Class 10.1

Electrochemistry

CHEM 102H

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Preliminary Concepts

- Electrochemistry: the electrical generation of, or electrical exploitation of oxidation reduction reactions.
- Electrochemical reactions involve some means of producing or consuming electrons from an external source. The reacting system is an electrochemical cell and the electrical current enters or exits via electrodes.

More Preliminary Concepts

- Electrodes:

  Reduction occurs at one electrode (Cathode)

  Oxidation occurs at the other electrode (Anode)
- Electrical Conduction: movement of electrical charges from one place to another - usually through some medium. If the medium is a wire, it is metallic conduction; if the medium is an electrolyte solution, the conduction is carried out by ions.

Electrochemical Cells

There are two kinds:

- Electrolytic: electrical current is used to drive otherwise nonspontaneous oxidation-reduction (redox) reactions
- Galvanic (Voltaic): Spontaneous redox reactions are used to create electrical current (and do electrical work).

Simple (innocent) Redox Reactions

The simplest Oxidation-Reduction (Redox) reactions are those wherein only electrons are transferred, eg.:

$$Co^{3+}(aq) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe^{3+}(aq)$$

$$Ce^{4+}(aq) + Fe^{2+}(aq) \rightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$$

In these reactions, $Fe^{2+}(aq)$ is the *reducing agent* (*reductant*); $Co^{3+}(aq)$ and $Ce^{4+}(aq)$ are *oxidizing agents* (*oxidants*).

$Fe^{2+}(aq)$ is oxidized (its oxidation state increases)

$Co^{3+}(aq)$ and $Ce^{4+}(aq)$ are reduced (their oxidation states decrease).

More on Redox Reactions

In the previous reactions, the uninvolved ions are not shown, but if they are it doesn't really change what is actually going on. e.g. in aqueous solution, the reaction

$$Co(NO_3)_3 + Fe(NO_3)_2 \rightarrow Co(NO_3)_2 + Fe(NO_3)_3$$

involves transfer of electrons among the metal ions.

Slightly more complicated are reactions involving bond breaking or making, e.g.,

$$2\ Cu^{+}(aq) + I_2(s) \rightarrow 2\ Cu^{2+}(aq) + 2\ I^{-}(aq)$$

$Cu^{+}(aq)$ is oxidized to Cu^{2+} (its oxidation state increases).

I_2 is reduced to I^{-} (oxidation states decreases).

More on Redox Reactions

Sometimes a redox reaction can involve fairly extensive structural rearrangement and atom transfer among the molecules involved:

$Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$ - <u>not</u> balanced

This shows the species that are oxidized and reduced, but doesn't indicate all the chemical species involved. This occurs in acidic solution, so we can assume that "protons" are involved with the oxygen atoms lost by the dichromate ions - and we must take account of the number of electrons transferred:

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

Things that must check: (1) atoms, (2) charge, (3) species shown "make sense" for an acidic solution

Half Reactions

$Co^{3+}(aq) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe^{3+}(aq)$

<u>Half-reactions</u>:

$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$ reduction reaction (Cathode reaction)

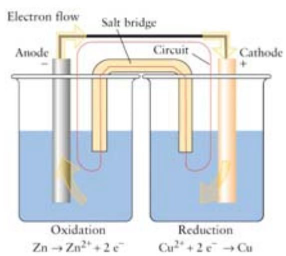
$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ oxidation reaction (Anode reaction)

Even though the electrons are never really "free" we can break up the redox process into half reactions for the purpose of "bookkeeping" in balancing equations.

Examples (Unbalanced)

1. $F_2(g) + H_2O(l) \rightarrow HF(aq) + O_2(g)$
2. $BrO_3^-(aq) + Br^-(aq) + H^+(aq) \rightarrow Br_2(l) + H_2O(l)$
3. $H_2S(g) + SO_2(g) \rightarrow S(s) + H_2O(l)$
4. $Ca_3(PO_4)_3(s) + SiO_2(g) + C(s) \rightarrow P_4(g) + CaSiO_3(s) + CO(g)$
5. $MnO_4^-(aq) + H^+(aq) + Cl^-(aq) \rightarrow Mn^{2+}(aq) + H_2O + Cl_2(g)$
6. $InCl(s) + xs\ H_2O(l) \rightarrow In(s) + In^{3+}(aq) + Cl^-(aq)$

Daniell Cell



Zn|Zn^{2+}(1.0M)||Cu^{2+}(1.0M)|Cu

"Separation" in a Galvanic cell:

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

Cathode reaction:

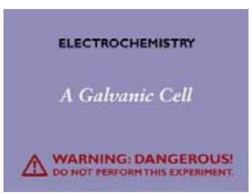
$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$

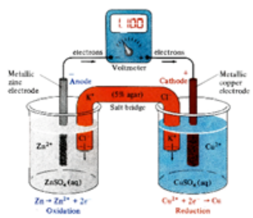
Anode reaction:

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

Note: Despite what the picture seems to imply, electrons don't carry the current in solution!

Galvanic (Voltaic) cells





Zn|Zn^{2+}(1.0M)||Cu^{2+}(1.0M)|Cu

The Free Energy of a redox reaction ($\Delta G°_{rxn}$) can be harnessed by separating the oxidizing and reducing agents and forcing the electrons through a load.

Another Redox Reaction

With a strong oxidant, Cu can donate electrons:

$2\,AgNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2\,Ag(s)$

The net ionic reaction is:

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

Again, the reaction is really an equilibrium, but K_{eq} is huge: $\Delta G°_{rxn} = \Sigma\Delta G°_{f,products} - \Sigma\Delta G°_{f,reactants} = -88.73$ kJ

Half Reactions

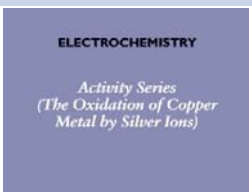
<u>Half-reactions</u>:

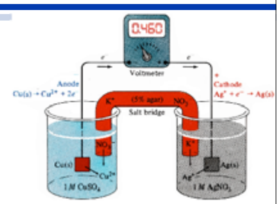
$Ag^+(aq) + e^- \rightarrow Ag(s)$ Cathode reaction (reduction reaction)

$Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$ Anode reaction (oxidation reaction)

Again, the reactions can be “separated” in a Galvanic cell.

Cu/Cu^{2+} anode, Ag/Ag^+ cathode



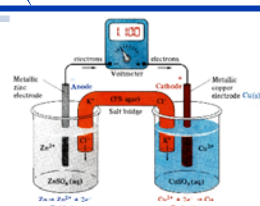


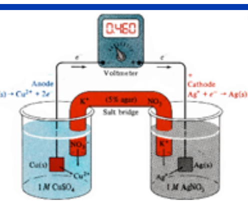
$Cu|Cu^{2+}(1.0M)||Ag^+(1.0M)|Ag$

$2\ Ag^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$

$\Delta G^\circ_{rxn} = \Sigma\Delta G^\circ_{f,products} - \Sigma\Delta G^\circ_{f,reactants} = -88.73\ kJ$

Additivity of Cell Potentials





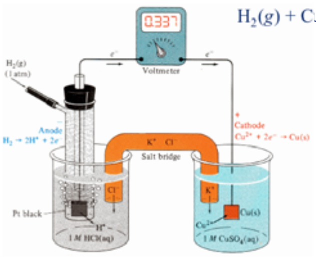
$2\ Ag^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2\ Ag(s)$

$E^\circ_{cell} = 1.100\ V + 0.460\ V = 1.56\ V$ (wired in series)

$\Delta G^\circ_{rxn} = \Sigma\Delta G^\circ_{f,products} - \Sigma\Delta G^\circ_{f,reactants} = -301.28\ kJ$

Standard Hydrogen Electrode, SHE

$Pt|H^+(1.0M), H_2(1\ atm)||Cu^{2+}(1.0M)|Cu$



$H_2(g) + Cu^{2+}(aq) \rightarrow 2\ H^+(aq) + Cu(s)$

$E°_{cell} = 0.337\ V$

All potentials can be referenced to one standard electrode. That electrode is the Standard Hydrogen Electrode shown here.