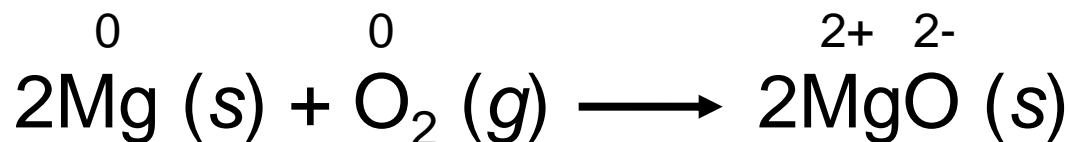# Electrochemistry

Chapter 19

1

***Electrochemical*** processes are oxidation-reduction reactions in which:

- the energy released by a spontaneous reaction is converted to electricity or

- electrical energy is used to cause a nonspontaneous reaction to occur

$$\overset{0}{2Mg} (s) + \overset{0}{O_2} (g) \longrightarrow \overset{2+\ 2-}{2MgO} (s)$$

$2Mg \longrightarrow 2Mg^{2+} + 4e^-$ ***Oxidation*** half-reaction (lose e^-)

$O_2 + 4e^- \longrightarrow 2O^{2-}$ ***Reduction*** half-reaction (gain e^-)

Oxidation number

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

1. Free elements (uncombined state) have an oxidation number of zero.

$$Na, Be, K, Pb, H_2, O_2, P_4 \; = 0$$
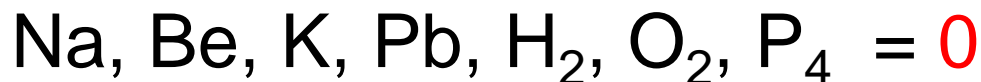
2. In monatomic ions, the oxidation number is equal to the charge on the ion.

$$Li^+, Li = +1; \; Fe^{3+}, Fe = +3; \; O^{2-}, O = -2$$

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

4. The oxidation number of hydrogen is +1 *except* when it is bonded to metals in binary compounds. In these cases, its oxidation number is −1. $Na^{+1}H^{-1} = 0$ $Ca^{2+} H_2^{-1} = 0$

5. Group IA metals are +1, IIA metals are +2 and fluorine is always −1.

6. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion. CO_2 $C + 2x{-}2 = 0$
$C{-}4 = 0; C = +4$

HCO_3^-

Oxidation numbers of all the atoms in HCO_3^- ?

$O = -2$ $H = +1$

CH_3COOH
$2C + 4x1{+} + 2x{-}2 = 0$
$2C +4 -4 = 0$
$2C = 0 ; C = 0/2 =$

$3x(-2) + 1 + ? = -1$

$C = +4$

Balancing Redox Equations

The oxidation of Fe^{2+} to Fe^{3+} by $Cr_2O_7^{2-}$ in acid solution?
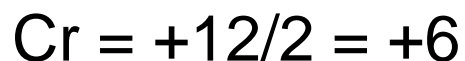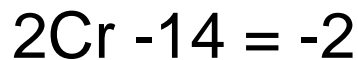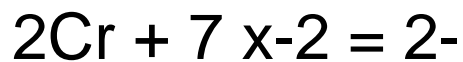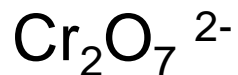
1. Write the unbalanced equation for the reaction in ionic form.

$Fe\ Cl_2$

$Fe + 2 \times -1 = 0$ $Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + Cr^{3+}$

$Fe = 2+$
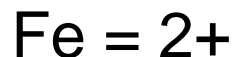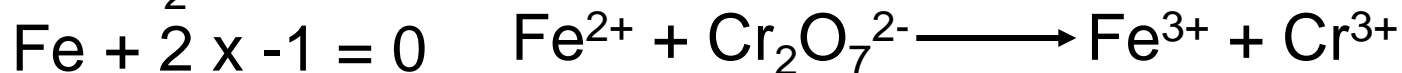
2. Separate the equation into two half-reactions.

$Cr_2O_7^{\ 2-}$

$2Cr + 7 \times -2 = 2-$

$2Cr -14 = -2$

$Cr = +12/2 = +6$

Oxidation: $\overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Fe^{3+}}$

Reduction: $\overset{+6}{Cr_2O_7^{2-}} \longrightarrow \overset{+3}{Cr^{3+}}$
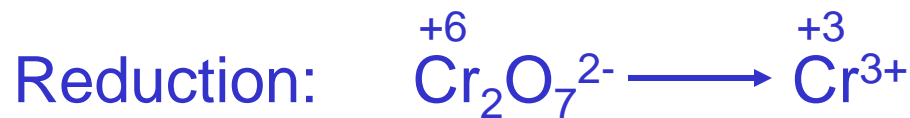
3. Balance the atoms other than O and H in each half-reaction.

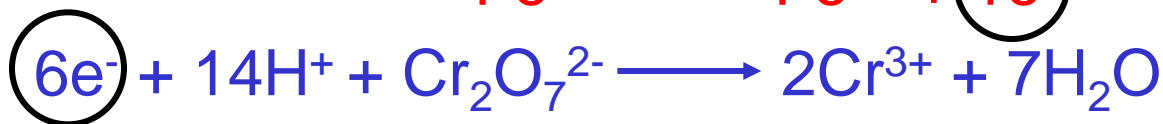$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

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Balancing Redox Equations

4. For reactions in acid, add H_2O to balance O atoms and H^+ to balance H atoms.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

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

5. Add electrons to one side of each half-reaction to balance the charges on the half-reaction.

$$Fe^{2+} \longrightarrow Fe^{3+} + \boxed{1e^-}$$

$$\boxed{6e^-} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$
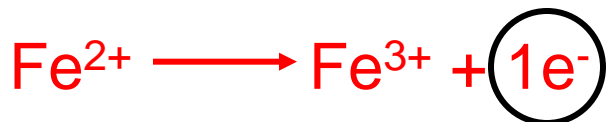
6. If necessary, equalize the number of electrons in the two half-reactions by multiplying the half-reactions by appropriate coefficients.

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$$

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$
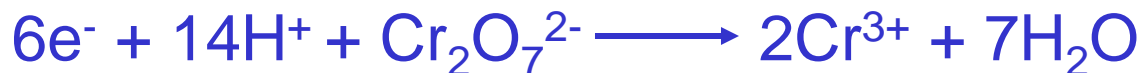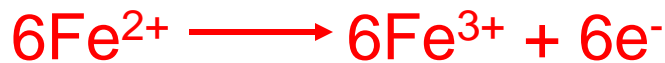
Balancing Redox Equations

7. Add the two half-reactions together and balance the final equation by inspection. **The number of electrons on both sides must cancel.**

Oxidation: $6Fe^{2+} \longrightarrow 6Fe^{3+} + \cancel{6e^-}$

Reduction: $\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

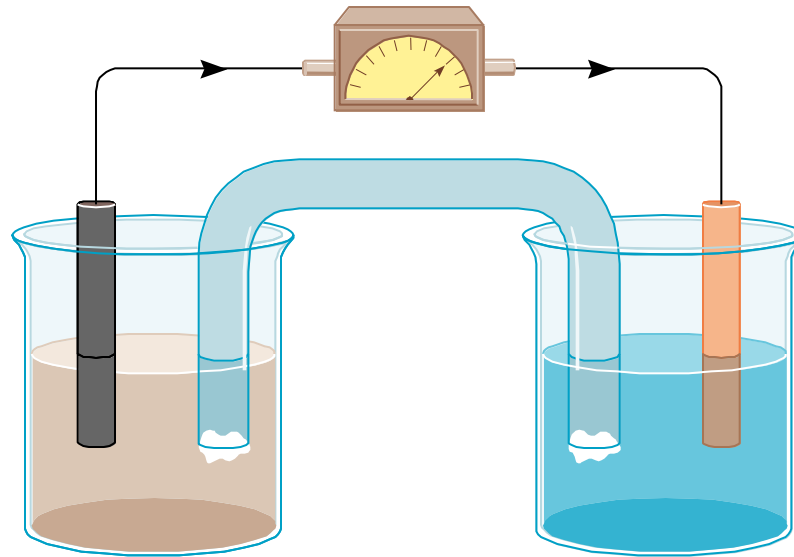$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

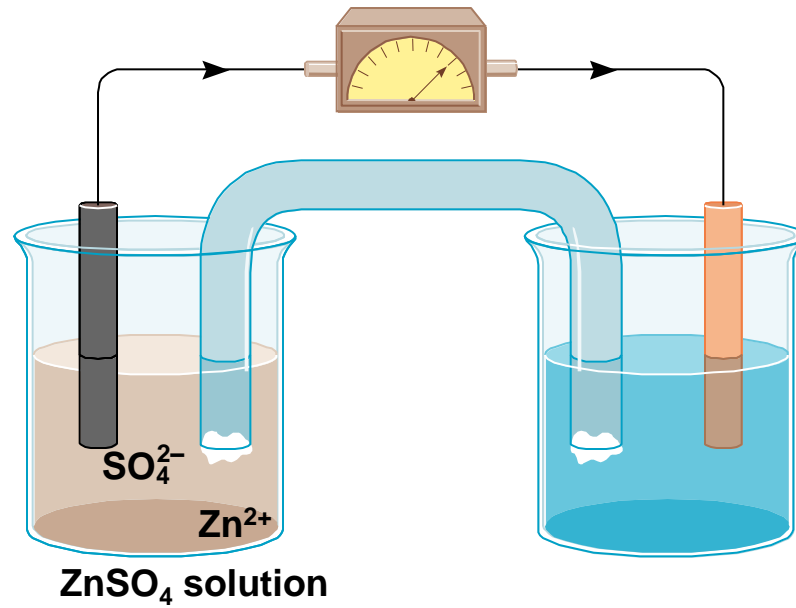8. Verify that the number of atoms and the charges are balanced.

$$14 \times 1 - 2 + 6 \times 2 = 24 = 6 \times 3 + 2 \times 3$$

9. For reactions in basic solutions, add OH^- to **both sides** of the equation for every H^+ that appears in the final equation.

Galvanic Cells

Galvanic Cells

SO$_4^{2-}$

Zn^{2+}

ZnSO$_4$ solution

Galvanic Cells

Galvanic Cells

Salt bridge

SO$_4^{2-}$

Zn^{2+}

ZnSO$_4$ solution

Cotton plugs

Cu^{2+}

SO$_4^{2-}$

CuSO$_4$ solution
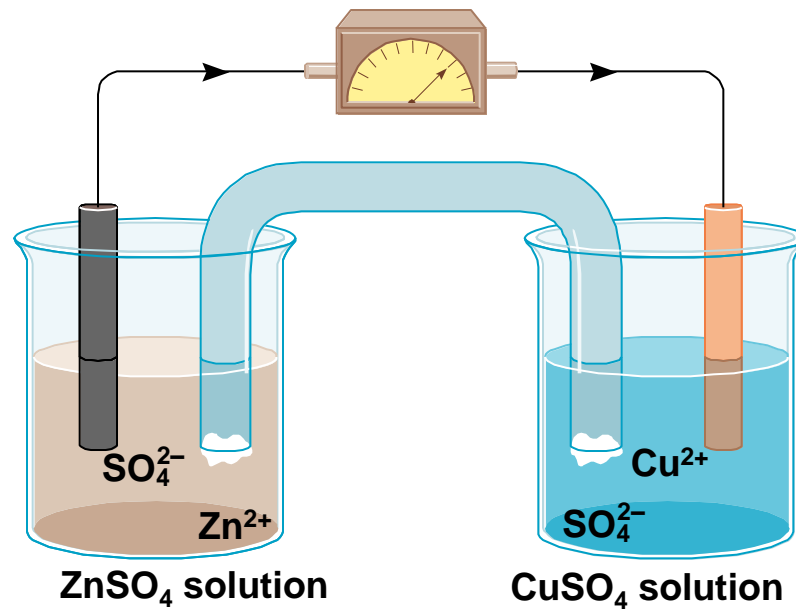
Galvanic Cells

Galvanic Cells

Galvanic Cells

Voltmeter

e^-

e^-

Zinc anode

Copper cathode

$\leftarrow$ Cl$^-$ K$^+$ $\rightarrow$

Salt bridge

Cotton plugs

SO_4^{2-}

Cu^{2+}

Zn^{2+}

SO_4^{2-}

ZnSO$_4$ solution

CuSO$_4$ solution

$2e^-$

Zn

Zn^{2+}

14

Galvanic Cells

Voltmeter

e^-

e^-

Zinc anode

← **Cl⁻**   **K⁺** →

Salt bridge

Copper cathode

Cotton plugs

SO_4^{2-}

Cu^{2+}

Zn^{2+}

SO_4^{2-}

ZnSO₄ solution

CuSO₄ solution

$2e^-$

Zn

Zn^{2+}

Zn is oxidized to Zn²⁺ at anode.

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

Galvanic Cells

Voltmeter

e^- e^-

Zinc anode

Copper cathode

← Cl⁻   K⁺ →

Salt bridge

Cotton plugs

SO_4^{2-}

Cu^{2+}

Zn^{2+}

SO_4^{2-}

ZnSO₄ solution

CuSO₄ solution

$2e^-$

Zn

Zn^{2+}

Cu

Zn is oxidized to Zn²⁺ at anode.

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

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Galvanic Cells

Voltmeter

e^- e^-

Zinc anode

Copper cathode

← Cl⁻   K⁺ →

Salt bridge

Cotton plugs

SO_4^{2-}

Zn^{2+}

Cu^{2+}

SO_4^{2-}

ZnSO₄ solution

CuSO₄ solution

$2e^-$

Zn

Zn^{2+}

$2e^-$

Cu^{2+}

Cu

Zn is oxidized to Zn²⁺ at anode.

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

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Voltmeter

Zinc anode — e^- ← Cl⁻ K⁺ → **Copper cathode**

Zinc anode

e^-

e^-

← Cl⁻   K⁺ →

Salt bridge

Copper cathode

SO_4^{2-}

Cotton plugs

Cu^{2+}

Zn^{2+}

SO_4^{2-}

ZnSO₄ solution

CuSO₄ solution

$2e^-$

Zn

Zn^{2+}

Cu^{2+}

$2e^-$

Cu^{2+}

Cu

**Zn is oxidized
to Zn²⁺ at anode.**

**Cu²⁺ is reduced
to Cu at cathode.** 18

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

$$2e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$$

Voltmeter

e^-

e^-

Zinc anode

$\leftarrow Cl^- \quad K^+ \rightarrow$

Salt bridge

Copper cathode

Daniell cell

SO_4^{2-}

Cotton plugs

Cu^{2+}

Zn^{2+}

SO_4^{2-}

ZnSO$_4$ solution

CuSO$_4$ solution

$2e^-$

Zn

Zn^{2+}

Cu^{2+}

$2e^-$

Cu^{2+}

Cu

Zn is oxidized to Zn^{2+} at anode.

Net reaction

Cu^{2+} is reduced to Cu at cathode 19

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

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

$$2e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$$

Galvanic Cells

Voltmeter

e^- e^-

**anode
oxidation**

Zinc
anode

← Cl⁻   K⁺ →

Salt bridge

Copper
cathode

**cathode
reduction**

Cotton
plugs

SO_4^{2-}

Zn^{2+}

Cu^{2+}

SO_4^{2-}

ZnSO₄ solution

CuSO₄ solution

$2e^-$

Zn

Zn^{2+}

$2e^-$

Cu^{2+}
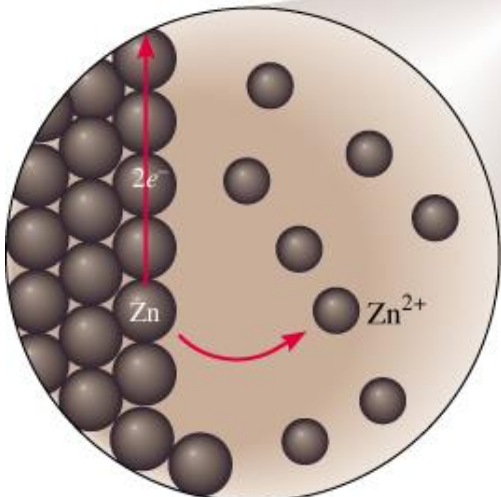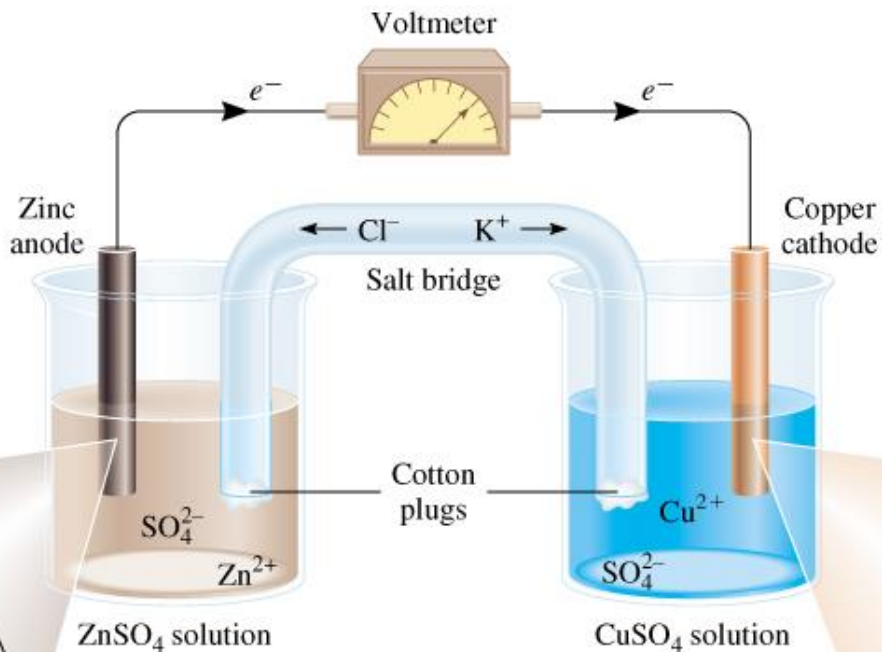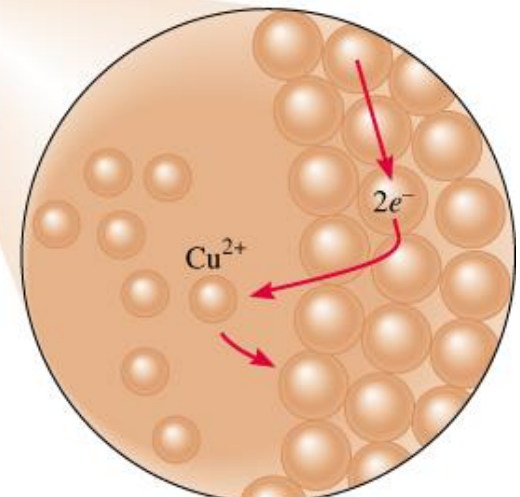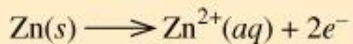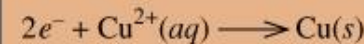
**spontaneous
redox reaction**
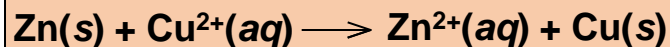
Zn is oxidized
to Zn^{2+} at anode.

Cu²⁺ is reduced
to Cu at cathode.

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

$$2e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$$

Net reaction

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

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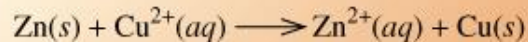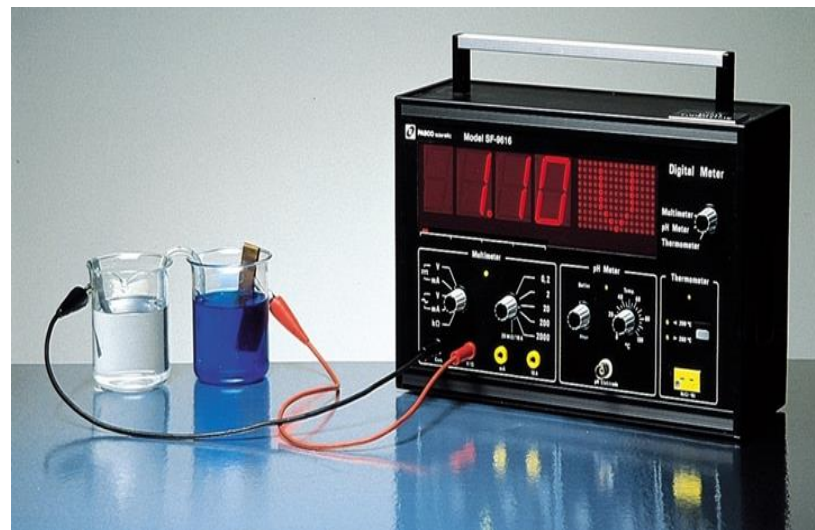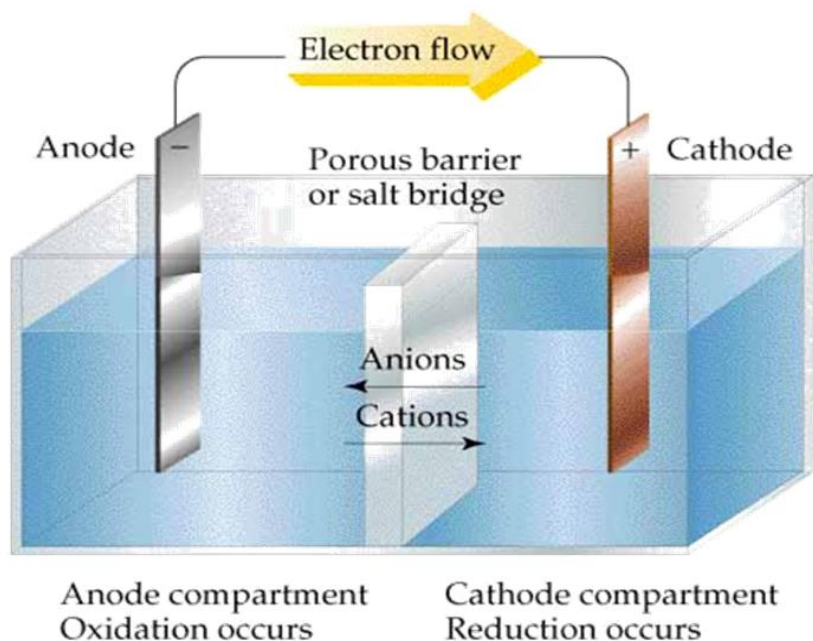
Galvanic Cells

Anode – electrode at which oxidation occurs

Cathode – electrode at which reduction occurs

Electrons always flow from anode to cathode

Salt bridge – tube that contains an electrolytes , maintains charge neutrality for a voltaic cell

Galvanic Cells

The difference in electrical potential between the anode and cathode is called:

- *cell voltage*

- *electromotive force (emf)*

- *cell potential*

Cell Diagram

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

$$[Cu^{2+}] = 1\ M\ \&\ [Zn^{2+}] = 1\ M$$

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

anode   cathode

22
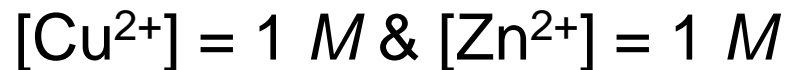
Standard Electrode Potentials

Standard reduction potential (E^0) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 *M* and all gases are at 1 atm.
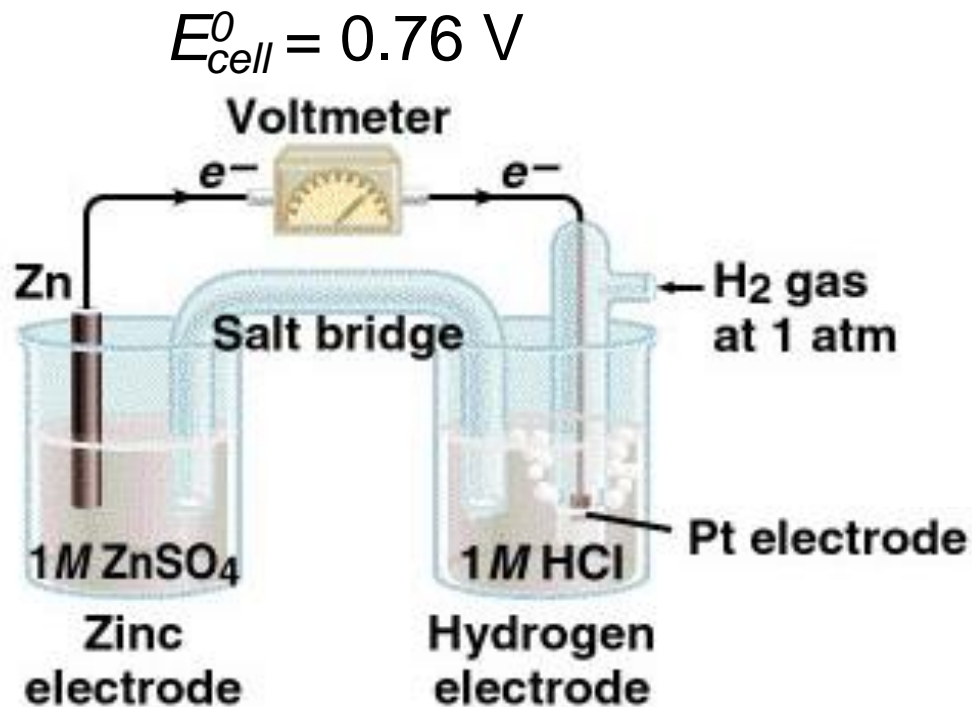
H₂ gas at 1 atm

Pt electrode

1*M* HCl

Reduction Reaction

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

$$E^0 = 0\ V$$

Standard hydrogen electrode (SHE)

Standard Electrode Potentials

$$\text{Zn (s)} \mid \text{Zn}^{2+} \text{ (1 M)} \parallel \text{H}^+ \text{ (1 M)} \mid \text{H}_2 \text{ (1 atm)} \mid \text{Pt (s)}$$

Anode (oxidation): $\text{Zn (s)} \longrightarrow \text{Zn}^{2+} \text{ (1 M)} + 2\text{e}^-$

Cathode (reduction): $2\text{e}^- + 2\text{H}^+ \text{ (1 M)} \longrightarrow \text{H}_2 \text{ (1 atm)}$

$$\text{Zn (s)} + 2\text{H}^+ \text{ (1 M)} \longrightarrow \text{Zn}^{2+} + \text{H}_2 \text{ (1 atm)}$$

Standard Electrode Potentials

$E^0_{cell} = 0.76$ V

Standard emf (E^0_{cell})

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

Zn (s) | Zn^{2+} (1 M) || H$^+$ (1 M) | H$_2$ (1 atm) | Pt (s)

$$E^0_{cell} = E^0_{H^+/H_2} - E^0_{Zn^{2+}/Zn}$$

$$0.76 \text{ V} = 0 - E^0_{Zn^{2+}/Zn}$$

$$E^0_{Zn^{2+}/Zn} = -0.76 \text{ V}$$

Zn^{2+} (1 M) + 2e$^-$ $\longrightarrow$ Zn $E^0 = -0.76$ V

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Standard Electrode Potentials

$E^0_{cell} = 0.34$ V

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

$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{H^+/H_2}$

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

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

Pt (s) | H_2 (1 atm) | H^+ (1 M) || Cu^{2+} (1 M) | Cu (s)

Anode (oxidation): H_2 (1 atm) $\longrightarrow$ $2H^+$ (1 M) + $2e^-$

Cathode (reduction): $2e^-$ + Cu^{2+} (1 M) $\longrightarrow$ Cu (s)

H_2 (1 atm) + Cu^{2+} (1 M) $\longrightarrow$ Cu (s) + $2H^+$ (1 M)

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TABLE 19.1

Standard Reduction Potentials at 25°C*

Half-Reaction	E°(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

+ve

Oxidizing agent

reducing agent

-ve

Increasing strength as oxidizing agent

Increasing strength as reducing agent

*For all half-reactions the concentration is 1 M for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

- E^0 is for the reaction as written

- The more positive E^0 the greater the tendency for the substance to be reduced

- The half-cell reactions are reversible

- The sign of E^0 changes when the reaction is reversed

- Changing the stoichiometric coefficients of a half-cell reaction **does not** change the value of E^0

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Example 6.1 What is the standard emf of an electrochemical cell made of a Cd electrode in a 1.0 M $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 M $Cr(NO_3)_3$ solution?

Cd^{2+} (aq) + 2e$^-$ ⟶ Cd (s) E^0 = -0.40 V   Cd is the stronger oxidizer

Cr^{3+} (aq) + 3e$^-$ ⟶ Cr (s) E^0 = -0.74 V   Cd will oxidize Cr

Anode (oxidation):   Cr (s) ⟶ Cr^{3+} (1 M) + 3e$^-$ x 2

Cathode (reduction): 2e$^-$ + Cd^{2+} (1 M) ⟶ Cd (s)   x 3

2Cr (s) + 3Cd^{2+} (1 M) ⟶ 3Cd (s) + 2Cr^{3+} (1 M)

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

E^0_{cell} = -0.40 – (-0.74)

E^0_{cell} = 0.34 V

Example 6.2: Use electrode potential to determine whether the following proposed reactions are spontaneous with all substances present at unit activity:

a) Cl_2 (g)+ $2I^-$ (aq) $\rightarrow 2Cl^-$ (aq)+I_2 (s)

b) $2Ag(s)+2H^+(aq) \rightarrow 2Ag^+(aq)+H_2(g)$

a) Fist we have to see who is reduced and who is oxidized .

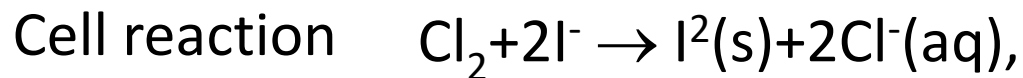Cl$_2$ is reduced I^- is oxidized

Cathode   Anode reactor

$Cl_2+2e- \rightarrow 2Cl^-$ $E^\circ_{Cl/Cl^-}=+1.36V$ $2I^- \rightarrow I_2$ (s) + 2e $E^\circ_{I/I^-} = +0.536V$

Cell reaction $Cl_2+2I^- \rightarrow I^2(s)+2Cl^-(aq)$,

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

$$E^\circ_{cell} = +1.36 - 0.536 = +0.824 \text{ V}$$

Since E°_{cell} is +ve the reaction is spontaneous

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b)$2Ag(s) + 2H^+(aq) \rightarrow 2Ag^+(aq) + H_2(g)$

H$^+$ is reduced

Cathode reaction:

$2H^+ + 2e^- \rightarrow H_2 (g)$ $E° = 0.00V$

Ag is oxidized

Anode reaction:

$2Ag(s) \rightarrow 2Ag^+(aq) + 2e$ $E°_{Ag+/Ag.} = +0.799V$

$2Ag + 2H^+(aq) \rightarrow 2Ag^+(aq) + H_2(g)$
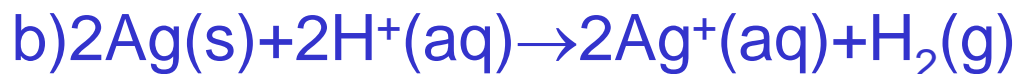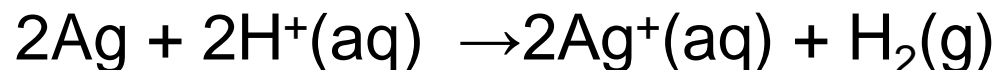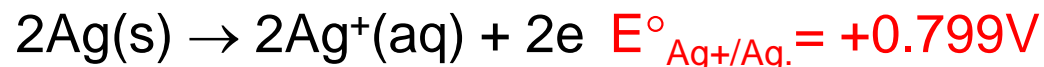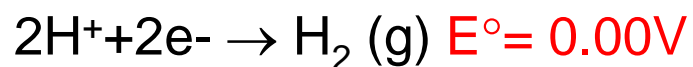
$E°_{cell} = E°_{cathode} - E°_{anode}$

$E°_{cell} = 0.0 - 0.799 = -0.799 \ V$

The result is nonspontaneous, $E°_{cell} = -ve$

Spontaneity of Redox Reactions

$\Delta G = -nFE_{cell}$ $\qquad$ n = number of moles of electrons in reaction

$\Delta G^0 = -nFE_{cell}^0$ $\qquad$ $F = 96,500 \dfrac{J}{V \cdot mol} = 96,500$ C/mol

$\Delta G^0 = -RT \ln K = -nFE_{cell}^0$

$E_{cell}^0 = \dfrac{RT}{nF} \ln K = \dfrac{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}{n \,(96,500 \text{ J/V}\cdot\text{mol})} \ln K$

$E_{cell}^0 = \dfrac{0.0257 \text{ V}}{n} \ln K$

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

$E_{cell}^\circ = \dfrac{RT}{nF} \ln K$

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

E_{cell}° $\qquad$ ΔG° $\qquad$ K
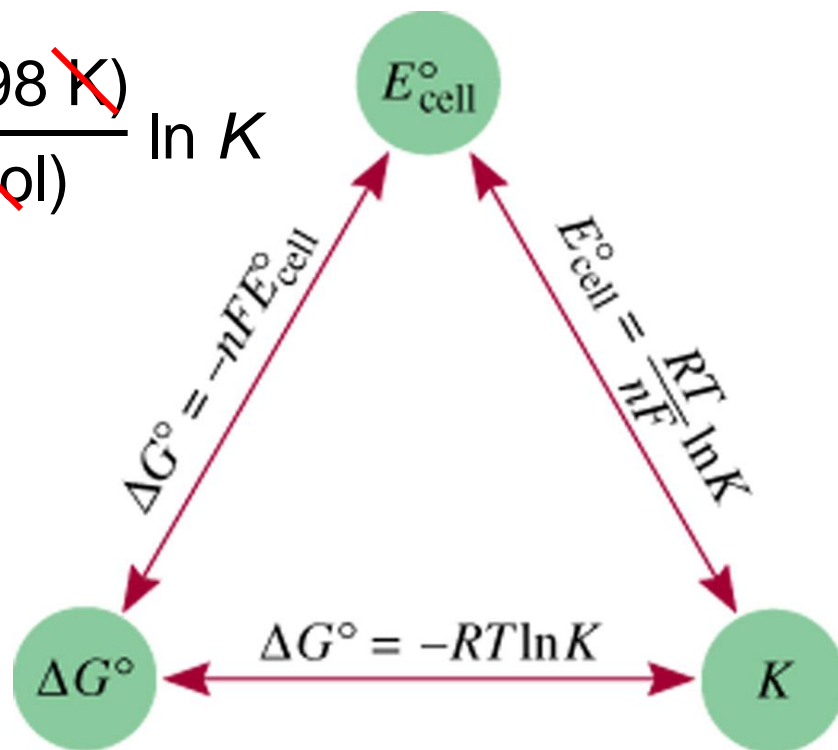
Spontaneity of Redox Reactions

TABLE 19.2

Relationships among $\Delta G°$, K, and $E°_{cell}$

$\Delta G°$	K	$E°_{cell}$	Reaction under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	=1	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

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Example 6.3 What is the equilibrium constant for the following reaction at 25^0C? Fe^{2+} (aq) + 2Ag (s) $\rightleftarrows$ Fe (s) + 2Ag$^+$ (aq)

$$E^0_{cell} = \frac{0.0257 \text{ V}}{n} \ln K$$

Oxidation: 2Ag $\longrightarrow$ 2Ag$^+$ + 2e$^-$

$n = 2$

Reduction: 2e$^-$ + Fe^{2+} $\longrightarrow$ Fe

$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Ag^+/Ag}$

$E^0 = -0.44 - (0.80)$

$E^0 = -1.24$ V

$$K = \exp\left[\frac{E^0_{cell} \times n}{0.0257 \text{ V}}\right] = \exp\left[\frac{-1.24 \text{ V} \times 2}{0.0257 \text{ V}}\right]$$

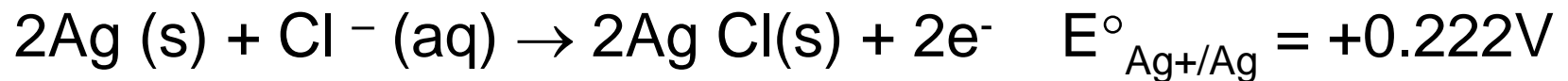$K = 1.23 \times 10^{-42}$

Example 6.4: a) Use electrochemical data to calculate the value of $\Delta G°$ for the reaction $2Ag\ (s)\ +\ Cl_2\ (g)\ \rightarrow\ 2AgCl\ (s)$
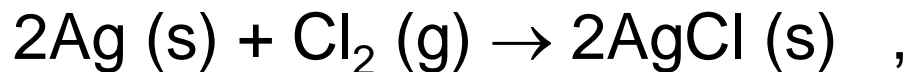
b) If $\Delta H° = -254.0\ K_S$, calculate $\Delta S°$

a) We have to calculate $E°_{cell}$ from the two half cell reactions.

Anode reaction:

$2Ag\ (s) + Cl^-\ (aq) \rightarrow 2Ag\ Cl(s) + 2e^-$ $E°_{Ag+/Ag} = +0.222V$

Cathode reaction:

$2e^- + Cl_2\ (s) \rightarrow 2\ Cl^-\ (aq)$, $E°_{Cl/Cl^-} = +1.369V$

$2Ag\ (s) + Cl_2\ (g) \rightarrow 2AgCl\ (s)$, $\Delta G° = -nf\ E°_{cell}$
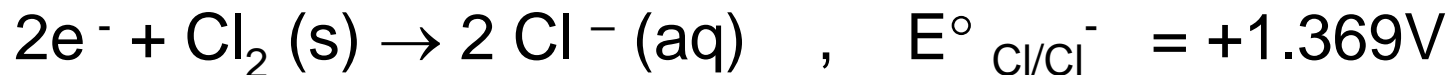
$E°_{cell} = E°_{Cl/Cl^-} - E°_{Ag+/Ag}$ $= -2 \times 96500 \times 1.137\ J$

$E°_{cell}\ = +1.369 - 0.222 = 1.137V$ $= -219.4\ kJ$

b) $\Delta G° = \Delta H° - T\Delta S°$

- 219.4 x 1000J = - 254.0 x 1000 J - 298 Δ SJ/K

$\Delta S° = -\dfrac{(254.0 - 219.4) 1000J}{298 \ K}$

= - 116 J/K

Example 6.5: Use electrochemical data to calculate the equilibrium constant K for the following reaction at 25ºC

$$Fe^{++} (aq) + Ag^+ (aq) \rightleftharpoons Fe^{+++}(aq) + Ag (s)$$

$$Fe^{++}(aq) \rightarrow Fe^{+++} (aq) + e^- \qquad E^o_{Fe3+/Fe2+} = +0.771V$$

$$e^- + Ag^+(aq) \rightarrow Ag(s) \qquad E^o_{Ag+/g} = 0.799V$$
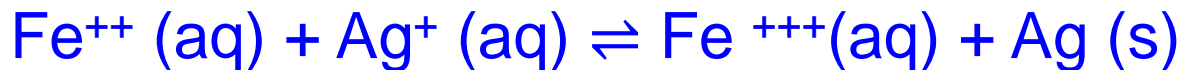
$n = 1$, T=25 °C= 298 K, F=96500

$$E°_{cell} = E°_{cath} - E°_{anode} \qquad E^o_{cell} = - (RT /nF) \ln K$$

$E^0 = 0.799-0.771$

$0.028 = - (8.314 \times 298 /1 \times 96500) \ln K$

$E^0 = 0.028$ V $\qquad \therefore \ln K = 1.091$

$$\therefore K = 2.98$$

The Effect of Concentration on Cell Emf

$\Delta G = \Delta G^0 + RT \ln Q$ $\qquad$ $\Delta G = -nFE$ $\qquad$ $\Delta G^0 = -nFE^0$
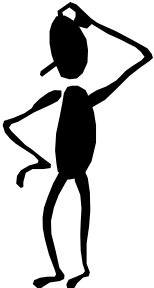
$$-nFE = -nFE^0 + RT \ln Q$$

Nernst equation

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

At 298

$$E = E^0 - \frac{0.0257 \text{ V}}{n} \ln Q$$

Ex 6.6 Will the following reaction occur spontaneously at 25^0C if $[Fe^{2+}] = 0.60\ M$ and $[Cd^{2+}] = 0.010\ M$?

$$Fe^{2+}\ (aq) + Cd\ (s) \rightleftharpoons Fe\ (s) + Cd^{2+}\ (aq)$$

Oxidation: $\qquad Cd \longrightarrow Cd^{2+} + 2e^-$

Reduction: $2e^- + Fe^{2+} \longrightarrow 2Fe$

$n = 2$

$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Cd^{2+}/Cd}$
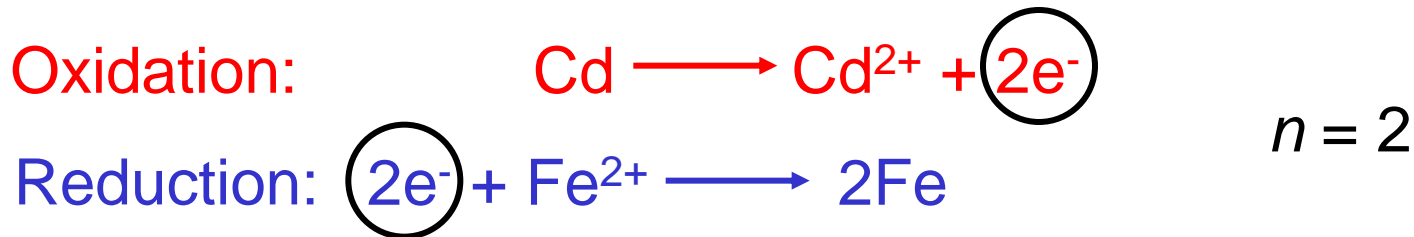
$E^0 = -0.44 - (-0.40)$

$E^0 = -0.04\ V$

$$E = E^0 - \frac{0.0257\ V}{n}\ \ln Q$$

$$E = -0.04\ V - \frac{0.0257\ V}{2}\ \ln \frac{0.010}{0.60}$$

$$E = 0.013$$

$E > 0 \qquad$ Spontaneous

Example 6.7: What is the electrode potential of Zn^{++}/Zn electrode in which the concentration of $Zn^{++} = 0.1M$.

$$Zn^{++}+2e^- \rightarrow Zn \, , \, E° = -0.76 \, V$$

At 298

$$E = E^0 - \frac{0.0257 \, V}{n} \ln Q$$

$$E = -0.76 - (0.0257/2 \ln (1/0.1)$$

$$= -0.79V$$

Example 6.8: What is the potential for the cell :
Ni / Ni^{++} (0.01M) // Cl $^-$ (0.2 M) / Cl$_2$ M) / Pt

$$Ni \rightarrow N_i^{++} + 2e^- \qquad E^\circ\,_{Ni2+/Ni} = -0.25V$$

$$2e^- + Cl_2\,(g) \rightarrow 2Cl^- \qquad E_{\circ\,Cl/Cl^-} = 1.36V$$

$$2Ni + Cl_2\,(g) \rightarrow 2Cl^-\,(aq) + Ni^{++}\,(aq)$$

$$E^\circ\,_{cell} = 1.36 - (-0.25) = 1.61V$$

$$E = E^0 - \frac{0.0257\ V}{n}\ \text{ln}\ Q$$

$$Q = [Cl^-]^2\ [Ni^{++}] / P_{Cl2} = ((0.2)2\ (0.01)/1 = 0.0004$$

$$E = 1.61 - [(0.0257/2) \times 0.0004]$$
$$= 1.71\ V$$

Example 6.9: Consider a cell reaction

$Mg(s) + 2H^+ (aq) \rightarrow Mg^{++}(aq) + H_2 (g)$, $E°_{cell} = 2.363V$

What is the concentration of H^+ (aq) in a cell in which $[Mg^{++}]$ = 1.00M and P_{H2} =1.0atm, if the Ecell = 2.099 V?

At 298 : $E = E^0 - \dfrac{0.0257\ V}{n} \ln Q$

$n = 2$

$Q = (Mg^{+2})\ P_{H2} / (H^+)^2 = (1)(1) / (H^+)^2$

$2.099 = 2.363 - (0.0257/ 2) \ln (1/ (H^+)^2)$

$2.099 - 2.363 = -0.0128 \ln [H^+]^{-2}$

$\ln [H^+]^{-2} = 20.625$

$[H^+]^{-2} = 906407915.01$
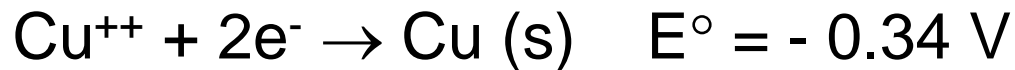
$[H^+] = 3.3 \times 10^{-5}\ M$

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Concentration cell : two half-cells composed of the same material but differing in ion concentrations

High concentration = reduction , low concentration = oxidation

Example 6.10: What is the   E for the cell :
Cu / Cu^{++} (0.01M) // Cu^{++} (0.1M) / Cu .

$$Cu^{++} + 2e^- \rightarrow Cu\ (s) \quad E° = -0.34\ V$$

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

$$E^0 cell = -0.34 - (-0.34) = 0.0\ V$$

$$E = E^0 - \frac{0.0257\ V}{n}\ \ln Q$$

$$E = 0.0 - (0.0257/2)\ \ln (0.01/0.1) = -0.0296\ V$$

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Electrolysis is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.

• In electrolytic solution, the charge is carried by ions.

• Ions must be free to move.

• Occurs at molten salts or aqueous solutions of electrolyte.
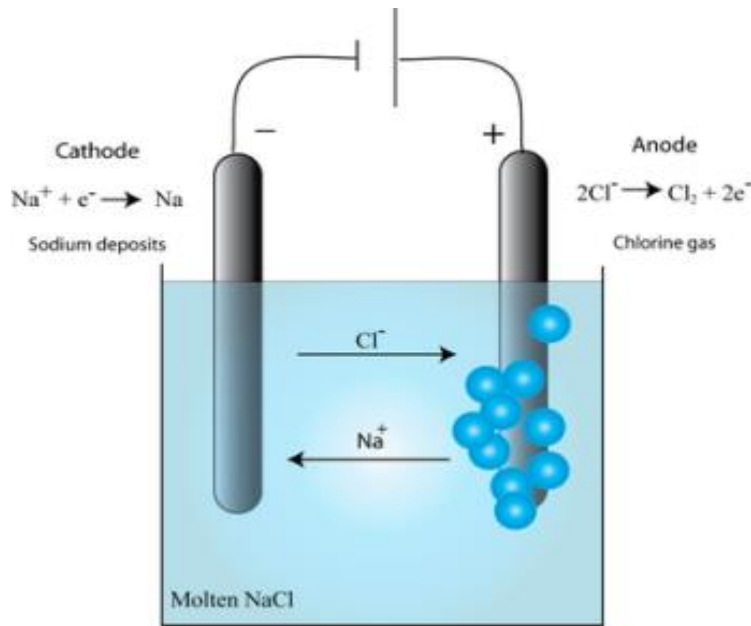
Cl$_2$ gas
NaCl

Liquid Na ←

→ Liquid Na

Iron cathode   Iron cathode
Carbon anode

Battery

e^- e^-

Anode   Cathode

Molten NaCl

Oxidation
$2Cl^- \longrightarrow Cl_2(g) + 2e^-$

Reduction
$2Na^+ + 2e^- \longrightarrow 2Na(l)$
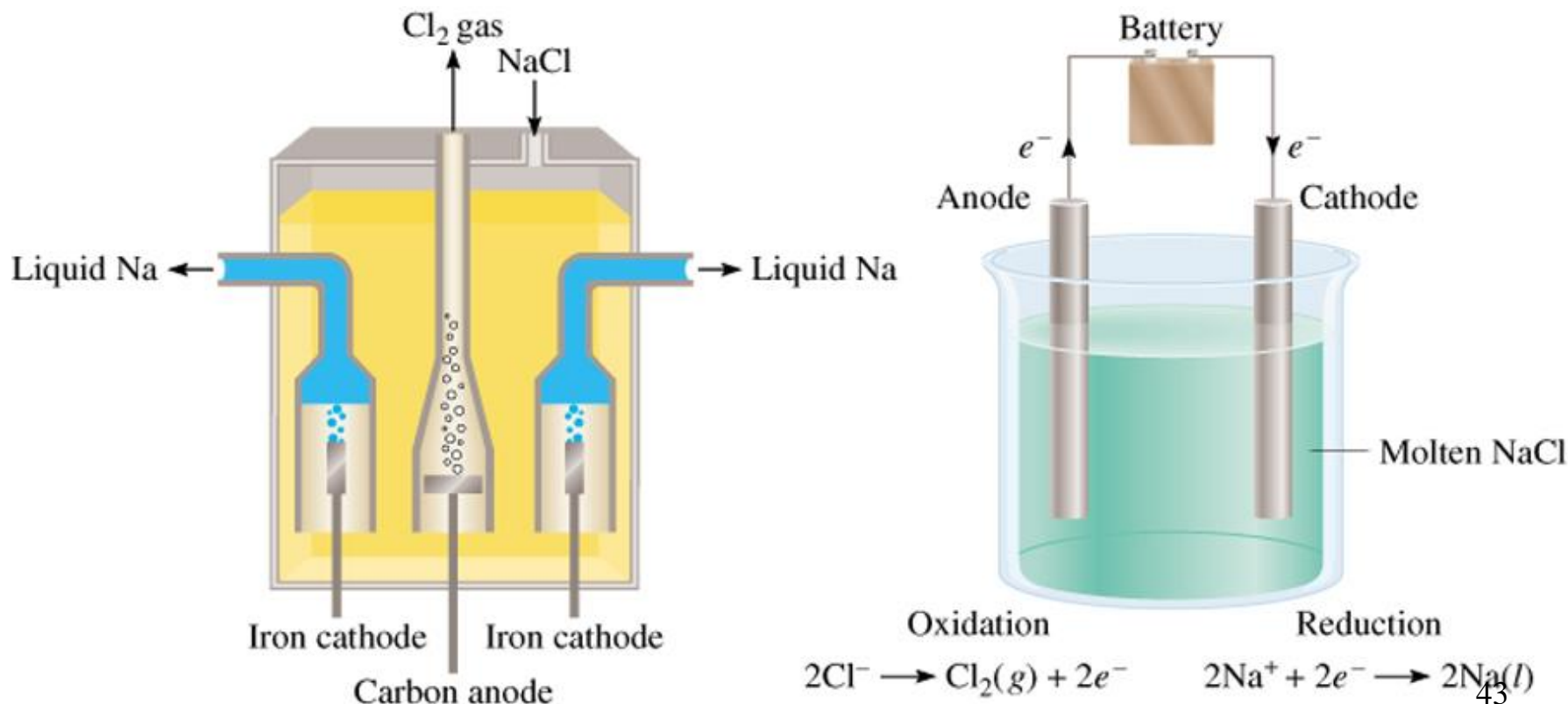
Electrolysis of molten NaCl

Cathode reaction

$$Na^+ + e^- \rightarrow Na$$

Always reduction occurs at the cathode

Anode reaction

$$2\ Cl^- \rightarrow Cl_2 + 2e^-$$

Always oxidization occurs at the anode

Cathode
$$Na^+ + e^- \rightarrow Na$$
Sodium deposits

Anode
$$2Cl^- \rightarrow Cl_2 + 2e^-$$
Chlorine gas

Cl^-

Na^+

Molten NaCl

Anode (oxidation):	$2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$
Cathode (reduction):	$2Na^+(l) + 2e^- \longrightarrow 2Na(l)$
Overall:	$2Na^+(l) + 2Cl^-(l) \longrightarrow 2Na(l) + Cl_2(g)$

Electrolysis and Mass Changes

| Current (amperes) and time | → | Charge in coulombs | → | Number of moles of electrons | → | Moles of substance reduced or oxidized | → | Grams of substance reduced or oxidized |
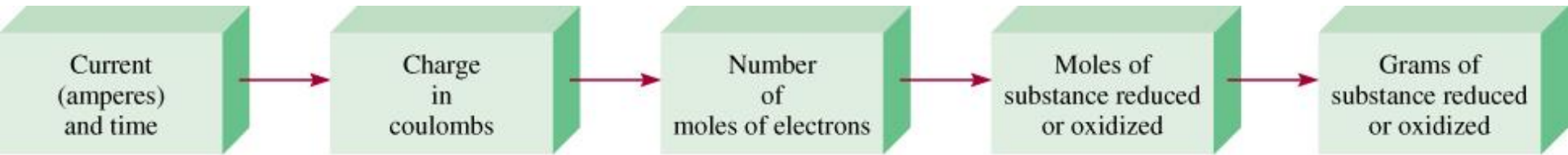
charge (C) = current (A) x time (s)

$$\boxed{\text{1 mole e}^- = 96{,}500 \text{ C}}$$

Ex 6.11: How much Ca will be produced in an electrolytic cell of molten $CaCl_2$ if a current of 0.452 A is passed through the cell for 1.5 hours?

Anode: $2Cl^- (l) \longrightarrow Cl_2 (g) + 2e^-$

Cathode: $Ca^{2+} (l) + 2e^- \longrightarrow Ca (s)$

$Ca^{2+} (l) + 2Cl^- (l) \longrightarrow Ca (s) + Cl_2 (g)$
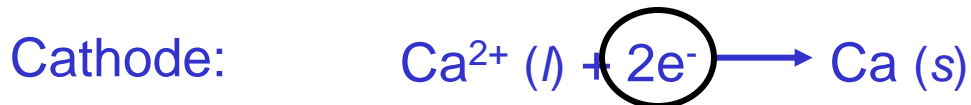
2 mole e^- = 1 mole Ca

96500 = 1mol e , So 2 moles of electrons requires = 2x 96500

Q = I x t = 0.452 x 1.5 x 3600 = 2440 C

193000 C = 1 mole Ca

2440 C   = x

X = 2440 x 1 / 193000 = 0.0126 mol Ca

Mass = 0.0126 x 40 = 0.5 g Ca

Example 6.12:a) In the electrolysis of $CuSO_4$, How much copper is plated out on the cathode by a current of 0.75 A in 10 min ?
b) What the volume of O_2 (g) at STP is liberated ?

a) C = A x t (s) = 0.75 x 10 x 60 = 450C

$$Cu^{++} + 2\ e^{-} \rightarrow\ Cu\ (s)$$

From the equation we have:

2 F = 2 x 96500C ≡ 1 mol Cu = 63.5g Cu

450 C =====➔ ?g of Cu

? g of Cu = 450 x 63.5g / 2 x 96500 = 0.148g Cu

b) $2H_2O \rightarrow O_2(g) + 4H^+ + 4\ e^-$
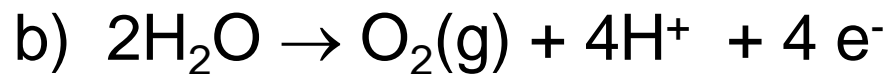
$PV=nRT$

$4\ F \equiv 4 \times 96500\ C = 1\ \text{mole}\ O_2 \equiv 24.5\ L$

$450C \rightarrow ?\ L$

$?L = 450 \times 24.5 / 4 \times 96500$

$\quad = 2.83 \times 10^{-2}\ L\ O_2\ (g)$

Example 6.13: a) What mass of copper is plated in the electrolysis of $CuSO_4$ in the same time 1.0g of Ag is plated in a silver coulometer that arranged in series with $CuSO_4$ cell ?
b) If 1.0 A is passed , how many minutes are required to plate this quantity ?

a) $Ag^+ + e^- \rightarrow Ag(s)$

$Cu^{++} + 2e^- \rightarrow Cu$
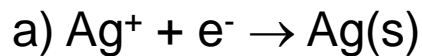
1 mole of e =1 F $\equiv$ 96500 C $\equiv$107.868 g Ag

2 mole of e = 2 F = 2 x 96500 C = 63.5 g

?C $\equiv$ 1.0 g

894.61 C = ? g

C= 1 x 96500 / 107.868 = 894.61 C

? G of Cu = 894.61 x 63.5 / 2x 96600

= 0.2948 g

b) C = A x t_s

894.61 = 1.0 x t_s

t = 894.615 s = 894.615 /60 = 14.9 min