ELECTROCHEMISTRY

Electrochemistry involves the relationship between **electrical energy** and **chemical energy.**

OXIDATION-REDUCTION REACTIONS

SPONTANEOUS REACTIONS

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Examples: voltaic cells, batteries.

NON-SPONTANEOUS REACTIONS

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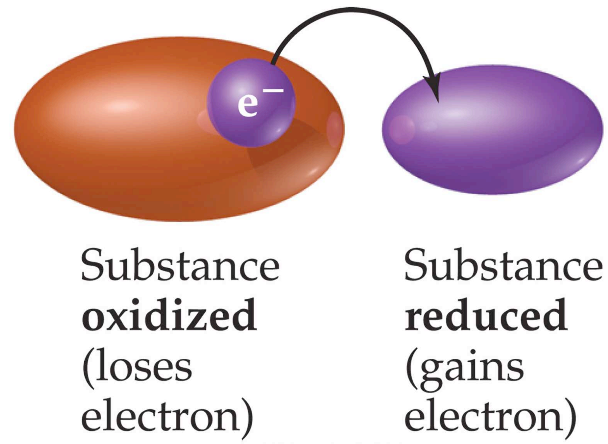
Examples: electrolysis, electrolytic cells.

QUANTITATIVE ASPECTS OF ELECTROCHEMICAL REACTIONS

Oxidation/Reduction



OXIDATION-REDUCTION

Oxidation = ____________________.
An oxidizing agent is a substance that causes oxidation (and is itself reduced).

Reduction = ____________________.
A reducing agent is a substance that causes reduction (and is itself oxidized).

LAnOx and GRedCat!

LAnOx: Lose electrons / Anode / Oxidized

GRedCat: Gain electrons / Reduced / Cathode

Rules for determining Oxidation States

1. **Oxidation state of atom in elemental form is zero.**
   e.g. Cl_2 O_2 P_4 C(s) S_8
2. **The oxidation number of a monatomic ion equals its charge.**
3. **Some elements have "common" oxidation numbers that can be used as reference in determining the oxidation numbers of other atoms in the compound.**

Alkali metals		**+1**
Alkaline earth metals		**+2**
Fluorine		**–1**
O	**usually**	**–2**
(peroxides (-1) & superoxides possible)		
H	**usually**	**+1**
(Hydrides: metal-H compounds (–1))		
Cl, Br, I	**almost always**	**–1**

4. **Sum of oxidation numbers is equal to overall charge of molecule or ion:**
   - **For a neutral compound the sum of oxidation numbers equals zero.**
   - **For a polyatomic ion, the sum of the oxidation numbers is equal to the charge on the ion.**
5. **Shared electrons are assigned to the more electronegative atom of the pair:**
   - **more electronegative atom will have a negative oxidation number.**

Single Displacement Reactions

Oxidation reduction reactions

$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

Ionic equation:

Net ionic equation

What is oxidized?

What is reduced?

What is the oxidizing agent?

What is the reducing agent?

Oxidation/Reduction

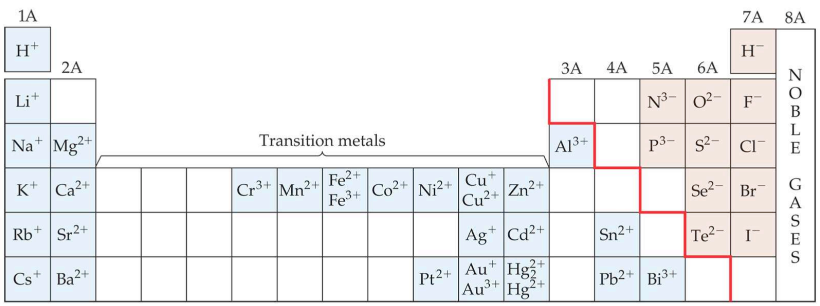
$$2NiO(OH)(s) + Cd(s) + 2H_2O(l) \rightarrow 2Ni(OH)_2(s) + Cd(OH)_2(s)$$

What is reduced?

What is oxidized?

Periodic trends in oxidation states

Driving force: atoms tend to lose or gain electrons to achieve an **inert gas configuration**



For main group elements (s and p block)

The **highest possible positive oxidation state** is equal to the ____________________!

(transition metals don't follow the rules)

Periodic trends in oxidation states

Can we rationalize these common oxidation states?

H -1 +1								
						O -2,-1	**F** -1	
			Al 3+		**P** 3+ 5+	**S** -2 +2,4,6	**Cl** -1 +1,3,5,7	
			Ga +3	**Ge** +2 +4	**As** 3+ 5+	**Se** -2 +2,4,6	**Br** -1 +1,3,5,7	
			In +1 +3	**Sn** +2 +4	**Sb** +3 +5	**Te** -2 +2,4,6	**I** -1 +1,3,5,7	
			Tl +1 +3	**Pb** **+2** +4	**Bi** +3 +5			

Blue: most common oxidation states in Group 5

BALANCING REDOX REACTIONS

1. Write incomplete half-reactions.

2. Balance each half-reaction separately.
   a. Balance atoms undergoing redox.
   b. Balance remaining atoms
      i. Add H_2O to balance oxygens.
      ii. Add H^+ to balance hydrogens.

3. Balance charges by adding electrons.

4. Multiply each half-reaction so that the *same number of electrons* are involved in the reduction and the oxidation.

5. Add the half-reactions.

6. In basic solutions, add OH^- to neutralize H^+

Half Reactions

Write the balanced half-reactions for:

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

1) **oxidation:** electrons are "products"

2) **reduction:** electrons are "reagents"

What is the balanced overall reaction?

Balancing Redox Reactions
in ACID SOLUTION

$$C(s) + HNO_3 \rightarrow NO_2 + CO_2 + H_2O$$

Balancing Redox Reactions
in BASE SOLUTION

$$PbO_2 + Cl^- + OH^- \rightarrow Pb(OH)_3^- + ClO^-$$

Balancing Redox Reactions

When the following reaction is balanced (in acid) what is the coefficient in front of water?

$NO_2(g) + H_2O(l) \rightarrow NO_3^-(aq) + NO(g)$

Circle your answer! 1 2 3 4

Spontaneous Redox Reactions

Is this reaction SPONTANEOUS?

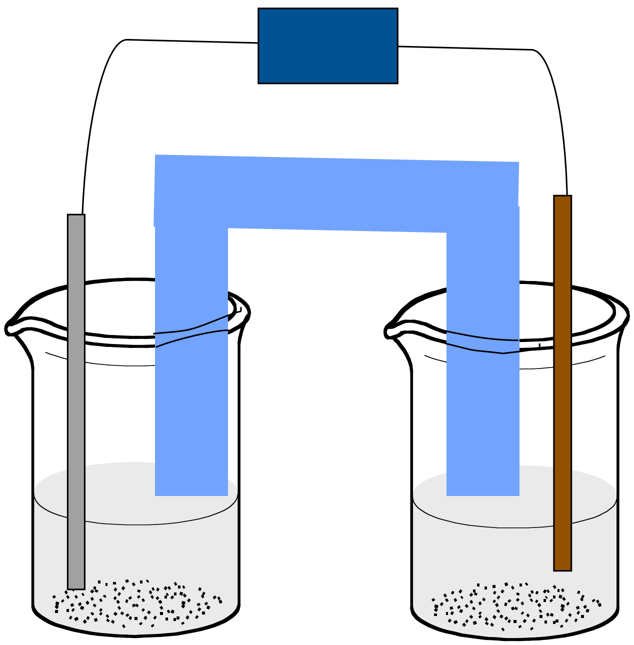
$$Zn^0(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu^0(s)$$

E released in a spontaneous redox reaction

Definition of Voltaic or galvanic cells:

Voltaic Cell

$Zn^0(s) + Cu(NO_3)_2(aq) \rightarrow Zn(NO_3)_2(aq) + Cu^0(s)$



What happens in a Voltaic Cell?

$Zn^0(s) + Cu(NO_3)_2(aq) \rightarrow Zn(NO_3)_2(aq) + Cu^0(s)$

What happens at the cathode?

What happens at the anode?

Which electrode will increase in mass?

Which electrode will decrease in mass?

Which direction do the electrons flow?

Why is a Salt Bridge needed?

Cathode: $Cu^{2+} + 2e^{-} \rightarrow Cu$

Cations move (how?____________) into the _________________ to neutralize the excess negatively charged spectator ions

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

Anions move (how?____________) into the __________________ to neutralize the excess Zn^{2+} ions formed by oxidation.

The electrons flow towards the cathode (through _______________) where they are used in the _____________ reaction.

Voltaic Cell

Voltaic cells consist of:

Anode: what process?___________________

Cathode: what process?___________________

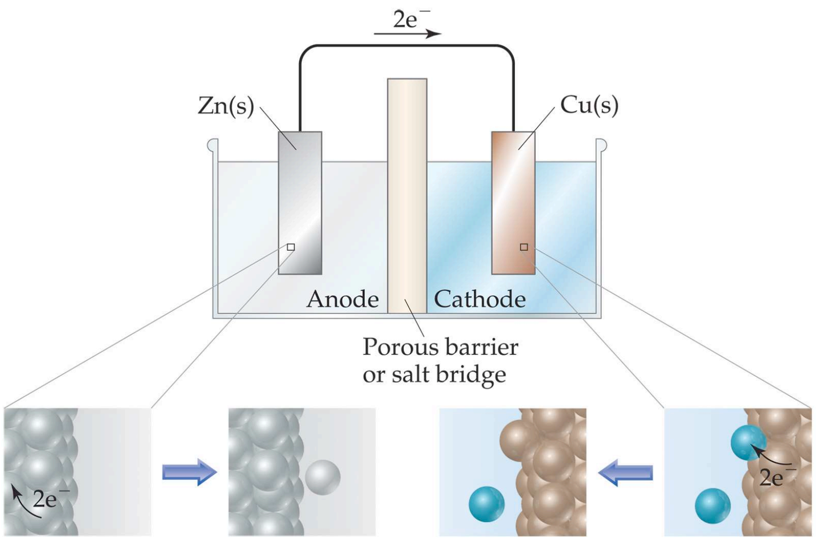
The two solid metals (cathode and anode) are the _____________ .

What does the Salt bridge or porous divider do?

"Rules" of voltaic cells:

1. At the anode electrons are products.
2. At the cathode electrons are reagents.
3. Electrons cannot swim!

Electrode at the Molecular Level



Voltaic Cell Potential

Spontaneous electrochemical reaction

Voltage:

1V =

This potential energy difference is called:

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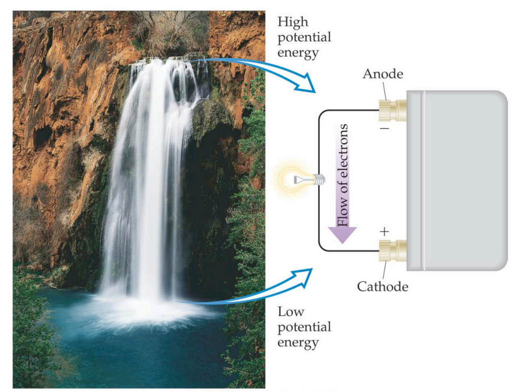

VOLTAIC CELL VOLTAGE

Cell voltage (EMF or E_{cell}) is the measure of ______________________

E_{cell} is an *Intensive* property:

E_{cell} is energy *per* electron

Cell voltage depends on:

1)

2)

3)

The more spontaneous a reaction,

-
-
-

STANDARD POTENTIAL FOR AN ELECTROCHEMICAL CELL

The *standard potential*:__________ potential (voltage) generated when reactants and products of a redox reaction are in their ***standard states***.

Standard States:
T = 25°C.
Gases, P = 1 atm partial pressure
[Solutions] = 1M

It is convenient to break redox reactions into half reactions.

When all substances are in standard state: Standard half-cell potentials

TABLE 20.1 Standard Reduction Potentials in Water at 25°C

Potential (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

HALF-CELL POTENTIAL

The *half-cell potential* is the potential associated with the half-reaction.

Rules for half-cell potentials:

1. **The sum of two half-cell potentials in a cell equals the overall cell potential:**

2. **For any half-reaction:**

3. **Standard half-cell is a hydrogen electrode:**

$$E°_{1/2}(oxid) = E°_{1/2}(reduc) = 0\ V\ (for\ SHE)$$