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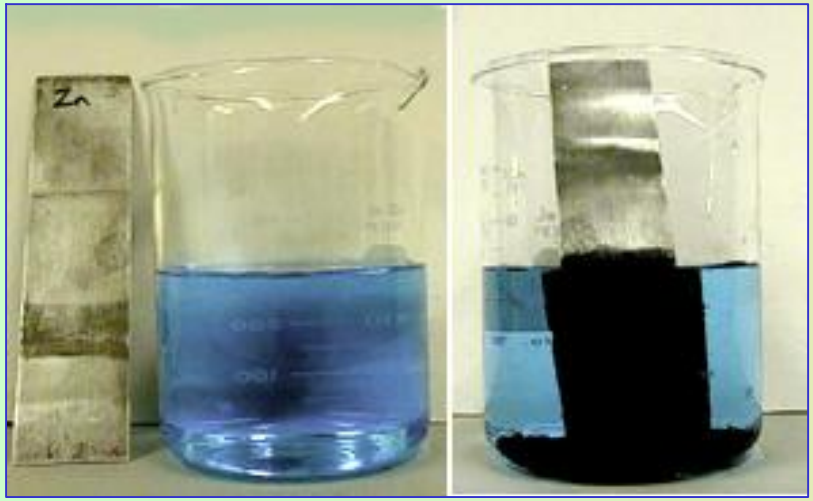
Redox: Spontaneity



When zinc metal is placed in a solution of copper sulfate, the copper is reduced and appears as a black coating on the zinc

http://genchem.chem.wisc.edu/demonstrations/Images/04chemrxn/sponoxred.jpg

Spontaneous reactions

If we know the electrode potentials, we can write a spontaneous redox reaction.

Let's choose a pair of half-reactions:

$Ag^+ (aq) + e^- \rightarrow Ag (s)$ $\quad E^0_{silver} = +0.80$ V

$Sn^{2+} (aq) + 2e^- \rightarrow Sn (s)$ $\quad E^0_{tin} = +0.14$ V

There are two steps involved:

Step #1. Reverse one of the half reactions into an oxidation step such that the sum of the electrode potentials gives a positive E^0_{cell} .

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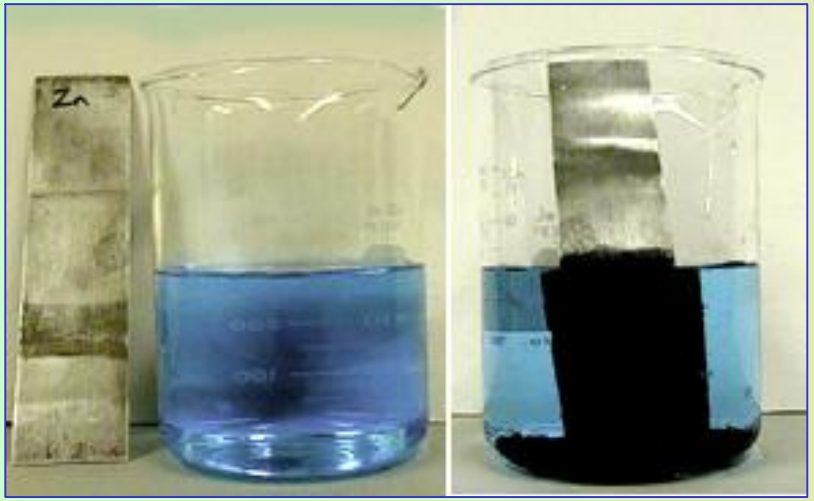

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Spontaneous reactions

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

$Sn (s) \rightarrow Sn^{2+} (aq) + 2e^-$ $\quad -E^0 = -0.14$ V

Step #2. Add the rearranged half-reactions to obtain a balanced overall equation.

$2\ Ag^+ (aq) + 2\ e^- \rightarrow 2\ Ag (s)$ $\quad E^0 = +0.80$ V

$Sn (s) \rightarrow Sn^{2+} (aq) + 2e^-$ $\quad -E^0 = -0.14$ V

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

$E^0_{cell} = +0.66$ V

Note that E^0 for the doubled silver half-reaction remains +0.80 V: changing the balancing coefficients of half-reactions does not change the E^0 value

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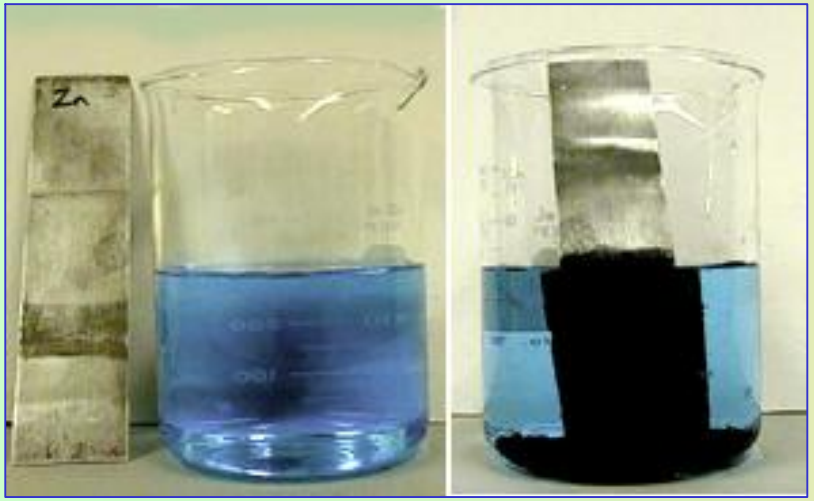

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Spontaneous reactions

If the process produces a **positive cell voltage**, the reaction will be **spontaneous**.

Therefore, this process is spontaneous:

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

$$E^{0}_{cell} = +0.66\ V$$

If the process produces a negative voltage the reaction will not occur in that direction.

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Worked example

Can iodine oxidize silver metal to Ag^+ ions?

DATA:

$$E^0_{I_2/I^-} = +0.54\ V$$

$$E^0_{Ag^+/Ag} = +0.80\ V$$

Solution

Let's write the half-equations for that process:

$I_2 + 2\ e^- \rightarrow 2\ I^-$ $E^0 = 0.54$ V [reduction]

$Ag \rightarrow Ag^+ + e^-$ $E^0 = -0.80$ V [oxidation]

By combining them, we can see that the cell potential is negative and, therefore, the reaction is not going to proceed spontaneously.

$I_2 + 2\ e^- \rightarrow 2\ I^-$ $E^0 = 0.54$ V

$2\ Ag \rightarrow 2\ Ag^+ + 2\ e^-$ $E^0 = -0.80$ V

$I_2 + 2\ Ag \rightarrow 2\ I^- + 2\ Ag^+$ $E^0_{cell} = -0.26$ V

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This photo shows the reaction between calcium metal and water. This is a displacement reaction in which hydrogen is displaced from the water; the bubbles you see are hydrogen gas.

http://www.uncp.edu/home/mcclurem/ptable/ca_2.jpg

Relative reactivities of metals

METALS THAT CAN DISPLACE H_2 FROM ACID

The standard hydrogen half-reaction represents the reduction of H^+ from acids to H_2:

$2\ H^+\ (aq) + 2\ e^- \rightarrow H_2\ (g) \quad E^0 = 0.00\ V$

[reduction]

To see which metals reduce H+ from metals we need the oxidation half-equation:

$2\ H^+\ (aq) + 2\ e^- \rightarrow H_2\ (g) \quad E^0 = 0.00\ V$

$M \rightarrow M^{n+}\ (aq) + n\ e^- \qquad E^0 = -\ E^0_{reduction}$

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TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2\,e^-$	$\longrightarrow 2\,F\,(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	$\longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	1.51	
	$Cl_2(g) + 2\,e^-$	$\longrightarrow 2\,Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$	$\longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	1.33	
	$O_2(g) + 4\,H^+(aq) + 4\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.23	
	$Br_2(l) + 2\,e^-$	$\longrightarrow 2\,Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2\,e^-$	$\longrightarrow 2\,I^-(aq)$	0.54	
	$O_2(g) + 2\,H_2O(l) + 4\,e^-$	$\longrightarrow 4\,OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2\,e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2\,e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2\,e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2\,e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2\,e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2\,e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2\,H_2O(l) + 2\,e^-$	$\longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3\,e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2\,e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

http://wps.prenhall.com/wps/media/objects/602/616516/Media_Assets/Chapter18/Text_Images/FG18_05-01UN.JPG

Relative reactivities of metals

METALS THAT CAN DISPLACE H_2 FROM ACID

The metals Li through Pb, those that lie below the standard hydrogen give a positive cell potential and the reaction of displacement of H_2 will be spontaneous in these cases

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	$Ni^{2+}(aq) + 2\,e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2\,e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2\,e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2\,e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2\,H_2O(l) + 2\,e^-$	$\longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3\,e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2\,e^-$	$\longrightarrow Mg(s)$	−2.37	
Weaker oxidizing agent	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	Stronger reducing agent
	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	

http://wps.prenhall.com/wps/media/objects/602/616516/Media_Assets/Chapter18/Text_Images/FG18_05-01UN.JPG

Relative reactivities of metals

METALS THAT CANNOT DISPLACE H_2 FROM ACID

Metals above the standard hydrogen half-reaction cannot reduce H^+ from acids.

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	$Cu^{2+}(aq) + 2\,e^-$	$\longrightarrow Cu(s)$	0.34	
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	$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2\,e^-$	$\longrightarrow Ni(s)$	−0.26	
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	$Fe^{2+}(aq) + 2\,e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2\,e^-$	$\longrightarrow Zn(s)$	−0.76	
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Weaker oxidizing agent	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	Stronger reducing agent
	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	

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Relative reactivities of metals

METALS THAT CAN DISPLACE OTHER METALS FROM SOLUTION

Any metal lower in the table can reduce the ion of a metal higher up; that is, it can displace that metal from solution.