Electrochemistry

"Redox" or oxidation-reduction reactions involve a change in the oxidation state of the chemical species involved in a chemical reaction. (Review handout on oxidation numbers.)

Example:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ gain of electron(s) = reduction

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ loss of electron(s) = oxidation

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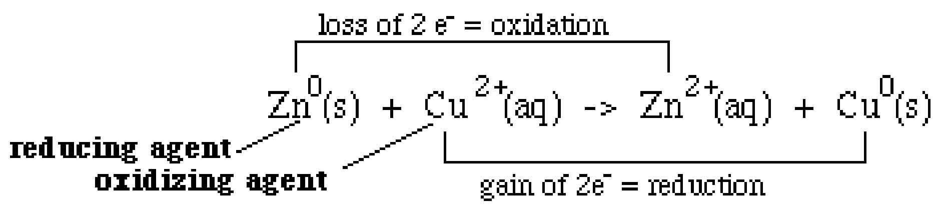
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ overall reaction

The two **half-cell** reactions combine to yield the overall reaction. The number of electrons gained in the reduction half-cell reaction must equal the number of electrons lost in the oxidation half-cell reaction.

The reactant which has undergone **reduction** caused the oxidation of another species and thus is termed the **oxidizing agent**.
The reactant which has undergone **oxidation** caused the reduction of another species and thus is termed the **reducing agent**.



Standard electrode potential ($E^o_{half\text{-}cell}$) is potential associated with a given half-cell reaction when all components are in standard states. The half-cell reaction is written as a reduction. The standard potential is also termed reduction potential. The chemical species closer to the top of the chart is more easily reduced, thus, a stronger oxidizing agent. The chemical species closer to the bottom of the chart is more easily oxidixed, thus, a stronger reducing agent.

Predicting Cell Reactions

Is the reaction $I_2(s) + Cu(s) \rightarrow Cu^{2+}(aq) + 2I^-(aq)$ spontaneous?

(1) Determine the reduction potential values for the two half-cell reactions.

$2e^- + I_2(s) \rightarrow 2I^-(aq)$ $E^o_{red} = +0.54V$

$2e^- + Cu^{2+}(aq) \rightarrow Cu(s)$ $E^o_{red} = +0.34V$

(2) Write oxidation and reduction half-cell reactions. Note the sign change for the oxidation half-cell reaction.

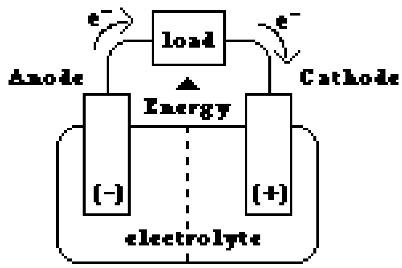
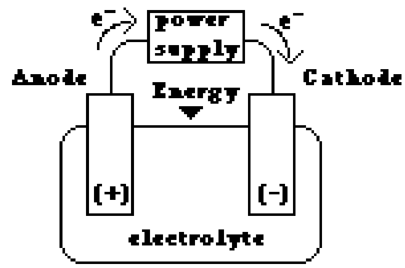
$2e^- + I_2(s) \rightarrow 2I^-(aq)$ $E^o_{red} = +0.54V$

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $E^o_{oxid} = -0.34V$

$I_2(s) + Cu(s) \rightarrow Cu^{2+}(aq) + 2I^-(aq)$ $E^o_{cell} = +0.20V$

So this reaction is spontaneous, E^o_{cell} has a positive value

Comparison of **Voltaic** versus **Electrolytic** Cells

Type of Cell	**Voltaic Cell**	**Electrolytic Cell**
Energy & Reaction Type	Energy is **released** from **spontaneous** redox reaction	Energy is **absorbed** to drive **nonspontaneous** redox reaction
System & Surroundings	System does work on load/ surroundings	Surroundings (power supply) does work on system (cell)
Diagram		
Oxidation = loss of e^- Oxidation half-cell	occurs at anode $X \rightarrow X^+ + e^-$	occurs at anode $A^- \rightarrow A + e^-$
Reduction = gain of e^- Reduction half-cell	occurs at cathode $e^- + Y^+ \rightarrow Y$	occurs at cathode $e^- + B^+ \rightarrow B$
Overall Reaction	$X + Y^+ \rightarrow X^+ + Y$ **$\Delta G < 0$**	$A^- + B^+ \rightarrow A + B$ **$\Delta G > 0$**
Electron flow	anode to cathode	anode to cathode
Charge on anode	**negative**	**positive**
Charge on cathode	**positive**	**negative**
Anions migrate	toward anode	toward anode
Cathode migrate	toward cathode	toward cathode
Requirements	need electrolyte (salt bridge, porous filter)	need electrolyte
Uses	fuel cells, batteries	plating, purifying active metals