

Oxidation-Reduction Reactions

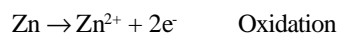
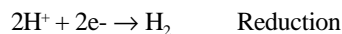
- Zn added to HCl yields the spontaneous reaction
$$\text{Zn}(s) + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g).$$
- The oxidation number of Zn has increased from 0 to 2+.
- The oxidation number of H has reduced from 1+ to 0.
- Zn is oxidized to Zn^{2+} while H^+ is reduced to H_2 .
- H^+ causes Zn to be oxidized and is the oxidizing agent.
- Zn causes H^+ to be reduced and is the reducing agent.
- Note that the reducing agent is oxidized and the oxidizing agent is reduced.

Balancing Oxidation-Reduction Reactions

- *Law of conservation of mass*: the amount of each element present at the beginning of the reaction must be present at the end.
- *Conservation of charge*: electrons are not lost in a chemical reaction.

Half Reactions

• Half-reactions are a convenient way of separating oxidation and reduction reactions.



Balancing Oxidation-Reduction Reactions

Half Reactions

- The half-reactions for
$$\text{Sn}^{2+}(aq) + 2\text{Fe}^{3+}(aq) \rightarrow \text{Sn}^{4+}(aq) + 2\text{Fe}^{2+}(aq)$$
are
$$\text{Sn}^{2+}(aq) \rightarrow \text{Sn}^{4+}(aq) + 2\text{e}^-$$
$$2\text{Fe}^{3+}(aq) + 2\text{e}^- \rightarrow 2\text{Fe}^{2+}(aq)$$
- Oxidation: electrons are products.
- Reduction: electrons are reagents.

Balancing Equations by the Method of Half Reactions

- Consider the titration of an acidic solution of $\text{Na}_2\text{C}_2\text{O}_4$ (sodium oxalate, colorless) with KMnO_4 (deep purple).
- MnO_4^- is reduced to Mn^{2+} (pale pink) while the $\text{C}_2\text{O}_4^{2-}$ is oxidized to CO_2 .
- The equivalence point is given by the presence of a pale pink color.
- If more KMnO_4 is added, the solution turns purple due to the excess KMnO_4 .

Balancing Equations by the Method of Half Reactions in acid

1. Write down the two half reactions.
2. Balance each half reaction:
 - a. First with elements other than H and O.
 - b. Then balance O by adding water.
 - c. Then balance H by adding H^+ .
 - d. Finish by balancing charge by adding electrons.
3. Make the number of electrons in each half-reaction equal by multiplying each half reaction by an integer.
4. Add the reactions together and simplify.
5. Check!

Balancing Equations for Reactions Occurring in Basic Solution

- We use OH^- and H_2O rather than H^+ and H_2O .
- The same method as above is used, but OH^- is added to “neutralize” the H^+ used.

Voltaic Cells

- The energy released in a spontaneous redox reaction is used to perform electrical work.
- Voltaic or galvanic cells are devices in which electron transfer occurs via an external circuit.
- Voltaic cells are spontaneous.
- If a strip of Zn is placed in a solution of CuSO_4 , Cu is deposited on the Zn and the Zn dissolves by forming Zn^{2+} .

Voltaic Cells

- Voltaic cells consist of
 - Anode: $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-$
 - Cathode: $\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$
 - Salt bridge (used to complete the electrical circuit): cations move from anode to cathode, anions move from cathode to anode.
- The two solid metals are the electrodes (cathode and anode).

As oxidation occurs, Zn is converted to Zn^{2+} and $2e^-$. The electrons flow towards the anode where they are used in the reduction reaction.

- We expect the Zn electrode to lose mass and the Cu electrode to gain mass.
- “Rules” of voltaic cells:
 1. At the anode electrons are products. (Oxidation)
 2. At the cathode electrons are reagents. (Reduction)
 3. Electrons cannot swim.
- Electrons flow from the anode to the cathode.
- Therefore, the anode is negative and the cathode is positive.
- Electrons cannot flow through the solution, they have to be transported through an external wire. (Rule 3.)

Voltaic Cells

- Anions and cations move through a porous barrier or salt bridge.
- Cations move into the cathodic compartment to neutralize the excess negatively charged ions (Cathode: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$, so the counterion of Cu is in excess).
- Anions move into the anodic compartment to neutralize the excess Zn^{2+} ions formed by oxidation.

Cell EMF

- The flow of electrons from anode to cathode is spontaneous.
- Electrons flow from anode to cathode because the cathode has a lower electrical potential energy than the anode.
- Potential difference: difference in electrical potential. Measured in volts.
- One volt is the potential difference required to impart one joule of energy to a charge of one coulomb:

Cell EMF

$$1 \text{ V} = \frac{1 \text{ J}}{1 \text{ C}}$$

- Electromotive force (emf) is the force required to push electrons through the external circuit.
- Cell potential: E_{cell} is the emf of a cell.
- For 1M solutions at 25 °C (standard conditions), the standard emf (standard cell potential) is called E°_{cell} .

Standard Reduction (Half-Cell) Potentials

- Convenient tabulation of electrochemical data.
- Standard reduction potentials, E°_{red} are measured relative to the standard hydrogen electrode (SHE).

The SHE is the cathode. It consists of a Pt electrode in a tube placed in 1 M H^+ solution. H_2 is bubbled through the tube.

- For the SHE, we assign $2\text{H}^+(aq, 1M) + 2e^- \rightarrow \text{H}_2(g, 1 \text{ atm})$
- E°_{red} of zero.
- The emf of a cell can be calculated from standard reduction potentials:

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- The emf of a cell can be calculated from standard reduction potentials:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}}(\text{cathode}) - E^{\circ}_{\text{red}}(\text{anode})$$

TABLE 20.1 Standard Reduction Potentials in Water at 25 °C

Potential (V)	Reduction Half-Reaction
+2.87	$\text{F}_2(g) + 2e^- \rightarrow 2\text{F}^-(aq)$
+1.51	$\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$
+1.36	$\text{Cl}_2(g) + 2e^- \rightarrow 2\text{Cl}^-(aq)$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l)$
+1.23	$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$
+1.06	$\text{Br}_2(l) + 2e^- \rightarrow 2\text{Br}^-(aq)$
+0.96	$\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l)$
+0.80	$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$
+0.77	$\text{Fe}^{3+}(aq) + e^- \rightarrow \text{Fe}^{2+}(aq)$
+0.68	$\text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2\text{O}_2(aq)$
+0.59	$\text{MnO}_4^-(aq) + 2\text{H}_2\text{O}(l) + 3e^- \rightarrow \text{MnO}_2(s) + 4\text{OH}^-(aq)$
+0.34	$\text{I}_2(s) + 2e^- \rightarrow 2\text{I}^-(aq)$
+0.40	$\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^-(aq)$
+0.34	$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$
0	$2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$
-0.28	$\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$
-0.44	$\text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s)$
-0.76	$\text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s)$
-0.83	$2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$
-1.66	$\text{Al}^{3+}(aq) + 3e^- \rightarrow \text{Al}(s)$
-2.71	$\text{Na}^+(aq) + e^- \rightarrow \text{Na}(s)$
-3.05	$\text{Li}^+(aq) + e^- \rightarrow \text{Li}(s)$

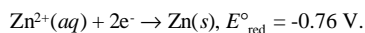
Consider $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-$.

We measure E_{cell} relative to the SHE (cathode):

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}}(\text{cathode}) - E^{\circ}_{\text{red}}(\text{anode})$$

$$0.76 \text{ V} = 0 \text{ V} - E^{\circ}_{\text{red}}(\text{anode}).$$

- Therefore, $E^{\circ}_{\text{red}}(\text{anode}) = -0.76 \text{ V}$.
- Standard reduction potentials must be written as reduction reactions:



- Since $E^{\circ}_{\text{red}} = -0.76 \text{ V}$ we conclude that the reduction of Zn^{2+} in the presence of the SHE is not spontaneous.
- The oxidation of Zn with the SHE is spontaneous.
- Changing the stoichiometric coefficient does not affect E°_{red} .
- Therefore, $2\text{Zn}^{2+}(aq) + 4e^- \rightarrow 2\text{Zn}(s), E^{\circ}_{\text{red}} = -0.76 \text{ V}$.
- Reactions with $E^{\circ}_{\text{red}} > 0$ are spontaneous reductions relative to the SHE.

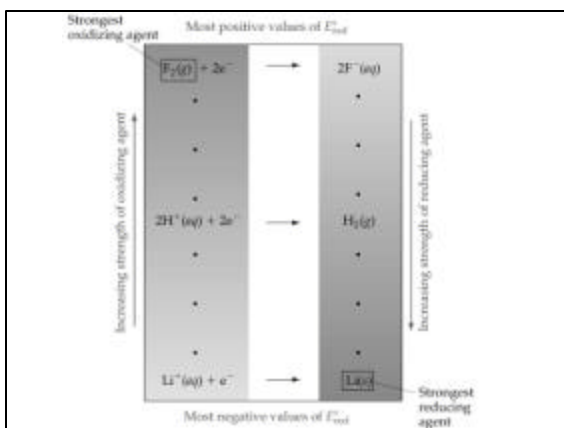
- Reactions with $E_{\text{red}}^{\circ} < 0$ are spontaneous oxidations relative to the SHE.
- The larger the difference between E_{red}° values, the larger E_{cell}° .
- In a voltaic (galvanic) cell (spontaneous) E_{red}° (cathode) is more positive than E_{red}° (anode).
- Recall

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode})$$

Cell EMF

Oxidizing and Reducing Agents

- The more positive E_{red}° the stronger the oxidizing agent on the left.
- The more negative E_{red}° the stronger the reducing agent on the right.
- A species on the higher to the left of the table of standard reduction potentials will spontaneously oxidize a species that is lower to the right in the table.
- That is, F_2 will oxidize H_2 or Li ; Ni^{2+} will oxidize $\text{Al}(\text{s})$.



Spontaneity of Redox Reactions

- In a voltaic (galvanic) cell (spontaneous) E_{red}° (cathode) is more positive than E_{red}° (anode) since

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode})$$
- More generally, for any electrochemical process

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{reduction process}) - E_{\text{red}}^{\circ}(\text{oxidation process})$$
- A positive E° indicates a spontaneous process (galvanic cell).
- A negative E° indicates a nonspontaneous process.

Spontaneity of Redox Reactions

EMF and Free-Energy Change

- We can show that

$$\Delta G = -nFE$$
- ΔG is the change in free-energy, n is the number of moles of electrons transferred, F is Faraday's constant, and E is the emf of the cell.
- We define

$$1F = 96,500 \text{ C/mol} = 96,500 \text{ J/V}\cdot\text{mol}$$
- Since n and F are positive, if $\Delta G > 0$ then $E < 0$.

Effect of Concentration on Cell EMF

The Nernst Equation

- A voltaic cell is functional until $E = 0$ at which point equilibrium has been reached.
- The point at which $E = 0$ is determined by the concentrations of the species involved in the redox reaction.
- The Nernst equation relates emf to concentration using

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$
 and noting that

$$-nFE = -nFE^{\circ} + RT \ln Q$$

Effect of Concentration on Cell EMF

The Nernst Equation

- This rearranges to give the Nernst equation:

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

- The Nernst equation can be simplified by collecting all the constants together using a temperature of 298 K:

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

- (Note that change from natural logarithm to base-10 log.)
- Remember that n is number of moles of electrons.

Effect of Concentration on Cell EMF

Concentration Cells

- We can use the Nernst equation to generate a cell that has an emf based solely on difference in concentration.
- One compartment will consist of a concentrated solution, while the other has a dilute solution.
- Example: $1.00 M Ni^{2+}(aq)$ and $1.00 \times 10^{-3} M Ni^{2+}(aq)$.
- The cell tends to equalize the concentrations of $Ni^{2+}(aq)$ in each compartment.
- The concentrated solution has to reduce the amount of $Ni^{2+}(aq)$ (to $Ni(s)$), so must be the cathode.

Effect of Concentration on Cell EMF

Cell EMF and Chemical Equilibrium

- A system is at equilibrium when $\Delta G = 0$.
- From the Nernst equation, at equilibrium and 298 K ($E = 0$ V and $Q = K_{eq}$):

$$0 = E^\circ - \frac{0.0592}{n} \ln K_{eq}$$

$$\log K_{eq} = \frac{nE^\circ}{0.0592}$$

Batteries

Lead-Acid Battery

- A 12 V car battery consists of 6 cathode/anode pairs each producing 2 V.
- Cathode: PbO_2 on a metal grid in sulfuric acid:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$
- Anode: Pb:

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

Lead-Acid Battery

- The overall electrochemical reaction is

$$PbO_2(s) + Pb(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

for which

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{red}(cathode) - E^\circ_{red}(anode) \\ &= (+1.685 \text{ V}) - (-0.356 \text{ V}) \\ &= +2.041 \text{ V.} \end{aligned}$$

- Wood or glass-fiber spacers are used to prevent the electrodes from touching.

Alkaline Battery

- Anode: Zn cap:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
- Cathode: MnO_2 , NH_4Cl and C paste:

$$2NH_4^+(aq) + 2MnO_2(s) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + 2H_2O(l)$$
- The graphite rod in the center is an inert cathode.
- For an alkaline battery, NH_4Cl is replaced with KOH .

Alkaline Battery

- Anode: Zn powder mixed in a gel:

$$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^{-}$$
- Cathode: reduction of MnO_2 .

Batteries

Fuel Cells

- Direct production of electricity from fuels occurs in a fuel cell.
- On *Apollo* moon flights, the $\text{H}_2\text{-O}_2$ fuel cell was the primary source of electricity.
- Cathode: reduction of oxygen:

$$2\text{H}_2\text{O}(l) + \text{O}_2(g) + 4e^{-} \rightarrow 4\text{OH}^{-}(aq)$$
- Anode:

$$2\text{H}_2(g) + 4\text{OH}^{-}(aq) \rightarrow 4\text{H}_2\text{O}(l) + 4e^{-}$$

Corrosion

Corrosion of Iron

- Since $E^{\circ}_{\text{red}}(\text{Fe}^{2+}) < E^{\circ}_{\text{red}}(\text{O}_2)$ iron can be oxidized by oxygen.
- Cathode: $\text{O}_2(g) + 4\text{H}^{+}(aq) + 4e^{-} \rightarrow 2\text{H}_2\text{O}(l)$.
- Anode: $\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^{-}$.
- Dissolved oxygen in water usually causes the oxidation of iron.
- Fe^{2+} initially formed can be further oxidized to Fe^{3+} which forms rust, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}(s)$.

Corrosion of Iron

- Oxidation occurs at the site with the greatest concentration of O_2 .

Preventing Corrosion of Iron

- Corrosion can be prevented by coating the iron with paint or another metal.
- Galvanized iron is coated with a thin layer of zinc.

Corrosion

Preventing Corrosion of Iron

- Zinc protects the iron since Zn is the anode and Fe the cathode:

$$\text{Zn}^{2+}(aq) + 2e^{-} \rightarrow \text{Zn}(s), E^{\circ}_{\text{red}} = -0.76 \text{ V}$$

$$\text{Fe}^{2+}(aq) + 2e^{-} \rightarrow \text{Fe}(s), E^{\circ}_{\text{red}} = -0.44 \text{ V}$$
- With the above standard reduction potentials, Zn is easier to oxidize than Fe.

Corrosion

Preventing Corrosion of Iron

- To protect underground pipelines, a sacrificial anode is added.
- The water pipe is turned into the cathode and an active metal is used as the anode.
- Often, Mg is used as the sacrificial anode:

$$\text{Mg}^{2+}(aq) + 2e^{-} \rightarrow \text{Mg}(s), E^{\circ}_{\text{red}} = -2.37 \text{ V}$$

$$\text{Fe}^{2+}(aq) + 2e^{-} \rightarrow \text{Fe}(s), E^{\circ}_{\text{red}} = -0.44 \text{ V}$$

Electrolysis

Electrolysis of Aqueous Solutions

- Nonspontaneous reactions require an external current in order to force the reaction to proceed.
- Electrolysis reactions are nonspontaneous.
- In voltaic and electrolytic cells:
 - reduction occurs at the cathode, and
 - oxidation occurs at the anode.
 - However, in electrolytic cells, electrons are forced to flow from the anode to cathode.

Electrolysis of Aqueous Solutions

In electrolytic cells the anode is positive and the cathode is negative. (In galvanic cells the anode is negative and the cathode is positive.)

- Example, decomposition of molten NaCl.
- Cathode: $2\text{Na}^+(l) + 2e^- \rightarrow 2\text{Na}(l)$
- Anode: $2\text{Cl}(l) \rightarrow \text{Cl}_2(g) + 2e^-$.
- Industrially, electrolysis is used to produce metals like Al.

Electrolysis

Electroplating

- Consider an active Ni electrode and another metallic electrode placed in an aqueous solution of NiSO_4 :
- Anode: $\text{Ni}(s) \rightarrow \text{Ni}^{2+}(aq) + 2e^-$
- Cathode: $\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$.
- Ni plates on the inert electrode.
- Electroplating is important in protecting objects from corrosion.

Electrolysis

Quantitative Aspects of Electrolysis

- We want to know how much material we obtain with electrolysis.
- Consider the reduction of Cu^{2+} to Cu.
 - $\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$.
 - 2 mol of electrons will plate 1 mol of Cu.
 - The charge of 1 mol of electrons is 96,500 C (1 F).
 - Since $Q = It$, the amount of Cu can be calculated from the current (I) and time (t) taken to plate.



Electrolysis

Electrical Work

- Free-energy is a measure of the maximum amount of useful work that can be obtained from a system.
- We know
$$\Delta G = w_{\text{max}}$$
$$\Delta G = -nFE$$
$$\therefore w_{\text{max}} = -nFE$$
- If work is negative, then work is performed by the system and E is positive.

Electrolysis

Electrical Work

- The emf can be thought about as a measure of the driving force for a redox process.
- In an electrolytic cell and external source of energy is required to force the reaction to proceed.
- In order to drive the nonspontaneous reaction the external emf must be greater than E_{cell} .
- From physics: work has units watts:
$$1 \text{ W} = 1 \text{ J/s.}$$