Oxidation & Reduction

Oxidation and Reduction reactions (redox)

e^-

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

Metal + Nonmetal : Transfer of electrons

$Na \rightarrow Na^+ + e^-$ Oxidized

$Cl + e^- \rightarrow Cl^-$ Reduced

Oxidation: a loss of electrons.

Reduction: a gain of electrons.

Oxidation States (Oxidation numbers)

Assigning charges to the various atoms in a compound.

Keep track of electrons in redox reactions.

Rules for assigning oxidation states

1. Charge (oxidation state) of a uncombined element is zero.

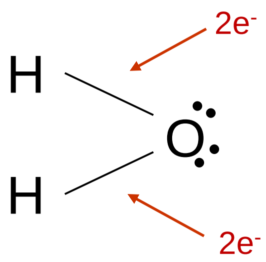
H_2, Cl_2, Ar, Na, K

2. The oxidation state of a monatomic ion is the same as its charge.

NaCl	Na^+ Cl^-	$\longrightarrow$	Na: +1 Cl: -1
Al_2S_3	Al^{3+} S^{2-}	$\longrightarrow$	Al: +3 S: -2

Rules for assigning oxidation states

For covalent compounds assume the most electronegative atom controls or possesses the shared electrons.



O gained two e^- from H → Oxidation state = -2

H lost one e^- → Oxidation state = +1

4. The oxidation state of H is +1 and O is -2 in covalent compounds.

Exception: Peroxide (O_2^{2-}) = -1 H_2O_2

Rules for assigning oxidation states

The most electronegative elements: F, O, N, and Cl

F: -1, O: -2, N: -3, Cl: -1

5. If two of these elements are found in the same compound, we assign them in order of electronegativity.

F > O > N > Cl

NO_2

O: $2 \times (-2) = -4$ So N must be +4

Rules for assigning oxidation states

6. Sum of oxidation states = 0 in a neutral compound.

7. Sum of oxidation states = charge in an ion.

NO_3^- O: $3 \times (-2) = -6$

N must be +5 for an overall charge of -1 for NO_3^-.

SO_4^{2-} O: $4 \times (-2) = -8$

S must be +6 for an overall charge of -2 for SO_4^{2-}.

Rules for assigning oxidation states

$K_2Cr_2O_7$	K = +1; Cr = +6; O = –2
CO_3^{2-}	C = +4; O = –2
MnO_2	Mn = +4; O = –2
PCl_5	P = +5; Cl = –1
SF_4	S = +4; F = –1

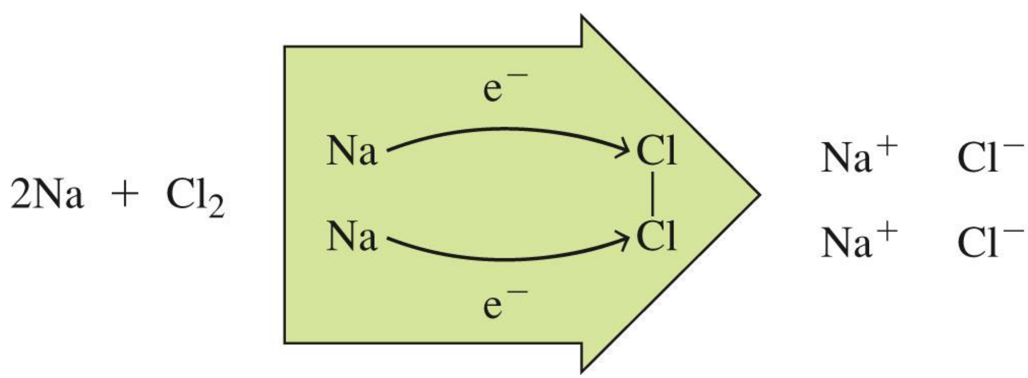
Oxidation-Reduction Reactions

In some redox reactions ions are produced.

e^-

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

Oxidation state:	0	0	+1 -1
	Element	Element	Na^+ Cl^-



Oxidation-Reduction Reactions

In some redox reactions ions are not produced (all nonmetals).

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

Oxidation state: -4 +1 (each H) 0 +4 -2 (each O) +1 (each H) -2

$$\underset{-4}{CH_4} \rightarrow \underset{+4}{CO_2} + 8e^-$$

C is oxidized.
CH_4 is a reducing agent.

$$\underset{0}{2O_2} + 8e^- \rightarrow CO_2 + 2H_2O$$

4(-2) = -8

O is reduced.
O_2 is an oxidizing agent.

Oxidation-Reduction Reactions

Oxidation: is an increase in oxidation state (a loss of e^-).

Reduction: is a decrease in oxidation state (a gain of e^-).

Oxidizing agent (electron acceptor): the reactant containing the element that is reduced.

Reducing agent (electron donor): the reactant containing the element that is oxidized.

$$CH_4 \rightarrow CO_2 + 8e^-$$

C is oxidized.
CH_4 is a reducing agent.

$$2O_2 + 8e^- \rightarrow CO_2 + 2H_2O$$

O is reduced.
O_2 is an oxidizing agent.

Half-Reaction Method for balancing

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

$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$ Reduction half-reaction

$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$ Oxidation half-reaction

Number of Electrons lost	must be equal to	Number of Electrons gained

Multiply by 2: $2Ce^{4+}(aq) + 2e^- \rightarrow 2Ce^{3+}(aq)$

$$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$$

$$2Ce^{4+}(aq) + Sn^{2+}(aq) + \cancel{2e^-} \rightarrow 2Ce^{3+}(aq) + Sn^{4+}(aq) + \cancel{2e^-}$$

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

Half-Reaction Method for balancing

1. Identify and write the equations for the oxidation and reduction half–reactions.

2. For each half–reaction:
   A. Balance all the elements except H and O.
   B. Balance O using H_2O.
   C. Balance H using H^+.
   D. Balance the charge using electrons.

3. If necessary, multiply one or both balanced half–reactions by an integer to equalize the number of electrons transferred in the two half–reactions.

4. Add the half–reactions, and cancel identical species.

5. Check that the elements and charges are balanced.

Half-Reaction Method for balancing

$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$

How can we balance this equation?

1. Separate into half-reactions.

2. Balance elements except H and O.

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

$$SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq)$$

Half-Reaction Method for balancing

3. Balance O's with H_2O and H's with H^+.

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

$$H_2O(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2H^+(aq)$$

4. How many electrons are involved in each half-reaction? Balance the charges.

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

$$H_2O(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$

Half-Reaction Method for balancing

5. Multiply whole reactions by a whole number to make the number of electrons gained equal the number of electrons lost.

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

$$3 \times (\ H_2O(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-\ )$$

6. Combine half-reactions cancelling out those reactants and products that are the same on both sides, especially the electrons.

$$\cancel{6e^-} + \overset{8}{14H^+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + \overset{4}{7H_2O}(aq)$$

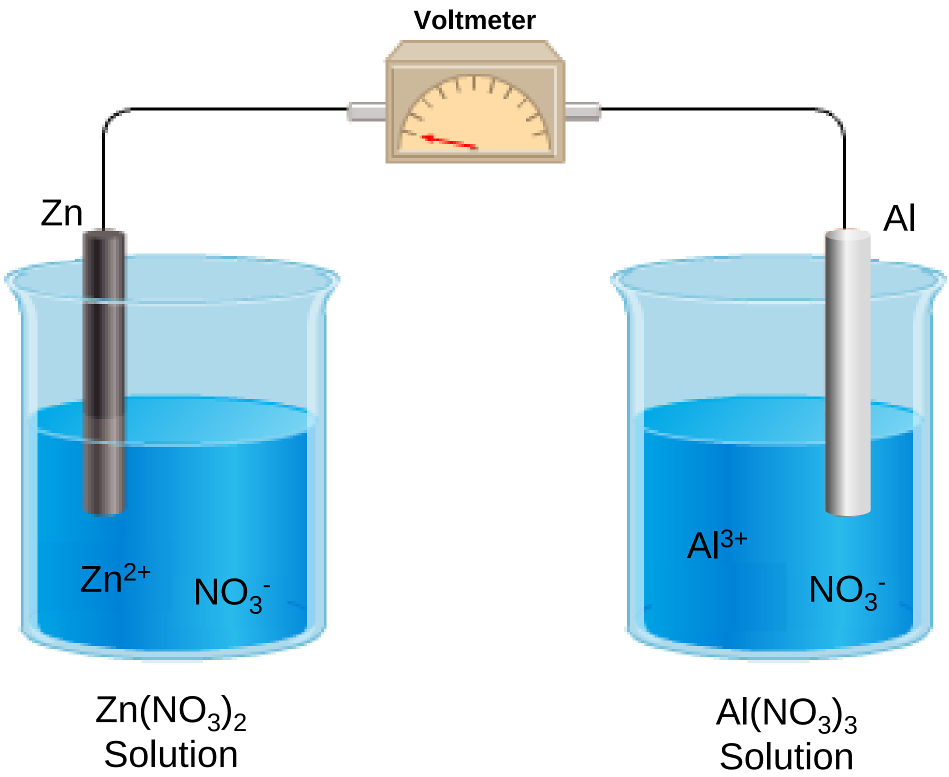
$$\cancel{3H_2O}(aq) + 3SO_3^{2-}(aq) \rightarrow 3SO_4^{2-}(aq) + \cancel{6H^+}(aq) + \cancel{6e^-}$$

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

Electrochemistry

Galvanic Cell

Electrochemistry



Standard Reduction Potentials

Potential (in volt): pressure of e^- to flow from one electrode to the other in a battery.

Increasing strength of oxidation agents

Ionic Concentration 1 M in water at 25°C, 1 atm.

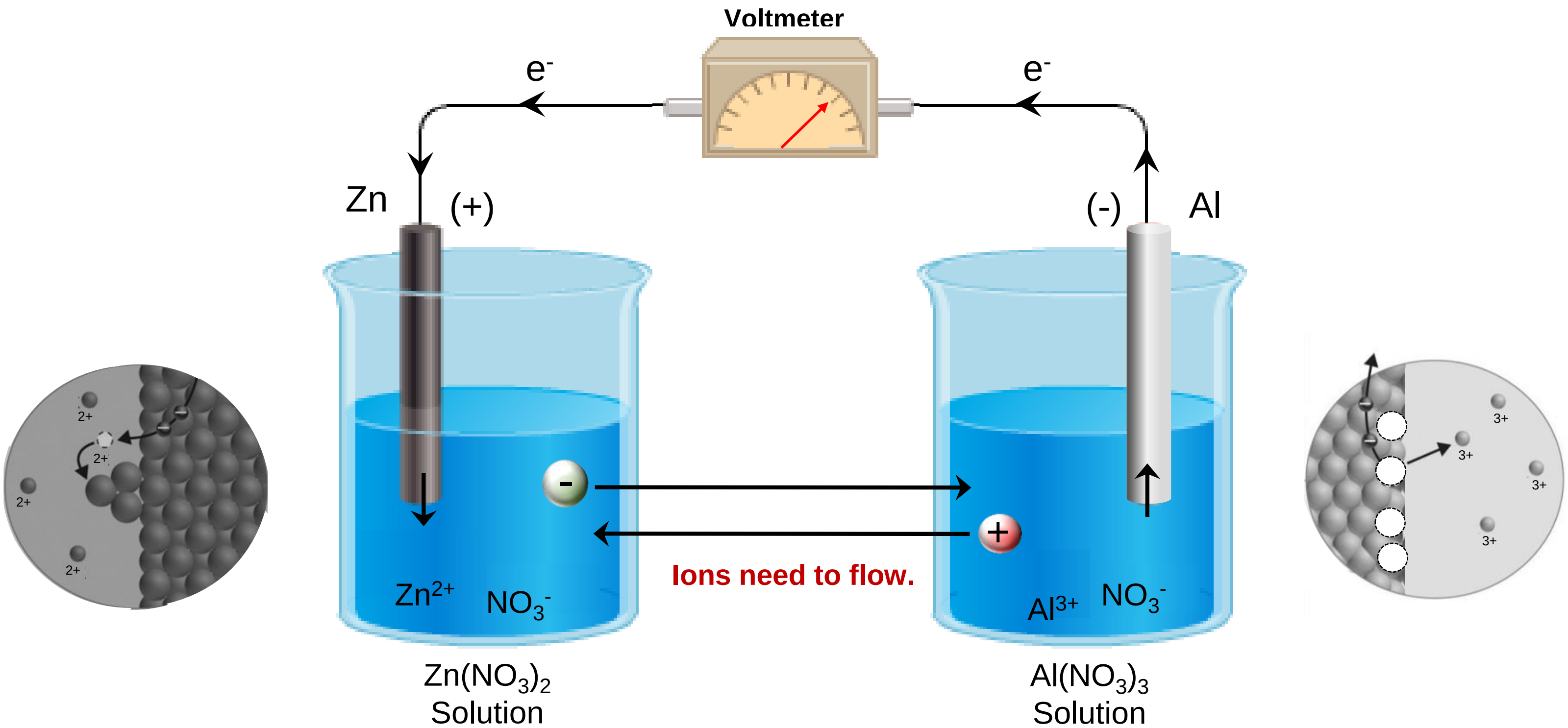
Half-Reaction	E° (volts)	Half-Reaction	E° (volts)
$F_2(g) + 2e^- \rightarrow 2F^-$	+2.87	$Pb^{2+} + 2e^- \rightarrow Pb(s)$	−0.13
$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51	$Sn^{2+} + 2e^- \rightarrow Sn(s)$	−0.14
$Au^{3+} + 3e^- \rightarrow Au(s)$	+1.50	$Ni^{2+} + 2e^- \rightarrow Ni(s)$	−0.26
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	+1.36	$Co^{2+} + 2e^- \rightarrow Co(s)$	−0.28
$14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.23	$Fe^{2+} + 2e^- \rightarrow Fe(s)$	−0.45
$4H^+ + O_2(g) + 4e^- \rightarrow 2H_2O$	+1.23	$Cr^{3+} + 3e^- \rightarrow Cr(s)$	−0.74
$4H^+ + MnO_2(s) + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.22	$\boxed{Zn^{2+} + 2e^- \rightarrow Zn(s)}$	$\boxed{-0.76}$
$Br_2(l) + 2e^- \rightarrow 2Br^-$	+1.09	$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g)$	−0.83
$Hg^{2+} + 2e^- \rightarrow Hg(l)$	+0.85	$Mn^{2+} + 2e^- \rightarrow Mn(s)$	−1.19
$Ag^+ + e^- \rightarrow Ag(s)$	+0.80	$\boxed{Al^{3+} + 3e^- \rightarrow Al(s)}$	$\boxed{-1.66}$
$Hg_2^{2+} + 2e^- \rightarrow 2Hg(l)$	+0.80	$Mg^{2+} + 2e^- \rightarrow Mg(s)$	−2.37
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77	$Na^+ + e^- \rightarrow Na(s)$	−2.71
$I_2(s) + 2e^- \rightarrow 2I^-$	+0.54	$Ca^{2+} + 2e^- \rightarrow Ca(s)$	−2.87
$Cu^+ + e^- \rightarrow Cu(s)$	+0.52	$Sr^{2+} + 2e^- \rightarrow Sr(s)$	−2.89
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	+0.34	$Ba^{2+} + 2e^- \rightarrow Ba(s)$	−2.91
$4H^+ + SO_4^{2-} + 2e^- \rightarrow SO_2(aq) + 2H_2O$	+0.17	$Cs^+ + e^- \rightarrow Cs(s)$	−2.92
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15	$K^+ + e^- \rightarrow K(s)$	−2.93
$\boxed{2H^+ + 2e^- \rightarrow H_2(g)}$	$\boxed{0.00}$	$Rb^+ + e^- \rightarrow Rb(s)$	−2.98
		$Li^+ + e^- \rightarrow Li(s)$	−3.04

Increasing strength of reducing agents

Zn is a better oxidizing agent → It is reduced

Al is a better reducing agent → It is oxidized

Galvanic Cell (Electrochemical Battery)



Cathode

Reduction

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

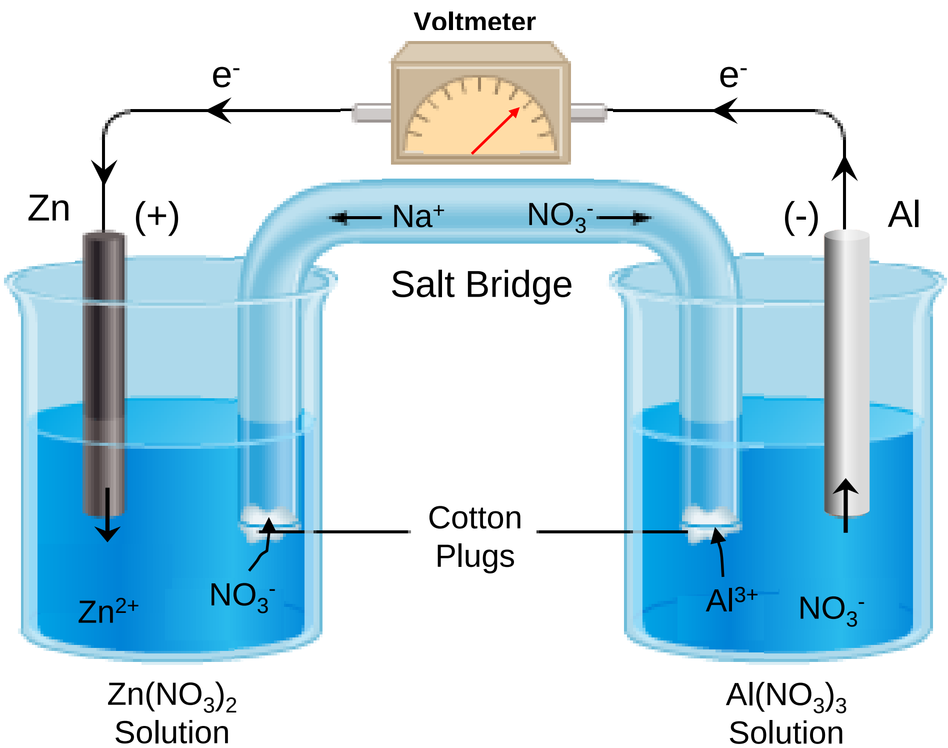
$Al(s) \rightarrow Al^{3+} + 3e^{-}$

Anode

Oxidation

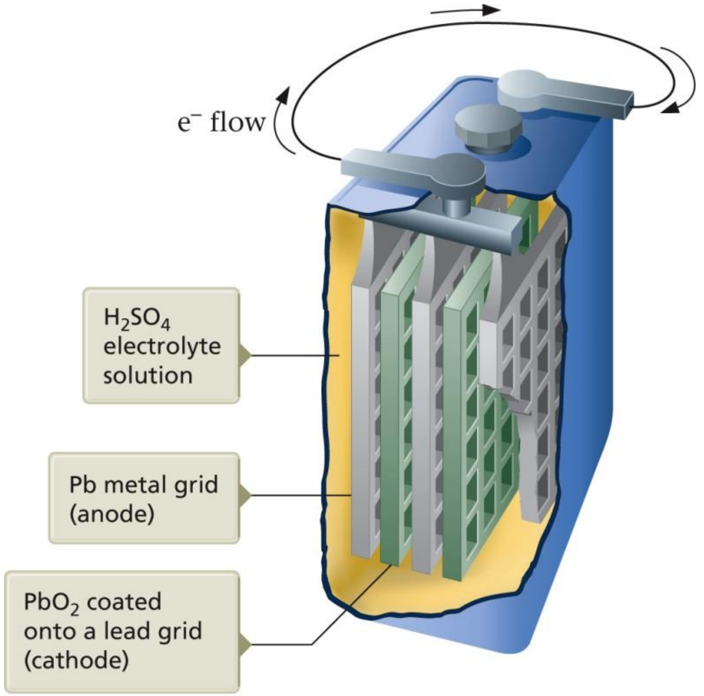
Redox reaction

Galvanic Cell (Electrochemical Battery)



Chemical Reaction ⇨ Electric Energy

Lead Storage Battery



Anode reaction – oxidation

$$Pb + H_2SO_4 \rightarrow PbSO_4 + 2H^+ + 2e^-$$

Cathode reaction – reduction

$$PbO_2 + H_2SO_4 + 2e^- + 2H^+ \rightarrow PbSO_4 + 2H_2O$$

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

Dry Cell Battery (Acid Version)

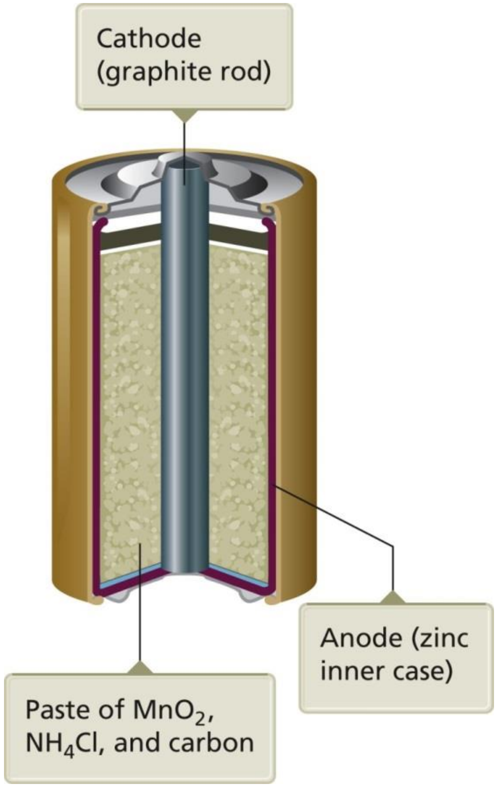
They do not contain a liquid electrolyte.

Anode reaction – oxidation

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$

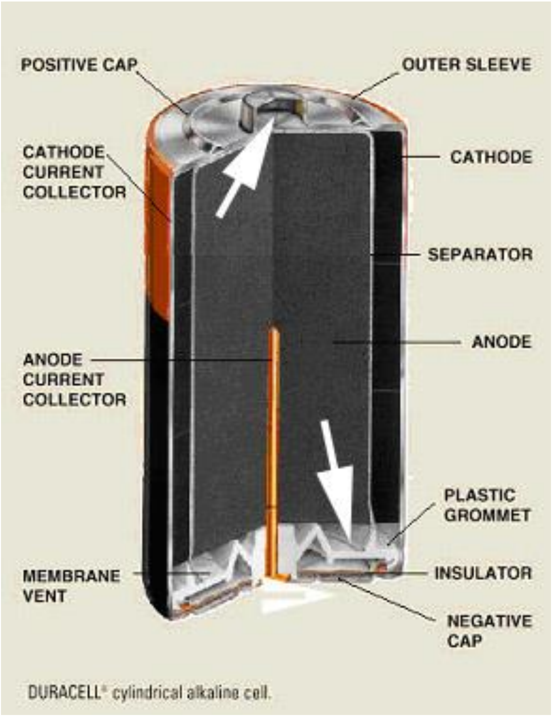
Cathode reaction – reduction

$$2NH_4^{+} + 2MnO_2 + 2e^{-} \rightarrow Mn_2O_3 + 2NH_3 + 2H_2O$$



Dry Cell Battery (Alkaline Version)

They do not contain a liquid electrolyte.



Anode reaction – oxidation

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$$

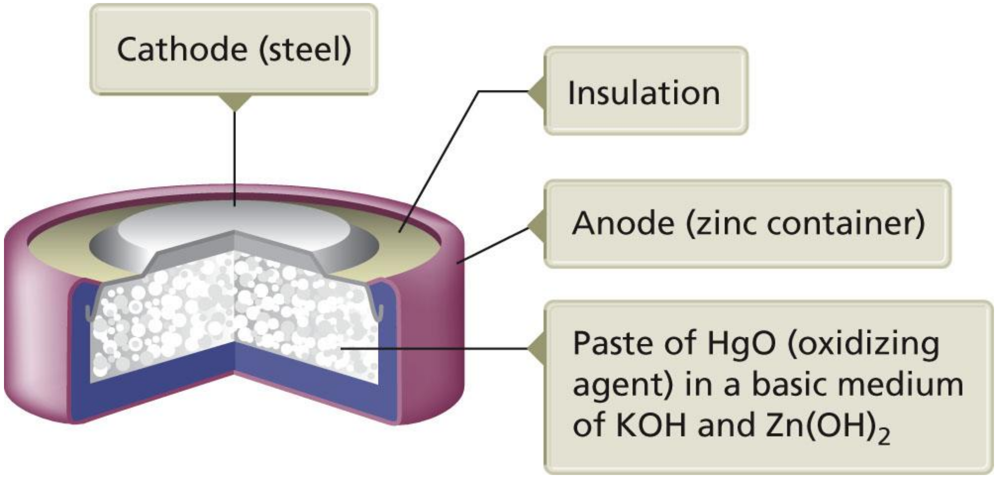
Cathode reaction – reduction

$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$$

Dry Cell Battery (Other Version)

Silver cell – Zn anode, Ag_2O cathode

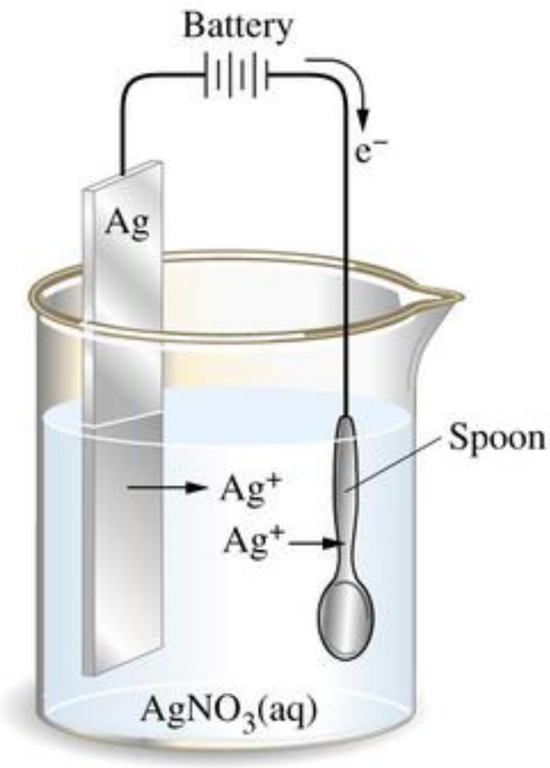
Mercury cell – Zn anode, HgO cathode



Nickel-cadmium – Rechargeable

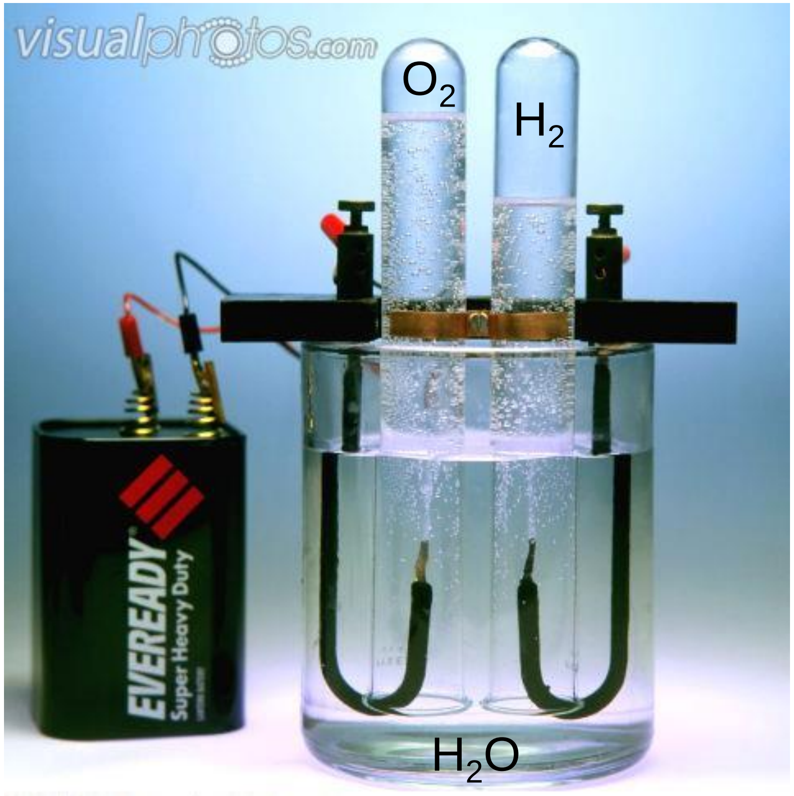
Electrolysis

Nonspontaneous



Electric Energy ⟹ Chemical Reaction

Electrolysis



$$2H_2O(l) \xrightarrow{\text{Forced electric current}} 2H_2(g) + O_2(g)$$