0\ \mathrm{V}$

oxidizing agent strength ↑

Substance	E^0 (volts)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+ 2.87
$Fe_3^+(aq) + e^- \rightarrow Fe_2^+(aq)$	+ 0.77
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00 (ref)
$Fe_2^+(aq) + e^- \rightarrow Fe(s)$	- 0.44
$Li^+(aq) + e^- \rightarrow Li(s)$	- 3.05

reducing agent strength ↓

Li is the best reducing agent, it is easy to be oxidized

F_2 is the best oxidizing agent, it is easy to be reduced

The more positive value of E^0 is, the greater the tendency for the substance to be reduced

Standard Cell Potential

E^0_{cell} is determined from standard reduction potentials E^0

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

The convention is cathode - anode

Changing stoichiometry does not change E^0 (neither size of electrode or amount of solution affects this)

Problem

Write the balanced cell reaction of the galvanic cell and calculate E^0_{cell}

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

Cathode (rd) $Cu^{2+}(1M) + 2\ e^- \rightarrow Cu(s)$ $E^0 = 0.34$ v
Anode (ox) $Zn(s) \rightarrow Zn^{2+}(1M) + 2\ e^-$ $E^0 = -0.76$ v

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Cell $Zn(s) + Cu^{2+}(1M) \rightarrow Zn^{2+}(1M) + Cu(s)$ $E^0_{cell} = 1.10$ v

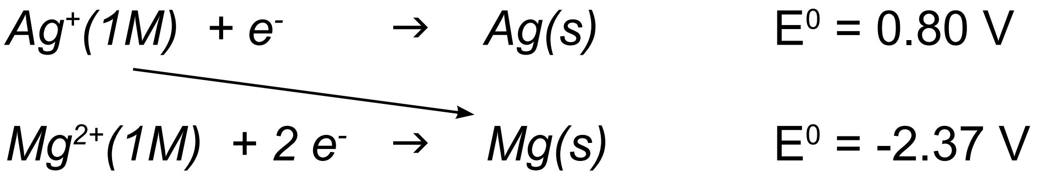
$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = 0.34\text{ v} - (-0.76\text{v}) = 1.10\text{ v}$$

Problem

A galvanic cell consists of a Mg electrode in 1 *M* $Mg(NO_3)_2$ solution and a Ag electrode in 1 *M* $AgNO_3$ solution. Calculate the standard cell potential E^0_{cell}

Data

Standard reduction potentials



$Ag^+(1M) + e^- \rightarrow Ag(s)$ $E^0 = 0.80$ V

$Mg^{2+}(1M) + 2e^- \rightarrow Mg(s)$ $E^0 = -2.37$ V

We apply the **diagonal rule**:

The half-reactions are written from the most positive to the most negative reduction potentials. A compound on the left of the first half-reaction will oxidize a compound on the right of the second half-reaction. The arrow indicates which compound will be oxidized

Therefore Ag^+ will oxidize Mg

Anode (ox) $Mg(s) \rightarrow Mg^{2+}(1M) + 2e^-$

Cathode (rd) $2\,Ag^+(1M) + 2e^- \rightarrow 2\,Ag(s)$

$$Mg(s) + 2\,Ag^{+}(1M) \rightarrow Mg^{2+}(1M) + 2\,Ag(s)$$

Note that in order to balance the overall reaction we multiplied the reduction of Ag^{+} by 2. However, the E^{0} is not affected by this procedure

$$E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode} = 0.80\text{ V} - (-2.37\text{ V}) = 3.17\text{ V}$$

Positive value of E^{0} shows that the forward reaction is favored

Thermodynamics of redox reactions

Electrical work

A work involved in a transformation of chemical energy into electrical energy

$$W_{max} = \Delta G \quad \text{(maximum work that can be taken from a system)}$$

A cell work is the total charged moved by the cell potential

$$W = - n F E_{cell}$$

The negative sign indicates that the electrical work is done by the system

n - the number of moles of electrons exchanged between the oxidized agent and the reducing agent in the redox reaction

F - Faraday constant, the charge of one mole of electrons

total charge = number of e^- x charge of one e^-

$1\ F = 6.022 \times 10^{23}\ e^-/\text{mol}\ e^- \times 1.602 \times 10^{-19}\ C/e^-$

$= 9.647 \times 10^{4}\ C/\text{mol}\ e^-$

Free energy is related to E_{cell} as follows

$$\Delta G = - n F E_{cell}$$

under standard conditions: use ΔG^0 and E^0_{cell}

Equilibrium constant

$$\Delta G^0 = - RT \ln K_c = - n F E^0_{cell}$$

$$E^0_{cell} = (RT / n F) \ln K_c$$

at 25 C, use values for R, T, and F

$$E^0_{cell} = (0.0257\ V) / (n)\ .\ \ln K_c$$

Problem

Calculate the equilibrium constant for the following reaction at 25 C

$$Sn\ (s) + 2\ Cu^{2+}\ (aq) \leftrightarrows Sn^{2+}\ (aq) + 2\ Cu^{+}\ (aq)$$

A hypotetical galvanic cell made up of two electrods (Sn^{2+}/Sn and Cu^{2+}/Cu^{+})

The half-cell reactions

Anode (ox) $Sn\ (s) \rightarrow Sn^{2+}\ (aq) + 2\ e^{-}$

Cathode (rd) $2\ Cu^{2+}\ (aq) + 2\ e^{-} \rightarrow 2\ Cu^{+}\ (aq)$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = E^0_{cu} - E^0_{sn}$$

$$= 0.15\ V - (-0.14\ V)$$

$$= 0.29\ V$$

$E^0_{cell} = (0.0257\ V) / (n) \ .\ \ln K_c$

$\ln K_c = (2 \times 0.29\ V) / (0.0257\ V)$

$= 22.6$

$K = e^{22.6} = 7 \times 10^9$

Problem

Calculate the standard free-energy change for the following reaction at 25 C

$$2\ Au\ (s)\ +\ 3\ Ca^{2+}\ (1.0M)\ \leftrightarrows\ 2\ Au^{3+}\ (1.0M)\ +\ 3\ Ca\ (s)$$

A hypotetical galvanic cell made up of two electrods (Au^{3+}/Au and Ca^{2+}/Ca)

The half-cell reactions

Anode (ox) $2\ Au\ (s) \rightarrow 2\ Au^{3+}\ (1.0M)\ +\ 6\ e^-$

Cathode (rd) $3\ Ca^{2+}\ (1.0M)\ +\ 6\ e^- \rightarrow 3\ Ca\ (s)$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = E^0_{ca} - E^0_{au}$$

$$= -2.87\ V - 1.50\ V$$

$$= -4.37\ V$$

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

$$= -(6)\ (96{,}500\ \text{J/V mol})\ (-4.37\ \text{V})$$

$$= 2.53 \times 10^3\ \text{kJ/mol}$$

The positive value of ΔG^0 indicates that the reaction favors the reactants at equilibrium. The result is consistent with the fact that E^0_{cell} for this galvanic cell is negative

Effect of concentration on cell potential

For a general reaction

$$a\,A \quad + \quad b\,B \quad \rightarrow \quad c\,C \quad + \quad d\,D$$

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

where

$$Q \quad = \quad ([C]^c\,[D]^d)\ /\ ([A]^a\,[B]^b)$$

$$\Delta G^0 = -\,n\,F\,E^0 \;;\quad \Delta G = -\,n\,F\,E\;;\quad \Delta G = \Delta G^0 + RT\ ln\ Q$$

$$-\,n\,F\,E \quad = \quad -\,n\,F\,E^0 + RT\ ln\ Q$$

$$E \quad = \quad E^0 \quad - \quad (R\,T)\ /\ (n\,F)\ .\ ln\ Q$$

Nernst Equation

$$E = E^0 - (R\,T) / (n\,F) \,.\, \ln Q$$

The Nernst Equation shows the relationship between the standard cell potential (E^0) and the cell potential (E) under actual, non-standard conditions

This can be simplified at 25 C to

$$E = E^0 - (0.0257\ V) / n \,.\, \ln Q$$

Major use of the Nernst Equation

- Positive value of E indicates that the redox reaction is spontaneous
- Determining E_{cell} from standard reduction potentials
- Use actual concentrations (i.e., Q) to calculate E_{cell}

Problem

Predict if the following reaction occur spontaneously at 25 C, given that $[Co^{2+}]$ = 0.15 *M* and $[Fe^{2+}]$ = 0.68 *M*?

$$Co\ (s) + Fe^{2+}(aq) \rightarrow Co^{2+}\ (aq) + Fe\ (s)$$

The half-cell reactions

Anode (ox) $Co\ (s) \rightarrow Co^{2+}\ (aq) + 2e^-$
Cathode (rd) $Fe^{2+}(aq) + 2e^- \rightarrow Fe\ (s)$

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

$$= E^0_{Fe} - E^0_{Co}$$

$$= -0.44\ V - (-0.28\ V)$$

$$= -0.16\ V$$

$$E = E^0 - (0.0257\ V) / n \cdot \ln Q$$

$$= E^0 - (0.0257\ V) / n \cdot \ln ([Co^{2+}] / [Fe^{2+}])$$

$$= -0.16\ V - (0.0257\ V) / 2 \cdot \ln (0.15 / 0.68)$$

$$= -0.14\ V$$

Because E is negative the reaction is not spontaneous

Concentration cells

A cell composed of two concentrations of the same ions

Example

$$Zn\ (s)\ |\ Zn^{2+}\ (0.1\ M)\ ||\ Zn^{2+}\ (1.0\ M)\ |\ Zn\ (s)$$

The half-reactions

Anode (ox)	$Zn\ (s) \rightarrow Zn^{2+}\ (0.1M) + 2e^-$
Cathode (rd)	$Zn^{2+}\ (1.0M) + 2e^- \rightarrow Zn\ (s)$
Cell	$Zn^{2+}\ (1.0M) \rightarrow Zn^{2+}\ (0.1M)$

$$E = E^0 - (0.0257\ V) / 2 \ .\ \ln ([Zn^{2+}]_{dil} / [Zn^{2+}]_{con})$$

$E^0 = 0$ (because we have the same electrods)

$$E = - (0.0257\ V) / 2 \ .\ \ln (0.1 / 1.0) = 0.0296\ V$$

Batteries

Electrochemical cell or a series of combined electrochemical cells that can be used as a source of electrical current at a constant voltage

Examples

- Dry cell battery (flashlights …..)
- Mercury battery (watches …..)
- Lead storage battery (automobiles – series of cells)
- Solid-state lithium battery (lightweight metal lithium and solid polymer electrolyte)
- Fuel cells (needs continuous supply of reactants: H_2 and O_2)

Corrosion

Deterioration of metals by an electrochemical process on a metal surface

The first step of the corrosion of iron

Anode (ox) $Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2\ e^{-}$

Cathode (rd) $O_2\ (g) + 4\ H^{+}(aq) + 4\ e^{-} \rightarrow 2\ H_2O\ (l)$

Cell $2\ Fe\ (s) + O_2\ (g) + 4\ H^{+}(aq) \rightarrow 2\ Fe^{2+}\ (aq) + 2\ H_2O\ (l)$

From the tables

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

$$= 1.23\ V - (-0.44\ V)$$

$$= 1.67\ V$$

Thus the cell reaction is spontaneous under standard conditions

Electrolysis

Process in which electrical energy is used to cause a nonspontaneous chemical reaction to occur

Electrolytic cell

Apparatus used for electrolysis

Example

Molten NaCl

Anode (ox) $2\ Cl^{-}(l) \rightarrow Cl_2(g) + 2\ e^{-}$

Cathode (rd) $Na^{+}(l) + e^{-} \rightarrow Na(l)$

Cl^{-} ions migrate toward the positive electrode and are oxidized
Na^{+} ions migrate toward the negative electrode and are reduced

A net cell reaction adds anode and cathode half-reactions and the number of electrons must cancel

Anode (ox)	$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$	E° = 1.36 V
Cathode (rd)	$2\,(Na^+ + e^- \rightarrow Na)$	E° = -2.71 V
Cell Reaction	$2\,Cl^- + 2\,Na^+ \rightarrow Cl_2 + 2\,Na$	

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

$$= -2.71\text{ V} - 1.36\text{ V}$$

$$= -4.07\text{ V}$$

The E° of the reaction is about -4 V, which indicates that this is a nonspontaneous process. Therefore minimum 4 V must be supplied to carry out the reaction

Example

Electrolysis of water

$$2\,H_2O\,(l) \rightarrow 2\,H_2\,(g) + O_2 \qquad \Delta G = 474.4 \text{ kJ/mol}$$

This reaction is not spontaneous under normal conditions (1 atm and 25 C) because standard free energy change is positive (and big)

Using electricity the following reaction is feasable (in an acetic medium)

$$2\,H_2O\,(l) \rightarrow 4\,H^+\,(aq) + O_2 + 4\,e^-$$

The overall reactions of the water electrolysis

Anode (ox)	$2\,H_2O\,(l) \rightarrow 4\,H^+\,(aq) + O_2(g) + 4\,e^-$
Cathode (rd)	$4\,[\,H^+\,(aq) + e^- \rightarrow 1/2\,H_2\,(g)\,]$
Cell	$2\,H_2O\,(l) \rightarrow 2\,H_2\,(g) + O_2\,(g)$

Applications of electrolysis

Preparation of Aluminum from molten Al_2O_3. We can't use Al^{3+} in solution since H_2O is easier to reduce

Anode (ox) $3\ (O^{2-} \rightarrow 1/2\ O_2 + 2\ e^-)$

Cathode (rd) $2\ (Al^{3+} + 3\ e^- \rightarrow Al)$

Cell Reaction $2\ Al^{3+} + 3\ O^{2-} \rightarrow 3/2\ O_2 + 2\ Al$

Electroplating : reduction of metal ions (from solution) to pure metals (Ag, Cr, Cu, etc.)

Quantitative aspects of electrolysis

Consider a cell with the cathode reaction

Cathode (rd) $Cr^{3+} + 3\ e^- \rightarrow Cr$ (chrome plating)

How much electrical current is needed and for how long to produce 1 mole of Cr metal

Stoichiometry: 1 mole Cr^{3+} ~ 3 moles e^- ~ 1 mole Cr

If a current equivalent to 3 moles of electrons is passed through the solution of Cr^{3+}, then 1 mole of Cr metal will be produced

1 Faraday (F) = 1 mole electrons
1 F = 96,500 coulombs
1 coulomb = 1 amp sec

Therefore to get 1 mole of Cr we need to apply the electrical current of

(3 moles of e^-) x (96,500 amp sec)

Problem

How long would it take to produce 25 g of Cr from a solution of Cr^{3+} by a current of 2.75 amp?

1 mole Cr ~ 3 moles e^- ~ 3 F ~ 3 x 96,500 coulombs

Number of Faradays needed to produce 25 g of Cr

25 g Cr x (1 mol Cr) / (52 g Cr) x (3 F) / (1 mol Cr) = 1.44 F

Number of coulombs (the total charge)

1.44 F x (96,500 coulombs) / (1 F) = 139,000 coulombs

charge = current x time

time = charge / current

Time of electrolysis (1 coulomb = 1 amp s)

(139,000 amp s) / (2.75 amp) x (1 hr) / (3600 s) = 14.0 hr

Problem

Consider an electrolysis of molten $CaCl_2$, using a current of 0.452 amp during 1.5 h. How much product will be formed at the cathode.

Anode (ox) $2\,Cl^-\,(l) \rightarrow Cl_2 + 2\,e^-$
Cathode (rd) $Ca^{2+}\,(l) + 2\,e^- \rightarrow Ca\,(l)$

Cell Reaction $Ca^{2+}\,(l) + 2\,Cl^-\,(l) \rightarrow Ca\,(l) + Cl_2$

2 mole of electrons (e^-) are required to reduce 1 mole of Ca^{2+} ions, and to form 1 mole of Ca metal on the cathode. 2 mole of electrons (e^-) correspond to the total charge of 2 x 96,500 coulomb.

1 mole of Ca → 19.3×10^4 coulomb

We have used the following charge

charge = current x time

charge = 0.452 amp x 1.5 x 3600 s

= 2.44 x 10^3 coulomb

Therefore we have formed the following amount of Ca in moles

1 mole of Ca → 19.3 x10^4 coulomb

x mole of Ca → 2.44 x 10^3 coulomb

x = 0.0126 mole of Ca

which correspond to the mass of Ca

1 mole of Ca → 40.08 g

0.0126 mole of Ca → x g

x = (40.08) (0.0126) g

= 0.507 g