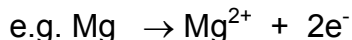


CHAPTER 19 ELECTROCHEMISTRY

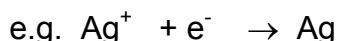
OXIDATION-REDUCTION REACTIONS – Review Pages 126-130

⇒ Oxidation number rules are provided on p. 129.

oxidation: loss of electrons (LEO); oxidation number of atom increases.



reduction: gain of electrons (GER); oxidation number of atom decreases.

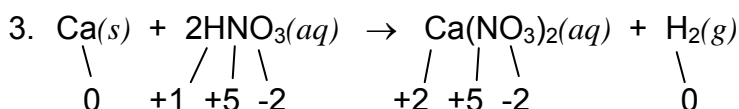


oxidizing agent: substance that causes oxidization; oxidizing agent is reduced.

reducing agent: substance that causes reduction; reducing agent is oxidized.

1. What is the oxidation number for Cl in HClO_4 ? +7

2. What is the oxidation number for Cr in $\text{Cr}_2\text{O}_7^{2-}$? +6



a. Which atom is oxidized (include oxidation #)? Ca (0)

b. Which atom is reduced (include oxidation #)? H^+

c. The atom that is oxidized goes from oxidation number 0 to +2.

d. The atom that is reduced goes from oxidation number +1 to 0.

e. Identify the oxidizing agent HNO_3

f. Identify the reducing agent Ca

19.1 REDOX REACTIONS

Rules for Balancing Redox Reactions Using Ion-Electron Half Reaction Method:

Acidic solution:

- 1) Separate the given reaction into 2 half reactions.
- 2) Balance all atoms except O, H.
- 3) Balance O atoms by adding H_2O 's.
- 4) Balance H atoms by adding H^+ ions.
- 5) Balance the charge by adding electrons (e^-) to the more positive side.
- 6) Multiply each reaction by an integer so that the # electrons gained = # electrons lost.
- 7) Combine the half reactions and simplify by canceling common species.

Basic solution:

- 1) Do steps 1-7 above.
- 2) Note the # of H^+ ions. Add this number of OH^- ions to both sides.
- 3) Combine OH^- and H^+ to form H_2O and simplify the reaction.

***If the equation is correctly balanced, the number of each type of atom and the net charge must be equal for both sides.**

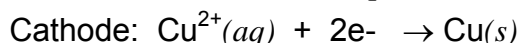
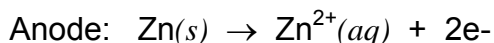
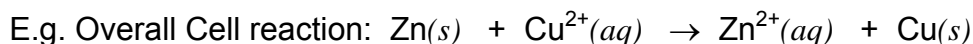
19.2 GALVANIC CELLS

Electrochemical Cell – A system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates electrical energy.

Voltaic cell – Electrochemical cell in which a spontaneous reaction generates electricity.

Cathode - Metal electrode where reduction occurs; mass of electrode increases as metal ions are reduced to form atoms that plate onto the cathode.

Anode - Metal electrode where oxidation occurs; mass of electrode decreases – the electrode is dissolving as metal atoms lose electrons to form ions in solution.

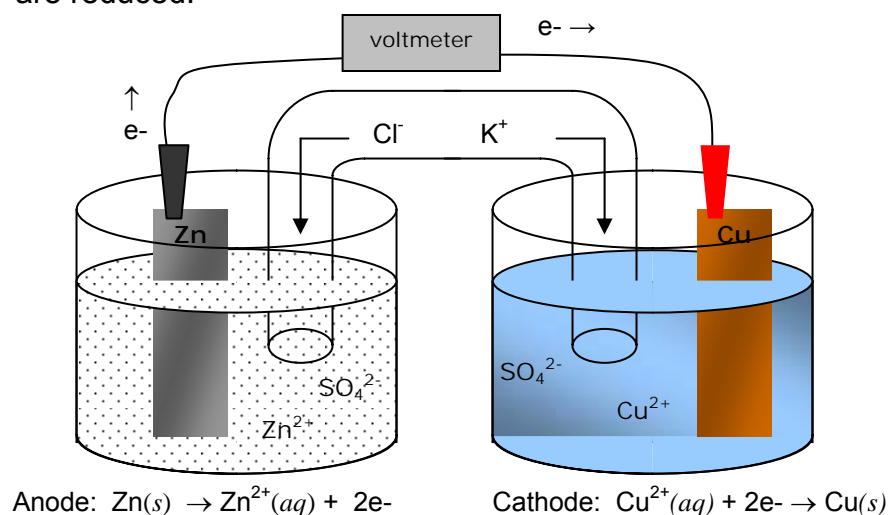


External Circuit - Electrons flow from the anode to the cathode via an external wire.

Salt Bridge - U shaped tube that contains an electrolyte gel or solution and that connects the two half cells in a voltaic cell; ions flow through the bridge to complete the electrical circuit.

Migration of ions maintains charge neutrality in both compartments:

- Anions move into the anodic cell where excess metal cations are formed by oxidation.
- Cations move into the cathodic cell where excess (-) charge builds up as the metal cations are reduced.



In an electrochemical cell, electrons flow from the anode to the cathode because the cathode has a lower electrical potential energy than the anode.

Electromotive Force, emf (E_{cell}): the maximum voltage difference between the electrodes in an electrochemical cell. This is the driving force that pushes electrons away from the anode and towards the cathode.

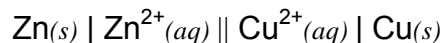
- E_{cell} is also referred to as the cell voltage; this is the cell potential measured in volts.

Notation For Voltaic Cells

| indicates a phase boundary between two phases in the same cell.



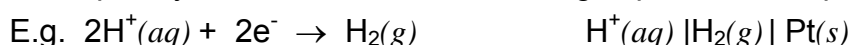
|| denotes the salt bridge that connects the two half reactions.



⇒ The anode is always written on the left side and the cathode on the right side.

⇒ The metal electrodes are written on the ends.

Pt frequently serves as an electrode for gas phase and aqueous reactions:



19.3 STANDARD REDUCTION POTENTIAL

Reduction potential – tendency of a species to be reduced (gain electrons) in a reduction half reaction.

⇒ Can't measure standard potential of a single half reaction; only the potential of the whole cell can be measured.

⇒ By convention, standard reduction potentials, E_{red}° are listed relative to the standard hydrogen electrode (SHE), which was assigned a standard reduction potential of zero. The SHE serves as a reference electrode. It consists of Pt in a tube containing 1 M H^+ solution; H_2 gas at 1 atm pressure is also bubbled through the tube.



⇒ Using other metals and solutions, we can measure E_{cell}° to obtain E_{ox}° .

E_{cell}° is the standard cell potential at 25 °C for 1 M solutions and gases at 1 atm pressure.

$E_{cell}^\circ = E_{red}^\circ(\text{cathode}) + E_{ox}^\circ(\text{anode})$	where $E_{ox}^\circ = -E_{red}^\circ$ for the reverse half reaction.
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• For this equation, make sure you change the sign of E_{ox}° , then add the two potentials.

(Alternately, the textbook uses $E_{cathode}^\circ - E_{anode}^\circ$; this is essentially the same equation because in either case we are making the potential for the anode negative and combining it with the cathode potential.)

Tabulated E_{red}° values for many half reactions are listed in Table 19.1

Important Information from Table 19.1:

- 1) Easiest substance to reduce has the most (+) reduction potential and is the strongest oxidizing agent. F_2 is strongest oxidizing agent; $E_{red}^\circ = +2.87 \text{ V}$. (Weakest oxidizing agent has the most (-) reduction potential; Li^+ has $E_{red}^\circ = -3.05 \text{ V}$).
- 2) Easiest substance to oxidize has the most (-) reduction potential (this is the most (+) oxidation potential) and is the strongest reducing agent. Reducing agents are oxidized (lose e^-), so the reaction occurs in the reverse direction. Li is the strongest reducing agent; $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$, $E_{ox}^\circ = +3.05 \text{ V}$. (Weakest reducing agent is F^-).
- 3) Active metals tend to be good reducing agents; active nonmetals tend to be good oxidizing agents.
- 4) E° is intensive; it does **not** depend on the # of moles involved. We don't need to multiply E° by a factor when a reaction has been multiplied by an integer.

E.g. a) Calculate E_{cell}° for $2\text{Al}(s) + 3\text{I}_2(s) \rightarrow 2\text{Al}^{3+}(aq) + 6\text{I}^-(aq)$ b) Is this reaction spontaneous?



19.4 SPONTANEITY OF REDOX REACTIONS

Electrical work is needed to move a charge through a conductor:

Electrical energy = charge x potential difference

Units: Joules = Coulombs x Volts

F is Faraday's constant; the electrical charge contained in 1 mol of e^- is equal to 96500 C.

$$1 F = \frac{96500 \text{ Coulombs}}{1 \text{ mol } e^-} = \frac{96500 J}{V \cdot \text{mol } e^-}$$

w_{\max} is the maximum work that can be done (maximum electricity obtained). From Chapter 18, we defined the maximum work obtained for a process as ΔG .

$$w_{\max} = -nFE \quad \text{or}$$

$$\Delta G = -nFE$$

n = number of moles of e^- transferred; E = Emf of cell; F = Faraday's constant

\Rightarrow spontaneous reaction: $\Delta G < 0$ and $E > 0$

\Rightarrow nonspontaneous reaction: $\Delta G > 0$ and $E < 0$

Under standard state conditions: $\Delta G^\circ = -nFE^\circ$

From section 18.5: $\Delta G^\circ = -RT \ln K$

Combining the two equations: $-nFE^\circ = -RT \ln K$

$$E^\circ = \frac{RT}{nF} \ln K = \frac{2.303RT}{nF} \log K$$

$R = 8.314 \text{ J/K}\cdot\text{mol}$; $F = 9.65 \times 10^4 \text{ J/V}\cdot\text{mol } e^-$, $T = 298 \text{ K}$

at 298 K

$$E^\circ = \frac{0.0592}{n} \log K$$

19.5 THE EFFECT OF CONCENTRATION ON CELL EMF

For a Voltaic cell the voltage keeps dropping as the spontaneous reaction proceeds right.

\Rightarrow The voltaic cell is functional until $E = 0$ at which point equilibrium is attained.

\Rightarrow The value of E_{cell} depends on the concentrations of reactants and products and on the temperature of the battery.

Recall: $\Delta G = \Delta G^\circ + RT \ln Q$ and $\Delta G^\circ = -nFE^\circ$

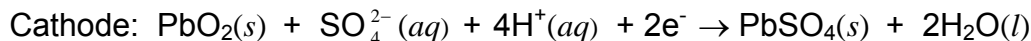
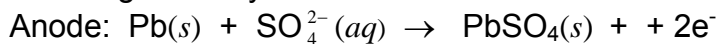
Nernst Equation: $E = E^\circ - \frac{RT}{nF} \ln Q$

at 298 K:
$$E = E^\circ - \frac{0.0592}{n} \log Q$$

19.6 BATTERIES

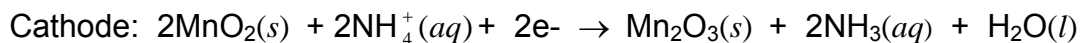
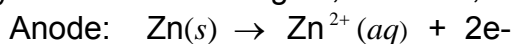
battery- A galvanic cell or a series of combined galvanic cells that can be use as a source of direct electrical current at constant voltage.

1) Lead Storage Battery used in automobiles



⇒ 12 V battery consist of 6 cathode/anode pairs: $E^\circ = 2.04 \text{ V}$ for each individual cell

2) Dry cell used in flashlights, cameras, etc.:



3) Nickel Cadmium Cell

4) Hydrogen-Oxygen Fuel Cell

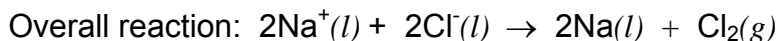
19.8 ELECTROLYSIS

Electrolytic cell - Electrochemical cell in which an electrical current is used to drive a nonspontaneous reaction.

For electrolytic cells:

1. Nonspontaneous reactions require an external current to force the reaction to proceed.
2. Electrons are forced to flow from the anode to the cathode.
3. Electrodes are generally composed of inert metals (E.g. Pt, Au).

E.g. Electrolysis of Molten NaCl:



Applications of electrolysis reactions

- electrolytic plating - protects objects from corrosion
- purification of metals

Quantitative Aspects of Electrolysis

charge = current x time

coulombs = amperes x seconds

coulomb - unit of electrical charge; this is the quantity of charge that passes a point in 1 second when a current of 1 ampere flows.

ampere: unit of electric current; this is the rate of flow of e^- .

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

⇒ Can use the above relationships along with Faraday's constant and the number of moles of e^- transferred to solve quantitative electrochemical problems.