Unit 11– ELECTROCHEMISTRY – GLUE INS

N42

Rules for Assigning Oxidation Numbers

1. Any uncombined element is 0.
2. Monatomic ion equals the charge on the ion.
3. The more-electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.
4. Fluorine in a compound is always -1
5. Oxygen is -2 unless it is combined with F, when it is +2, or it is in a peroxide, such as H_2O_2, when it is -1
6. Hydrogen in most of its compounds is +1 unless it is combined with a metal, in which case it is -1
7. In compounds, the elements of groups 1 and 2 as well as aluminum have oxidation numbers +1, +2 and +3 respectively.
8. The sum of the oxidation numbers of all atoms in a neutral compound is 0.
9. The sum of the oxidation numbers of all atoms in a polyatomic ion equals charge of the ion.

Mnemonics

LEO goes GER
Loss of Electrons is Oxidation
Gain of Electrons is Reduction

OIL RIG
Oxidation is Loss of Electrons
Reduction is Gain of Electrons

$$1\,A = \frac{1\,Coulomb}{1\,second} = \frac{6.242 \times 10^{18} e^-}{1\,second}$$

$$1\,Volt = \frac{1\,Joule}{1\,Coulomb} \qquad 1\,Faraday = \frac{96,500\,Coulombs}{1\,mol\,e^-}$$

Balancing Redox Equations

More complicated than balancing normal reactions.

You have to balance the electrons, not just the atoms!

Steps

1. Assign oxidation numbers to determine which things are oxidized and which are reduced.
2. Split the rxn into two halves – oxidation half and reduction half. Include electrons.
3. Balance the atoms.
4. Balance the charge by balancing the number of electrons.
5. Add half reactions back together, simplify, and CHECK.

Anode is Oxidation

Reduction at the Cathode

Anode The electrode where oxidation occurs

Cathode The electrode where reduction occurs

Oxidation and Reduction Recap

Oxidation is the process that occurs when
- the oxidation number of an element increases,
- an element loses electrons,
- a compound adds oxygen,
- a compound loses hydrogen, or
- a half-reaction has electrons as products.

Reduction is the process that occurs when
- the oxidation number of an element decreases,
- an element gains electrons,
- a compound loses oxygen,
- a compound gains hydrogen, or
- a half-reaction has electrons as reactants.

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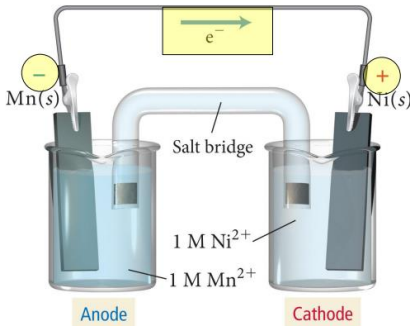
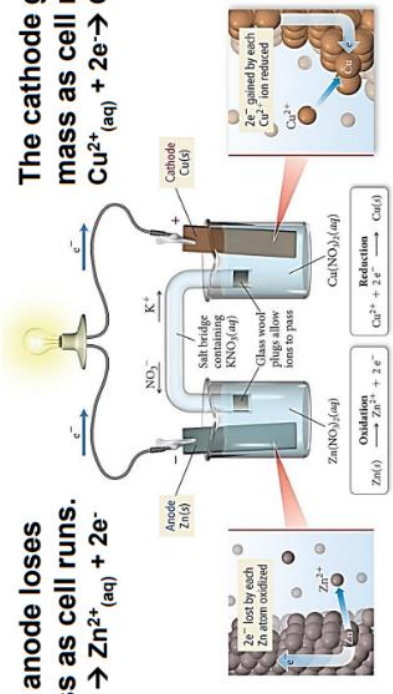


Galvanic
- Converts chemical energy into electrical energy.
- Positive cell potential, E°_{cell} = +
- Spontaneous, negative free energy difference, ΔG = -
- Anode = - and Cathode = +
- Electrons supplied by the chemical being oxidized.
- Electrons flow from anode to cathode.

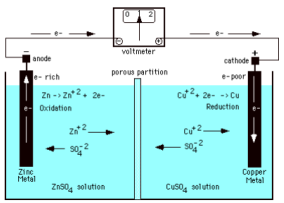
Electrolytic
- Converts electrical energy into chemical energy
- Negative cell potential, E°_{cell} = -
- NOT spontaneous, positive free energy difference, ΔG = +
- Anode = + and Cathode = -
- Electrons supplied by an external source
- Electrons enter from the cathode and come out at the anode.

The cathode gains mass as cell runs. $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

The anode loses mass as cell runs. $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$



Line Notation



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

Anode material | Anode solution || Cathode solution | Cathode material

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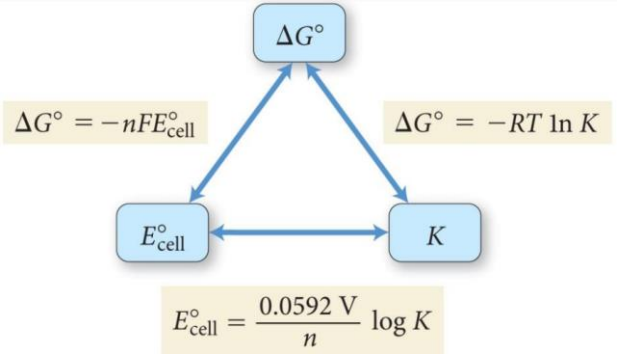


In all electrochemical cells, oxidation occurs at the anode, reduction occurs at the cathode.

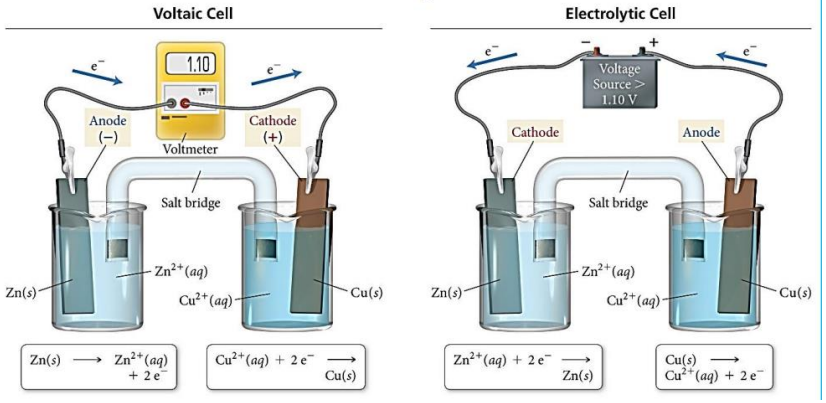
In voltaic cells

- Anode is the source of electrons and has a (−) charge.
- Cathode draws electrons and has a (+) charge.

In electrolytic cells

- Electrons are drawn off the anode, so it must have a place to release the electrons—the positive terminal of the battery.
- Electrons are forced toward the anode, so it must have a source of electrons—the negative terminal of the battery.

Voltaic versus Electrolytic Cells

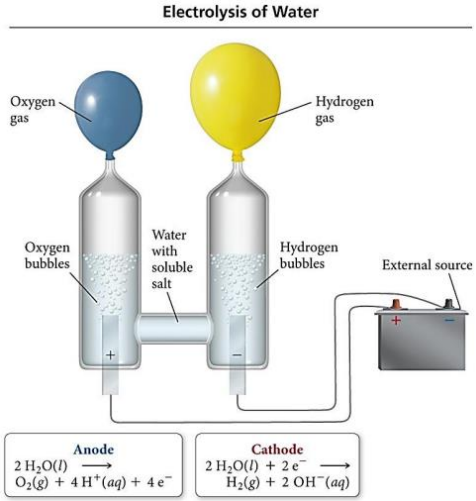


Standard Conditions and Nonstandard Conditions for the Zn/Cu Galvanic Cell

Equation	$E°$	$\Delta G°$	K
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	+1.10 V	−212 kJ/mol	1.5×10^{37}

$$E = E^{o} - \frac{RT}{nF} \ln Q \qquad Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Farther Away From Equilibrium than Standard Conditions	Standard Conditions	Closer To Equilibrium than Standard Conditions	At Equilibrium The cell is "dead"
$Q < 1$	$Q = 1$	$Q > 1$	$Q = K = 1.5 \times 10^{37}$
$E > E°$	$E = E°$	$E < E°$	E = zero
$[Zn^{2+}] < [Cu^{2+}]$ decreased [product] or increased [reactant] compared to standard conditions	$[Zn^{2+}] = [Cu^{2+}]$ [product] = [reactant]	$[Zn^{2+}] > [Cu^{2+}]$ increased [product] or decreased [reactant] compared to standard conditions	$[Zn^{2+}] >> [Cu^{2+}]$



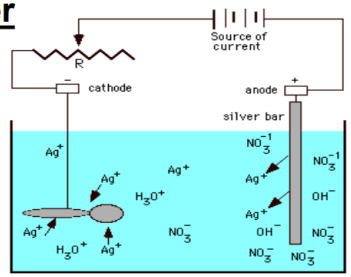
Electroplating of Silver

Anode reaction:

Ag → Ag⁺ + e⁻

Cathode reaction:

Ag⁺ + e⁻ → Ag



Electroplating requirements:

1. Solution of the plating metal
2. Anode made of the plating metal
3. Cathode with the object to be plated
4. Source of current