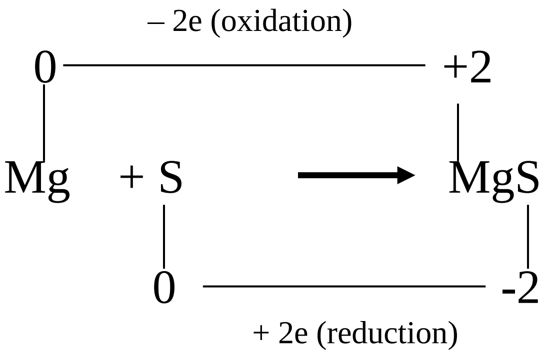
OXIDATION-REDUCTION REACTIONS

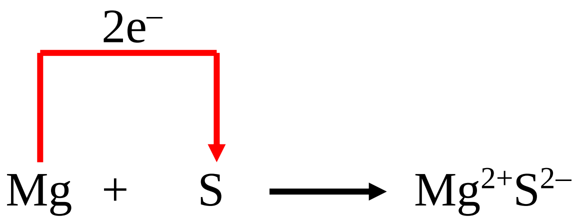
- Some of the most important reaction in chemistry are ***oxidation-reduction (redox)*** reactions. In these reactions, electrons transfer from one reactant to the other. The rusting of iron, bleaching of hair and the production of electricity in batteries involve redox reactions.

- Synthesis, decomposition, single replacement and combustion reactions are all examples of redox reactions. In these reactions, one substance loses electrons (**oxidized**) while another substance gain electrons (**reduced**). Therefore, ***oxidation*** is defined as loss of electrons, while ***reduction*** is defined as gain of electrons.

- For example in reaction of magnesium metal and sulfur to form magnesium sulfide:



Mg :	- is **oxidized** (loses electrons) - causes the reduction of S - called **Reducing Agent**	S:	- is **reduced** (gains electrons) - causes the oxidation of Mg - called **Oxidizing Agent**



- **Oxidation-Reduction** reactions can be represented by half-reactions:

<u>**Oxidation Half-Reaction**</u>	<u>**Reduction Half-Reaction**</u>
$Mg \longrightarrow Mg^{2+} + 2\,e^-$	$S + 2e^- \longrightarrow S^{2-}$

OXIDATION NUMBERS OR STATES

- Identifying the oxidation-reduction nature of reactions between metals and non-metals is straight forward because of ion formation. However, redox reactions that occur between two non-metals is more difficult to characterize since no ions are formed.

- Chemists have devised a scheme to track electrons before and after a reaction in order to simplify this process. In this scheme, a number (***oxidation state or number***) is assigned to each element assuming that the shared electrons between two atoms belong to the one with the most attraction for these electrons. The oxidation number of an atom can be thought of as the "charge" the atom would have if all shared electrons were assigned to it.

- The following rules are used to assign oxidation numbers to atoms in elements and compounds. (Note: these rules are hierarchical. If any two rules conflict, follow the rule that is higher on the list)

  1. The oxidation number of an atom in a free element is 0.

  2. The oxidation number of a monatomic ion is equal to its charge.

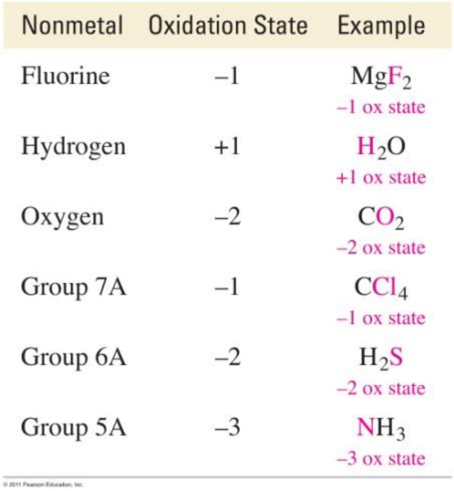
  3. The sum of the oxidation number of all atoms in:

     - A neutral molecule or formula is equal to 0.
     - An ion is equal to the charge of the ion.

  4. In their compounds, metals have a positive oxidation number.

     - Group 1A metals always have an oxidation number of +1.
     - Group 2A metals always have an oxidation number of +2.

  5. In their compounds non-metals are assigned oxidation numbers according to the table at right. Entries at the top of the table take precedence over entries at the bottom of the table.



Nonmetal	Oxidation State	Example
Fluorine	–1	MgF_2 –1 ox state
Hydrogen	+1	H_2O +1 ox state
Oxygen	–2	CO_2 –2 ox state
Group 7A	–1	CCl_4 –1 ox state
Group 6A	–2	H_2S –2 ox state
Group 5A	–3	NH_3 –3 ox state

Examples:

1. Determine the oxidation number for chlorine in the following compounds:

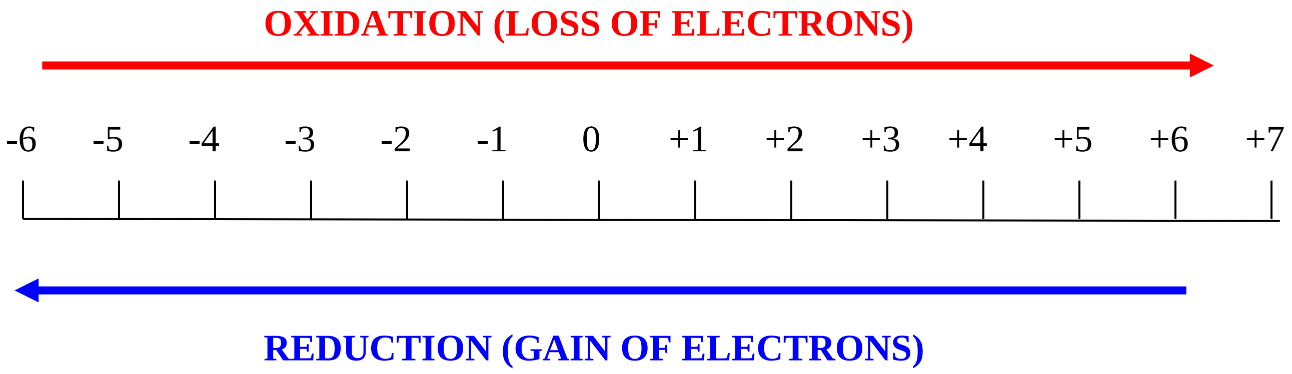
   a) HCl ______
   b) HClO ______
   c) $HClO_2$ ______
   d) $HClO_3$ ______
   e) $HClO_4$ ______

OXIDIDATION-REDUCTION REACTIONS

- Oxidation numbers (or states) can be used to identify redox reactions and determine which substance is oxidized and which is reduced.

- To do so, assign oxidation numbers to all elements in the reactants and products, then track which elements change oxidation numbers from reactants to products.

- Elements that increase their oxidation numbers lose electrons, and are therefore oxidized. Elements that decrease their oxidation numbers gain electrons, and are therefore reduced.



<u>Examples:</u>
For each reaction below, determine whether or not it is a redox reaction. If the reaction is a redox reaction, determine which element is oxidized and which is reduced and the number of electrons transferred in the reaction:

1) $Sn\ (s) + 4\ HNO_3\ (aq) \rightarrow SnO_2\ (s) + 4\ NO_2\ (g) + 2\ H_2O\ (g)$

2) $Hg_2(NO_3)_2\ (aq) + 2\ KBr\ (aq) \rightarrow Hg_2Br_2\ (s) + 2\ KNO_3\ (aq)$

3) $C_3H_8\ (g) + 5\ O_2\ (g) \rightarrow 3\ CO_2\ (g) + 4\ H_2O\ (g)$

HALF–REACTIONS

- Redox Reactions are discussed (sometimes balanced) by writing two Half-Reactions:

OXIDATION HALF-REACTION	**REDUCTION HALF-REACTION**
• involves loss of electrons	• involves gain of electrons
• increase in Oxidation Number	• decrease in Oxidation Number
$\mathbf{Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^{-}}$	$\mathbf{2Ag^{+}(aq) + 2e^{-} \longrightarrow 2Ag\,(s)}$

NOTE:

Number of electrons lost in Oxidation reaction	=	Number of electrons gained in Reduction reaction

CONCLUSION:

Oxidation–Reduction (Redox) Reactions

- are reactions in which the Oxidation Numbers of at least two elements change
- involve transfer of electrons:
  - ➢ from : the element that is oxidized (called **Reducing Agent**)
  - ➢ to: the element that is reduced (called **Oxidizing Agent**)

Examples:

1. Determine the oxidized and reduced species and write half-reactions for the reaction of zinc and sulfur to form zinc sulfide:

$$Zn\,(s) \;+\; S\,(s) \;\rightarrow\; ZnS\,(s)$$

Examples:

2. Determine the oxidized and reduced species and write half-reactions for the reaction of aluminum and iodine to form zinc aluminum iodine:

$$2\ Al\ (s) + 3\ I_2\ (s) \rightarrow 2\ AlI_3\ (s)$$

3. Determine the oxidized and reduced species and write half-reactions for the reaction shown below:

$$Mg\ (s) + 2\ HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2\ (g)$$

BALANCING REDOX REACTIONS IN ACIDIC & BASIC SOLUTIONS

- When balancing all redox reactions (acidic and basic solutions), follow these steps:

1. Assign oxidation numbers.
2. Write each half-reaction.
3. Balance each half-reaction for atoms and charge.
4. Equalize the number of electrons lost and gained.
5. Add the two resulting half-reactions.

Balancing half-reactions in acidic solution:

- ***In acidic solutions, H^+ and H_2O are readily available.***
- To balance half-reactions in acidic solution:

1. Balance electrons based on changes in oxidation number of element oxidized or reduced.

2. Balance elements other than O or H.

3. To balance O, add the appropriate number of H_2O molecules to the deficient side.

4. To balance H, add H^+ to the deficient side.

5. Check for balance of atoms and charges in the final equation.

Balancing half-reactions in basic solution:

- ***In acidic solutions, OH^- and H_2O are readily available.***
- To balance half-reactions in basic solution:

1. Balance electrons based on changes in oxidation number of element oxidized or reduced.

2. Balance elements other than O or H.

3. To balance O, add ***two (2) hydroxides (OH^-) to the deficient side***, and **add *one (1) water (H_2O), to the other side***.

4. To balance H, add ***one (1) water (H_2O), to the deficient side***, and add ***one (1) hydroxide (OH^-), to the other side***.

5. Check for balance of atoms and charges in the final equation.

- Balance the following redox reaction that takes place in acidic solution:

$$Zn(s) + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + NH_4^+(aq) \qquad \text{(acidic solution)}$$

Step 1: Assign oxidation numbers and determine the oxidized and reduced species and number of electrons involved.

$$\overset{0}{\mathbf{Zn}} + \overset{+5}{\mathbf{NO_3^-}} \longrightarrow \overset{+2}{\mathbf{Zn^{2+}}} + \overset{-3}{\mathbf{NH_4^+}}$$

Step 2: Set up half-reactions.

Oxidation half-reaction	**Reduction half-reaction**
$Zn \rightarrow Zn^{2+} + 2\,e^-$	$NO_3^- + 8\,e^- \rightarrow NH_4^+$

Step 3: Balance atoms; H_2O molecules and H^+ ions may be added as needed

Oxidation half-reaction	**Reduction half-reaction**
$Zn \rightarrow Zn^{2+} + 2\,e^-$ **(balanced; no action needed)**	$NO_3^- + 8\,e^- \rightarrow NH_4^+$ Balance O atoms by adding H_2O molecules: $NO_3^- + 8\,e^- \rightarrow NH_4^+ + 3\,H_2O$ Balance H atoms by adding H^+ ions: $NO_3^- + 10\,H^+ + 8\,e^- \longrightarrow NH_4^+ + 3\,H_2O$

Step 4: Equalize loss and gain of electrons.

Oxidation half-reaction	**Reduction half-reaction**
$[\,Zn \rightarrow Zn^{2+} + 2\,e^-\,] \times 4$ $4\,Zn \rightarrow 4\,Zn^{2+} + 8\,e^-$	$[\,NO_3^- + 10\,H^+ + 8\,e^- \rightarrow NH_4^+ + 3\,H_2O\,] \times 1$ $NO_3^- + 10\,H^+ + 8\,e^- \rightarrow NH_4^+ + 3\,H_2O$

Step 5: Add up half-reactions and cancel electrons.

$$4\,Zn + NO_3^- + 10\,H^+ \Rightarrow 4\,Zn^{2+} + NH_4^+ + 3\,H_2O$$

- **Check to see that atoms and charges are balanced for the overall reaction**

Examples:

Balance the following redox reaction in acidic solution:

1. $Br_2\ (l) + SO_2\ (g) \rightarrow Br^-\ (aq) + SO_4^{2-}\ (aq)$

2. $H_2O_2\ (aq) + MnO_4^-\ (aq) \rightarrow Mn^{2+}\ (aq) + O_2\ (g)$

- Balance the following redox reaction that takes place in basic solution:

$$MnO_4^-(aq) + \quad SO_3^{2-}\,(aq) \quad \rightarrow \quad MnO_2\,(s) \;\; + SO_4^{2-}\,(aq) \qquad \text{(basic solution)}$$

Step 1: Assign oxidation numbers and determine the oxidized and reduced species and number of electrons involved.

$$\overset{+7}{\mathbf{MnO_4^-}}\mathbf{(aq)} \quad + \quad \overset{+4}{\mathbf{SO_3^{2-}}}\,\mathbf{(aq)} \longrightarrow \overset{+4}{\mathbf{MnO_2}}\mathbf{(s)} \quad + \quad \overset{+6}{\mathbf{SO_4^{2-}}}\mathbf{(aq)}$$

Step 2: Set up half-reactions.

Oxidation half-reaction	**Reduction half-reaction**
$\mathbf{SO_3^{2-} \rightarrow SO_4^{2-} + 2\,e^-}$	$\mathbf{MnO_4^- + 3\,e^- \rightarrow MnO_2}$

Step 3: Balance atoms; H_2O molecules and OH^- ions may be added as needed

Oxidation half-reaction	**Reduction half-reaction**
$\mathbf{SO_3^{2-} \rightarrow SO_4^{2-} + 2\,e^-}$	$\mathbf{MnO_4^- + 3\,e^- \rightarrow MnO_2}$
Balance O atoms by adding 2 OH^- and 1 H_2O molecules: $\mathbf{2\,OH^- + SO_3^{2-} \rightarrow SO_4^{2-} + 2\,e^- + H_2O}$	Balance O atoms by adding 4 OH^- and 2 H_2O molecules: $\mathbf{2\,H_2O + MnO_4^- + 3\,e^- \rightarrow MnO_2 + 4\,OH^-}$
Balance H atoms: (no action needed) $\mathbf{2\,OH^- + SO_3^{2-} \rightarrow SO_4^{2-} + 2\,e^- + H_2O}$	Balance H atoms: (no action necessary) $\mathbf{2\,H_2O + M\ nO_4^- + 3\,e^- \rightarrow MnO_2 + 2\,OH^-}$

Step 4: Equalize loss and gain of electrons.

Oxidation half-reaction	**Reduction half-reaction**
$[2\ OH^- + SO_3^{2-} \rightarrow SO_4^{2-} + 2\ e^- + H_2O]$ x 3	**$[2\ H_2O + M nO_4^- + 3\ e^- \rightarrow MnO_2 + 2\ OH^-]$ x 2**
$6\ OH^- + 3\ SO_3^{2-} \rightarrow 3\ SO_4^{2-} + 6\ e^- + 3\ H_2O$	**$4\ H_2O + 2\ M nO_4^- + 6\ e^- \rightarrow 2\ MnO_2 + 4\ OH^-$**

Step 5: Add up half-reactions and cancel electrons.

$$H_2O + 3\ SO_3^{2-} + 2\ MnO_4^- \Rightarrow 3\ SO_4^{2-} + 2\ MnO_2 + 2\ OH^-$$

- **Check to see that atoms and charges are balanced for each half-reaction,**

Examples:
Balance the following redox reactions in basic solution:

1. $I^-\ (aq) + MnO_4^-\ (aq) \rightarrow I_2\ (aq) + MnO_2\ (s)$

2. $MnO_4^-\ (aq) + Br^-\ (aq) \rightarrow MnO_2\ (s) + BrO_3^-\ (aq)$

ELECTROCHEMICAL CELLS

- Electrochemical cells are systems consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current
- There are of two types of electrochemical cells:

1. **Voltaic Cells** (galvanic cells, or battery cells)
    - These are electrochemical cells in which a spontaneous reaction generates an electric current
    - Example: An ordinary battery

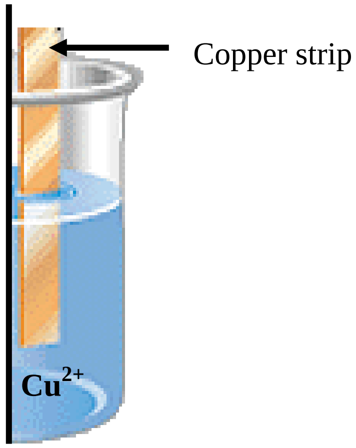
2. **Electrolytic Cells**
    - These are electrochemical cells in which an electric current drives a non-spontaneous reaction.
    - Example: Electroplating of Metals

Voltaic Cells

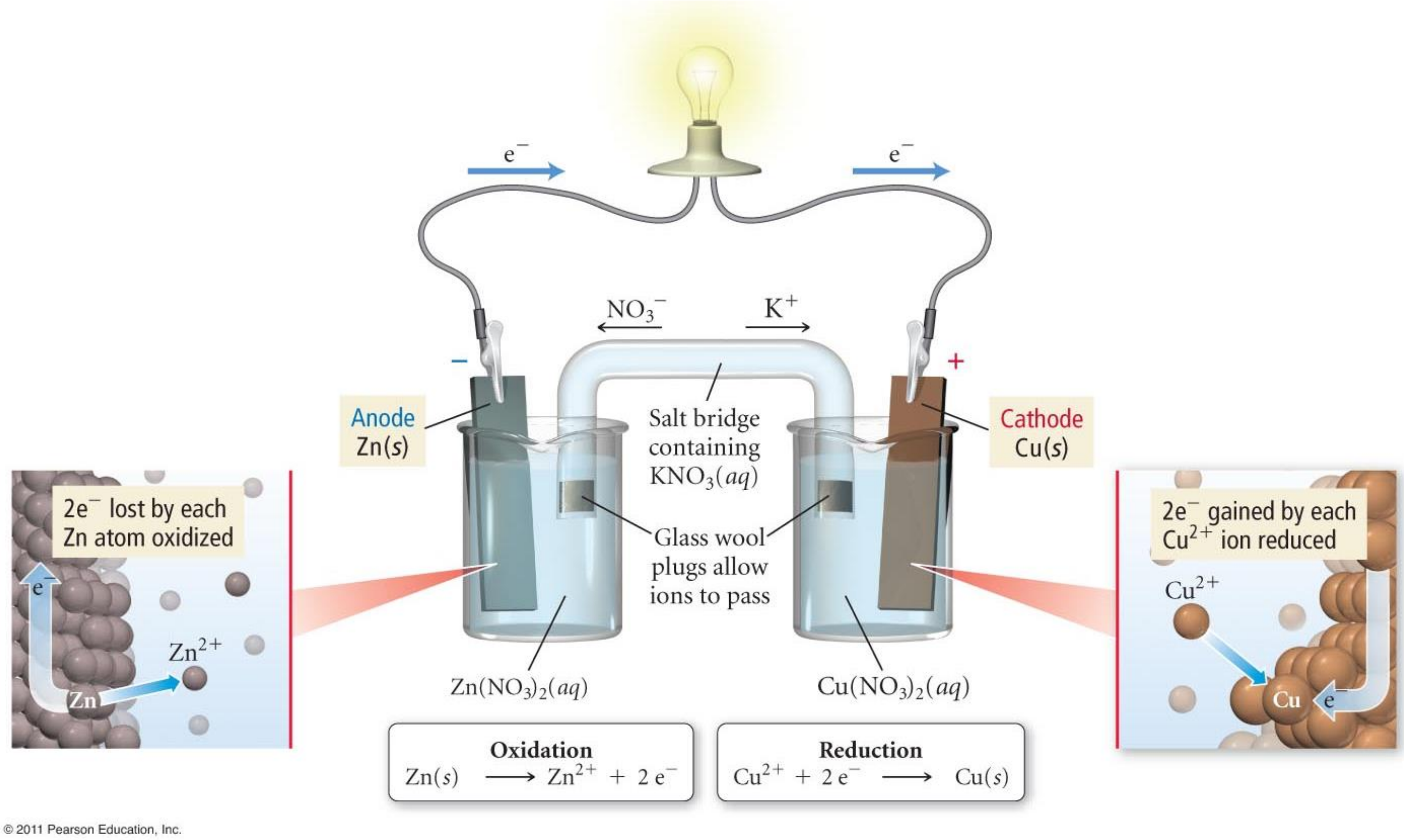
- Voltaic cells consist of two half-cells that are electrically connected. Each half-cell is made from a metal strip that dips into a solution of its metal ion.
- A voltaic cell cannot operate if a charge differential exits between the two half-cells. The charges built in each half-cell can be equalized through an internal connection, called the ***salt bridge***.
- The salt bridge is filled with charges that do not interfere with the redox reaction. This process equalizes the charges built in the two half-cells during the reaction.

Zinc – Zinc Ion Half-Cell
(zinc electrode)

Copper – Copper Ion Half-Cell
(copper electrode)



VOLTAIC CELLS



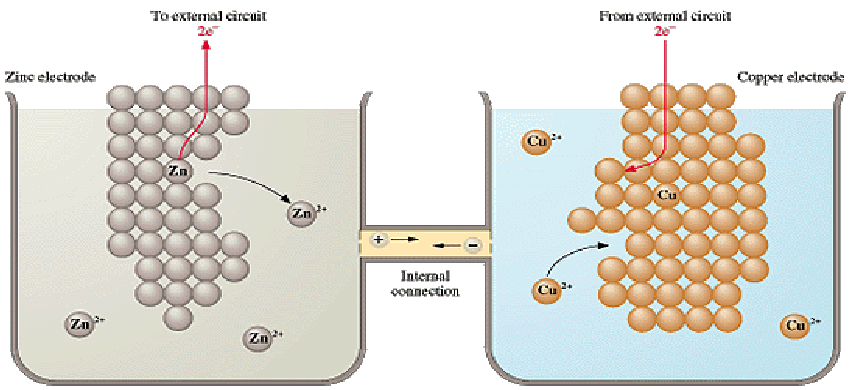
- When sketching and labeling a voltaic cell, follow the following guidelines:

	Anode	**Cathode**
The Electrodes:	• is the more negatively charged electrode (labeled –) • is the more active metal	• is the more positively charged electrode (labeled +) • is the less active metal
Electron Flow:	• Away from the anode	• Towards the cathode
Cell Reaction:	• Oxidation half-reaction	• Reduction half-reaction

VOLTAIC CELLS

- How does the voltaic cell function?

- Basic Idea: zinc tends to lose electrons more readily than copper (Zn is more active than Cu)

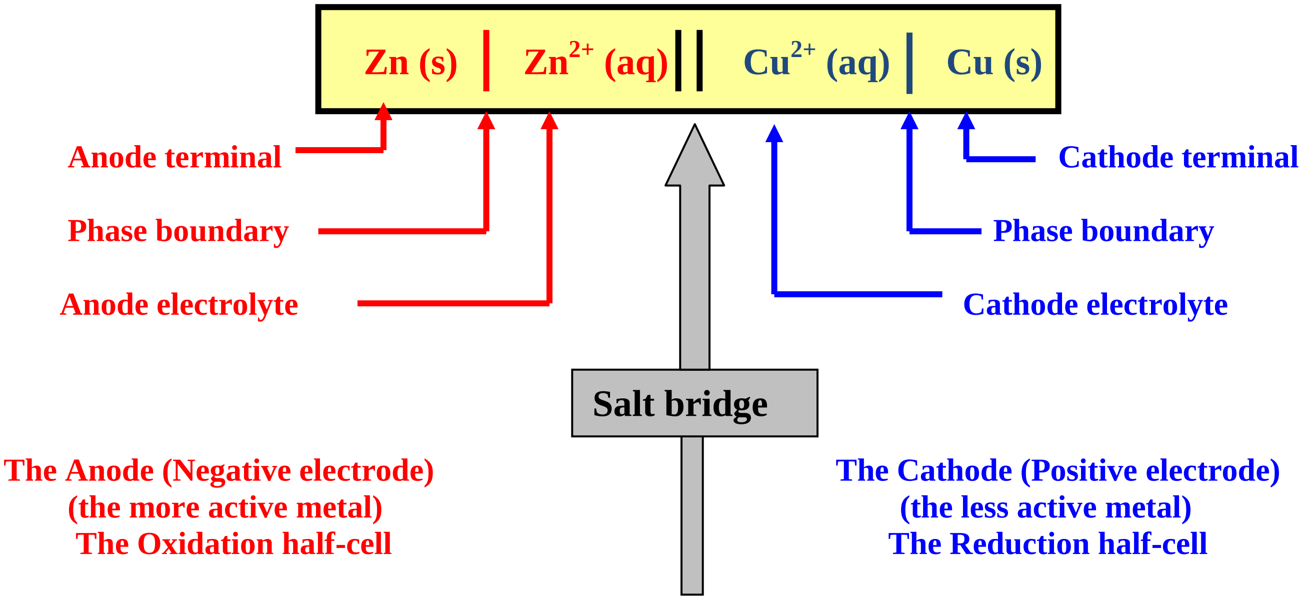


Oxidation half-reaction	**Reduction half-reaction**
$Zn (s) \rightarrow Zn^{2+} (aq) + 2 e^-$ - The electrons flow away from the zinc strip into the external circuit and form Zn^{2+} resulting buildup of positive charge in solution. - The Zinc strip is used up. - The electrons within the salt bridge flow to neutralize the accumulation of positive charge at the anode.	**$Cu^{2+} (aq) + 2 e^- \rightarrow Cu (s)$** - The electrons come from the external circuit and reduce Cu^{2+}, resulting buildup of negative charge in solution. - The Cu^{2+} ions plate out as solid copper. - The positive ions flow to neutralize the accumulation of negative charge at the cathode.

➢ **Net Result: An electric current is generated through the external circuit.**

ELECTROCHEMICAL CELL NOTATION

- Electrochemical cells are often represented by a compact notation, called ***cell notation***:



- When participants in a half-reaction are all in aqueous phase, a conductive surface is needed for electron transfer to take place. In such cases, an inert electrode of graphite or platinum is often used.

- For example, for the redox reaction shown below:

$$5\ Fe\ (s) + 2\ MnO_4^{-}\ (aq) + 16\ H^{+}\ (aq) \rightarrow 5\ Fe^{2+}\ (aq) + 2\ Mn^{2+}\ (aq) + 8\ H_2O\ (l)$$

the half-reactions are:

Oxidation: $Fe\ (s) \rightarrow Fe^{2+}\ (aq)$
Reduction: $MnO_4^{-}\ (aq) + 5\ e^{-} + 8\ H^{+}\ (aq) \rightarrow Mn^{2+}\ (aq) + 4\ H_2O\ (l)$

Since the main species in the reduction half-reaction are aqueous, a Pt electrode is used to allow electron transfer. The cell notation for this cell is then written as:

$$Fe\ (s) \mid Fe^{2+}\ (aq) \parallel MnO_4^{-}\ (aq),\ H^{+}\ (aq),\ Mn^{2+}\ (aq) \mid Pt$$

Examples:

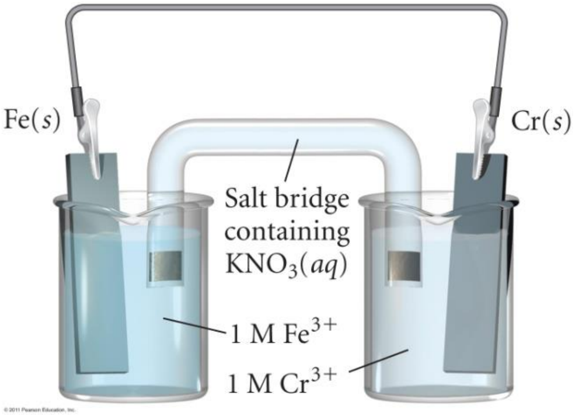
1. Write the cell notation for the reaction shown below:

$$2\ \text{Al (s)} + 3\ \text{Zn}^{2+}\ \text{(a)} \rightarrow 2\ \text{Al}^{3+}\ \text{(aq)} + 3\ \text{Zn (s)}$$

2. Write the half-reactions and the overall reaction for the redox reaction that occurs in the voltaic cell shown below:

$$\text{Sc (s)} \mid \text{Sc}^{3+}\ \text{(aq)} \parallel \text{Ag}^{+}\ \text{(aq)} \mid \text{Ag (s)}$$

3. Consider the voltaic cell shown below. (a) Identify and label the anode and the cathode, (b) determine the direction of the electron flow and (c) write a balanced equation for the overall reaction.

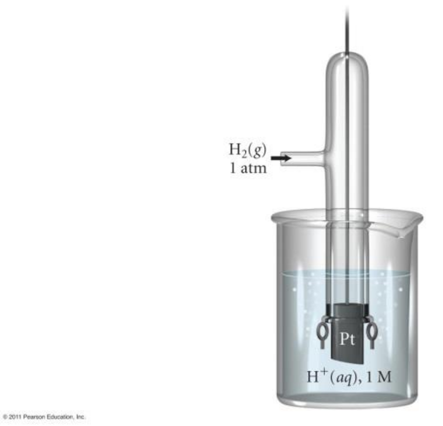


STANDARD HYDROGEN ELECTRODE

- A half-cell electrode that is normally chosen as a standard (having a potential of zero) is the ***standard hydrogen electrode (SHE)***.

- This half-cell consists of an inert platinum electrode immersed in 1 M HCl with hydrogen gas at 1 atm bubbling through the solution, as shown below:

Standard Hydrogen Electrode (SHE)



- The two half-reactions that can occur at this electrode are shown below:

$$2\,H^+(aq) + 2\,e^- \underset{\text{Anode Reaction}}{\overset{\text{Cathode Reaction}}{\rightleftharpoons}} H_2(g)$$

- Cell notations for the standard hydrogen electrode are as follows:

As an Anode

$Pt \mid H_2(g) \mid H^+(aq)$

As a Cathode

$H^+(aq) \mid H_2(g) \mid Pt$

Anode Reaction:

$H_2(g) \longrightarrow 2\,H^+(aq) + 2\,e^-$

Cathode Reaction:

$2\,H^+(aq) + 2e^- \longrightarrow H_2(g)$

Example:

1. Write the notation for a cell in which the electrode reactions are:

$2\ H^+(aq)\ +\ 2\ e^- \rightarrow H_2(g)$
$Zn\ (s) \rightarrow Zn^{2+}(aq)\ +\ 2\ e^-$

2. Give the overall cell reaction for the voltaic cell with the notation shown below:

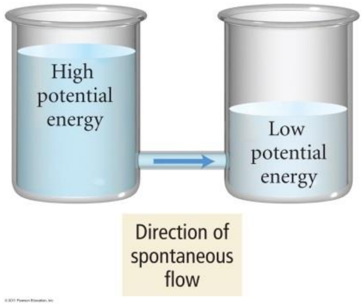
$Cd\ (s) \mid Cd^{2+}(aq) \parallel H^+(aq) \mid H_2(g) \mid Pt$

STANDARD ELECTRODE POTENTIALS

- The standard cell potential ($E°_{cell}$) for an electrochemical cell depends on the specific half-reactions occurring in the half-cells and is a measure of the potential energy difference between the two electrodes.

- Each half-cell can be thought of having its own individual potential, called the ***standard electrode potential***. The overall ***standard cell potential ($E°_{cell}$)*** is the ***difference between the two standard electrode potentials***.

- Similar to the analogy of two connecting water tanks, each half-cell in an electrochemical cell has its own electric potential, and when connected, electrons flow from the electrode with the more negative charge (greater potential energy) to the electrode with more positive charge (less potential energy).



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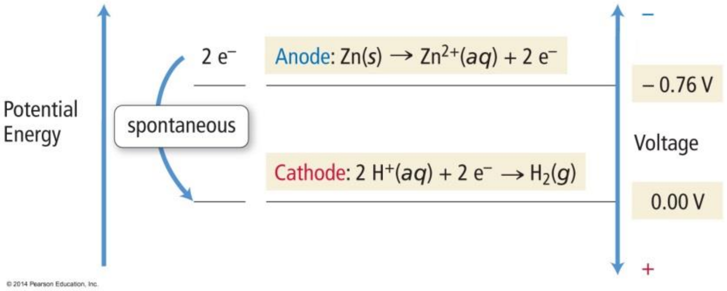
- Experimentally it is not possible to measure the potential of a single electrode. However, it is possible to measure potential of cell constructed from various electrodes connected to a chosen "reference electrode".

- The "reference electrode" chosen is arbitrarily assigned a Potential of Zero, under standard conditions. This electrode is the standard Hydrogen electrode (SHE) discussed earlier.

- Since electrons travel from anode to cathode, $E°_{cell}$, can be defined as the difference in voltage between the cathode (final state) and the anode (initial state):

$$\mathbf{E°_{cell} = E°_{cathode} - E°_{anode}}$$

- The measured $E°_{cell}$ can then be used to determine the standard electrode potential for any cell. For example, the potential for a Zn/H^+ cell is measured as + 0.76 V. The anode in this cell has a more negative potential than the cathode. Since the cathode was assigned a potential of zero, the standard electrode potential of the anode can be determined as shown below:



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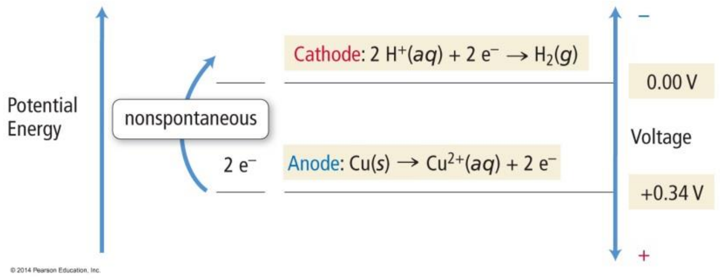
$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$0.76\ V = 0.00\ V - E°_{anode}$$
$$E°_{anode} = -0.76\ V$$

STANDARD ELECTRODE POTENTIALS

- Similarly, the potential for a Cu/H^+ cell is measured as –0.34 V. The anode in this cell has a more positive standard potential than the cathode. Since the cathode was assigned a potential of zero, the standard electrode potential of the anode can be determined as shown below:



$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$-0.34\text{ V} = 0.00\text{ V} - E^\circ_{anode}$$
$$E^\circ_{anode} = +0.34\text{ V}$$

- The standard electrode potential for a number of common half-reactions are listed on the next page. These electrode potentials are sometimes called “reduction potentials”.

<u>Summarizing Standard Electrode Potentials:</u>

- The electrode potential of the standard hydrogen electrode (SHE) is exactly zero.

- The electrode of any half-cell for a substance that is more easily reduced than H^+ is positively charged, and has a (+) value of **E°**.

- The electrode of any half-cell for a substance that is less easily reduced than H^+ is negatively charged, and has a (–) value of **E°**.

- The cell potential of any electrochemical cell (E°_{cell}) is the difference between the electrode potentials of the cathode and the anode ($E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$).

- E°_{cell} is positive for spontaneous reactions and negative for nonspontaneous reactions.

TABLE 18.1 Standard Electrode Potentials at 25 °C

Reduction Half-Reaction		E° (V)
$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$	$\longrightarrow PbSO_4(s) + 2H_2O(l)$	1.69
$MnO_4^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow MnO_2(s) + 2H_2O(l)$	1.68
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Au^{3+}(aq) + 3e^-$	$\longrightarrow Au(s)$	1.50
$PbO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow Pb^{2+}(aq) + 2H_2O(l)$	1.46
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$MnO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	1.21
$IO_3^-(aq) + 6H^+(aq) + 5e^-$	$\longrightarrow \frac{1}{2}I_2(aq) + 3H_2O(l)$	1.20
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$VO_2^+(aq) + 2H^+(aq) + e^-$	$\longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00
$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow NO(g) + 2H_2O(l)$	0.96
$ClO_2(g) + e^-$	$\longrightarrow ClO_2^-(aq)$	0.95
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$MnO_4^-(aq) + e^-$	$\longrightarrow MnO_4^{2-}(aq)$	0.56
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.52
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow H_2SO_3(aq) + H_2O(l)$	0.20
$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.16
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Fe^{3+}(aq) + 3e^-$	$\longrightarrow Fe(s)$	−0.036
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.23
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Cr^{3+}(aq) + e^-$	$\longrightarrow Cr^{2+}(aq)$	−0.50
$Cr^{3+}(aq) + 3e^-$	$\longrightarrow Cr(s)$	−0.73
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^-$	$\longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^-$	$\longrightarrow Ca(s)$	−2.76
$Ba^{2+}(aq) + 2e^-$	$\longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.92
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Examples:

Without calculating the $E°_{cell}$, predict whether each of the following redox reactions is spontaneous.

1) $Fe\ (s) + Mg^{2+}\ (aq) \rightarrow Fe^{2+}\ (aq) + Mg\ (s)$

2) $Fe\ (s) + Pb^{2+}\ (aq) \rightarrow Fe^{2+}\ (aq) + Pb\ (s)$

3) Which metal is the best reducing agent: Mn, Ni, Al or Cr?

4) A solution contains both NaI and NaBr. Which oxidizing agent could you add to the solution to selectively oxidize I^- (aq) but not Br^-(aq)?

   a) Cl_2 b) H_2O_2 c) $CuCl_2$ d) HNO_3

CALCULATING STANDARD POTENTIALS FOR ELECTROCHEMICAL CELLS

- The standard electrode potentials can be used to calculate the standard cell potential ($E°_{cell}$) for any redox reaction by using the following steps:

  1. Identify the oxidized and reduced species and write half-reactions representing each.
  2. Look up the standard electrode potentials for each half-reaction in the table of Reduction Potentials. For the substance that is actually oxidized, reverse the sign of the electrode potential.
  3. Add the 2 half-reactions to obtain the overall redox reaction. Add the two cell potentials obtained in step 2 to get the standard electrode potential ($E°_{cell}$).

Examples:

1. A voltaic cell is based on the following two half-reactions, shown below. Determine the overall reaction for this cell, and calculate the standard potential ($E°_{cell}$).

$Cd^{2+} (aq) + 2\ e^- \rightarrow Cd (s)$ $E°_{cell} = –0.40$

$Sn^{2+} (aq) + 2\ e^- \rightarrow Sn (s)$ $E°_{cell} = –0.14$

2. Using standard cell potentials in your text, calculate the $E°_{cell}$ for a cell that operates on the following overall reaction:

$$2\ Al (s) + 3\ I_2 (s) \rightarrow 2\ Al^{3+} (aq) + 6\ I^- (aq)$$

PREDICTING SPONTANEITY FOR REDOX REACTIONS

- To determine the spontaneous direction of oxidation-reduction reactions, examine the electrode potential of the two relevant half-reactions.

- The half-reaction with the more negative electrode potential will become oxidized, while the half-reaction with the more positive electrode potential will undergo reduction.

- Calculate the cell potential for the cell configured above. A positive cell potential indicates spontaneous reaction.

Examples:

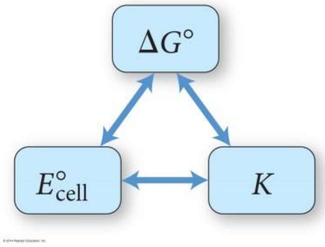
1. Does the following reaction occur spontaneously in the direction indicated, under standard conditions?

$$Cu^{2+}(aq) + 2\,I^{-}(aq) \rightarrow Cu(s) + I_2(s)$$

2. Which is the stronger oxidizing agent, $NO_3^{-}(aq)$ in acidic solution or $Ag^{+}(aq)$?

CELL POTENTIAL, FREE ENERGY & EQUILIBRIUM CONSTANT

- A positive standard cell potential ($E^{\circledcirc}_{cell}$) corresponds to a spontaneous redox reaction. Previously we learned that the spontaneity of a reaction is determined by the sign of free energy change ($\Delta G^{\circledcirc}$). We also know that $\Delta G^{\circledcirc}$ for a reaction is related to the equilibrium constant (K). Therefore, $E^{\circledcirc}_{cell}$, and K must also be related.

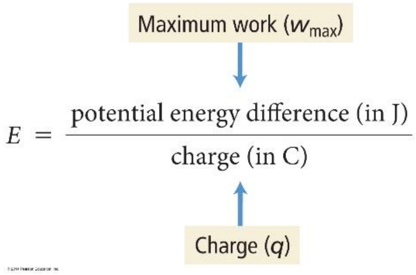


- The following general relationships should be remembered about the relationships of E°_{cell}, ΔG°, and K:

Spontaneous Redox Reactions	***Nonspontaneous Redox Reactions***
ΔG° is negative (< 0)	ΔG° is positive (>0 0)
E°_{cell} is positive (> 0)	E°_{cell} is negative (< 0)
$K > 1$	$K < 1$

RELATIONSHIP BETWEEN ΔG° AND $E°_{cell}$

- Based on the definition of potential difference, it is the measure of the difference in potential energy per unit of charge (q).



- The potential energy difference represents the maximum work (w_{max}), and can be determined as shown below:

$$w_{max} = -q\, E°_{cell}$$

- The charge that flows into an electrochemical cell is equal to Faraday's constant (F), which is the charge in coulombs per 1 mol of electrons:

$$F = \frac{96500\ C}{mol\ e^-}$$

- In a reaction, the total charge is determined by the number of moles of electrons based on the balanced equation, and is calculated as:

$$q = n\, F$$

- Combining this with the equation above for the maximum work:

$$w_{max} = -n\, F\, E°_{cell}$$

- Since ΔG° represents the maximum amount of work,

$$\mathbf{\Delta G° = -n\, F\, E°_{cell}}$$

EQUILBRIUM CONSTANTS AND E°$_{CELL}$

- For a voltaic cell, ΔG° and $E°_{cell}$ are related as shown below:

$$\Delta G° = -nFE°_{cell}$$

- Previously we found the relationship between ΔG° and K:

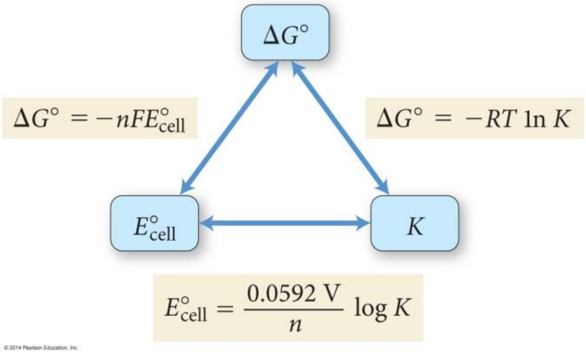
$$\Delta G° = -RT\ln K$$

- Combining these two equations give another method for obtaining the equilibrium constant for a reaction:

$$nFE°_{cell} = RT\ln K \qquad \text{or} \qquad E°_{cell} = \frac{RT}{nF}\ln K = \frac{2.303\,RT}{nF}\log K$$

- Substituting values for constants R and F at 25°C gives the equation shown below:

$$\boxed{E°_{cell} = \frac{0.0592}{n}\log K \qquad (\text{at } 25\ °C)}$$



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Examples:

1. Use the tabulated electrode potentials to calculate ΔG° for the reaction below:

$$I_2\ (s)\ +\ 2\ Br^-\ (aq)\ \rightarrow\ 2\ I^-\ (aq)\ +\ Br_2\ (l)$$

2. The standard cell potential for a Zn/Cu voltaic cell is 1.10 V. Calculate the equilibrium constant for the reaction shown below:

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

$$E^\circ_{cell} = \frac{0.0592}{n} \log K$$

3. Calculate the equilibrium constant for the following reaction from the standard electrode potentials:

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

CELL POTENTIAL AND CONCENTRATION

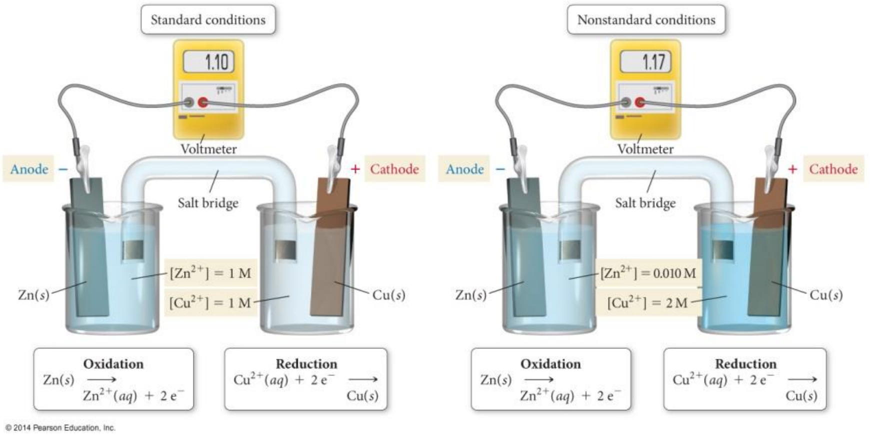
- We have previously discussed calculating E°_{cell} under standard conditions. For example, when $[Cu^{2+}] = 1$ M and $[Zn^{2+}] = 1$ M, the reaction shown below produces 1.10 V.

$$Zn\ (s) + Cu^{2+}\ (aq, 1\ M) \rightarrow Zn^{2+}\ (aq, 1\ M) + Cu\ (s) \qquad E^\circ_{cell} = 1.10\ V$$

- However, what if the concentrations of ions are not standard; e.g $[Cu^{2+}] > 1$ M and $[Zn^{2+}] < 1$ M.

$$Zn\ (s) + Cu^{2+}\ (aq, 2\ M) \rightarrow Zn^{2+}\ (aq, 0.010\ M) + Cu\ (s) \qquad E_{cell} = ???$$

- Remembering Le Chatelier's principle, we can predict that the reaction above would have a greater tendency to occur in the forward direction, and that E_{cell} therefore would be greater than +1.10 V.



- To calculate $E_{cell,}$ recall that free energy change, ΔG, and standard free energy change, ΔG°, were related as shown below:

$$\mathbf{\Delta G = \Delta G^\circ + RT\ ln\ Q}$$

Therefore,

$$\mathbf{-nFE_{cell} = -nFE^\circ_{cell} + RT\ ln\ Q}$$

- Rearrangement leads to the ***Nernst*** equation shown below:

$$\mathbf{E_{cell} = E^\circ_{cell} - \frac{RT}{nF} ln\ Q \qquad or \qquad E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} log\ Q}$$

- Substituting values for constants R and F at 25°C gives the equation shown below:

$$\mathbf{E_{cell} = E^\circ_{cell} - \frac{0.0592}{n} log\ Q \qquad (at\ 25\ ^\circ C)}$$

CELL POTENTIAL AND CONCENTRATION

Examples:

1. Calculate E_{cell} for a Daniell cell (Zn/Cu) with the following concentration of ions:

   $[Zn^{2+}] = 1.00 \text{x} 10^{-5}$ M and $[Cu^{2+}] = 0.100$ M

   $$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} =$$

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

2. What is the E_{cell} for the following voltaic cell?

   $Zn \mid Zn^{2+}$ (0.200 M) $\|$ Ag^{+} (0.00200 M) $\mid$ Ag (s)

3. Calculate E_{cell} for an electrochemical cell based on the following two half-reactions:

   Oxidation: Ni (s) $\rightarrow$ (Ni^{2+} (aq, 2.0 M) + 2 e^{-}

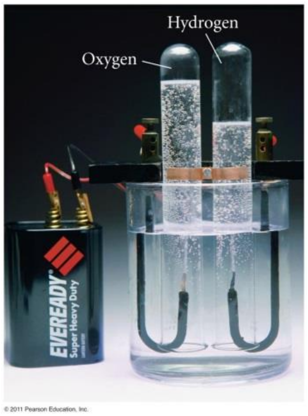
   Reduction: VO_2^{+} (aq, 0.010 M) + 2 H^{+} (aq, 1.0) + e^{-} $\rightarrow$ VO^{2+} (aq, 2.0 M) + H_2O (l)

ELECTROLYSIS & ELECTROCHEMICAL CELLS

- In an ***electrolytic cell***, electric current drives a non-spontaneous redox reaction through a process called ***electrolysis***.

- For example, decomposition of water (a non-spontaneous reaction) can be done in an electrolytic cell to obtain hydrogen and oxygen gases.

$$2\ H_2O\ (l) \rightarrow 2\ H_2\ (g) + O_2\ (g)$$



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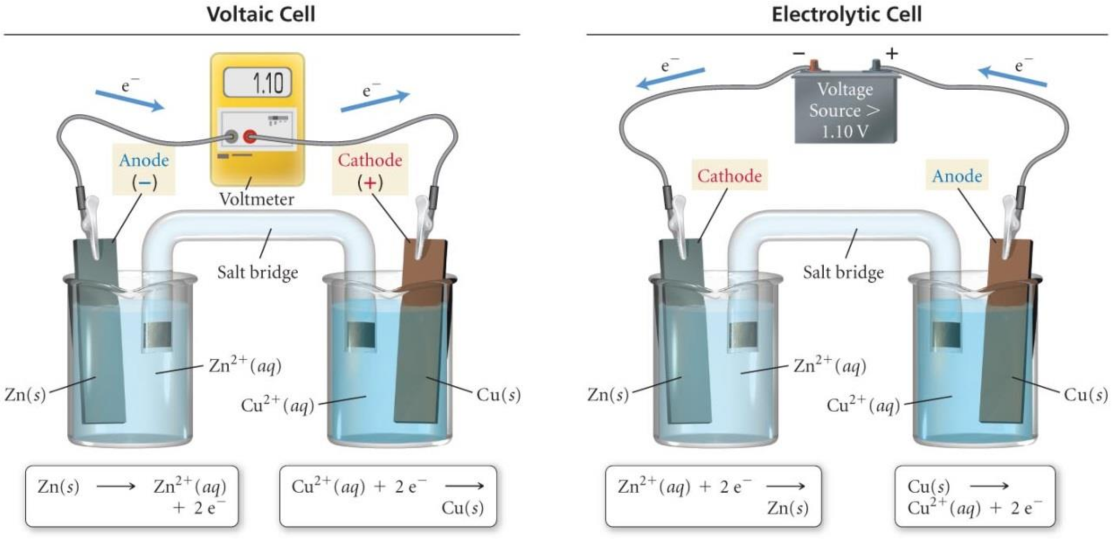
- In all electrochemical cells:
  - Oxidation occurs at the anode.
  - Reduction occurs at the cathode.

- **In voltaic cells:**
  - The anode is the source of electrons and has a negative charge (anode –).
  - The cathode draws electrons and has a positive charge (cathode +).

- **In electrolytic cells:**
  - The electrons are drawn away from the anode, which must be connected to the positive terminal of the external power (anode +).
  - The electrons are forced to the cathode, which must be connected to the negative terminal of the power source (cathode –).



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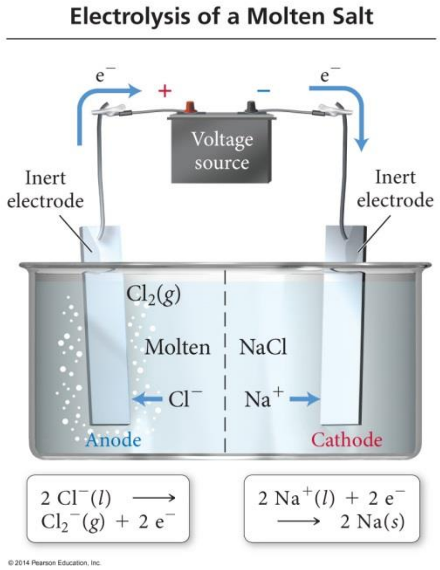
PREDICTING PRODUCTS OF ELECTROLYSIS

- Predicting the products of electrolysis can be simple or complex, depending on the type of substance used. Two examples for simple cases are given below:

Pure Molten Salts:


Electrolysis of a Molten Salt

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- The electrolysis of a pure molten salt contains only one cation and one anion. For example, electrolysis of NaCl, Na^+ and Cl^- are the only species present in the cell. The Cl^- cannot be further reduced (-1 is the lowest oxidation state for Cl), so it must be oxidized. The Na^+ cannot be oxidized further (+1 is the highest oxidation state for Na), so it must be reduced.

- Thus the half-reactions can be written as shown below:

Oxidation (Anode): $2\ Cl^-\ (l) \rightarrow Cl_2\ (g) + 2\ e^-$
Reduction (Cathode): $2\ Na^+\ (l) + 2\ e^- \rightarrow 2\ Na\ (s)$
Overall: $2\ Na^+\ (l) + 2\ Cl^-\ (l) \rightarrow 2\ Na\ (s) + Cl_2\ (g)$

- In the ***electrolysis*** of pure molten salts, ***anion is oxidized*** and ***cation is reduced***.

Mixture of Cations or Anions:

- In electrolysis of molten salt containing a mixture of cations or anions, we compare the electrode potentials of the appropriate ions and determine which would more easily oxidize or reduce. For example, in a mixture of NaCl and KCl, since there is only one anion (Cl^-), it would oxidize at the anode.

- For the cathode reaction, we would have to compare the relative ease of reduction of Na vs. K. Although the values of electrode potentials of aqueous solutions discussed earlier do not apply to molten salts, the relative ordering of these does reflect the ease of reduction of the cations.

$Na^+\ (aq) + e^- \rightarrow Na\ (s)$ $E° = -2.71\ V$ (for aqueous solution)
$K^+\ (aq) + e^- \rightarrow K\ (s)$ $E° = -2.92\ V$ (for aqueous solution)

- The larger (more positive) electrode potential of Na^+ indicates that it would reduce with more ease than K^+. Therefore, reduction of Na^+ to sodium metal would occur at the cathode.

- Similarly, if the molten salt contains a mixture of anions, we would compare the electrode potentials of each anion and determine which would more easily oxidize.

Summary:

- The cation that is most easily reduced (more positive electrode potential) is reduced first.

- The anion that is most easily oxidized (more negative electrode potential) is oxidized first.

Examples:

1. Molten NaCl can be decomposed to Na and Cl_2 using an electrolytic cell. Sketch a simple cell showing the polarity of the terminals, anode and cathode and the half-reactions that occur at each.

2. Predict the half-reactions occurring at the cathode and the anode for electrolysis of a mixture of molten $AlBr_3$ and $MgBr_2$.

ANSWERS TO IN-CHAPTER PROBLEMS:

Page	***Example No.***	***Answer***
3	1	Sn oxidized; N reduced; 4 electrons transferred
	2	Not Redox
	3	C oxidized; O reduced; 20 electrons transferred
4	1	$Zn \rightarrow Zn^{2+} + 2\ e^{-}$ $S + 2\ e^{-} \rightarrow S^{2-}$
5	2	$Al \rightarrow Al^{3+} + 3\ e^{-}$ $I_2 + 2\ e^{-} \rightarrow 2\ I^{-}$
	3	$Mg \rightarrow Mg^{2+} + 2\ e^{-}$ $2\ H^{+} + 2\ e^{-} \rightarrow H_2$
7	1	$Br_2 + SO_2 + 2\ H_2O \rightarrow 2\ Br^{-} + SO_4^{2-} + 4\ H^{+}$
	2	$5\ H_2O_2 + 2\ MnO_4^{-} + 6\ H^{+} \rightarrow 2\ Mn^{2+} + 5\ O_2 + 8\ H_2O$
10	1	$4\ H_2O + 2\ MnO_4^{--} + 6\ I^{-} \rightarrow 3\ I_2 + 2\ MnO_2 + 8\ OH^{-}$
	2	$H_2O + 2\ MnO_4^{-} + Br^{-} \rightarrow 2\ MnO_2 + BrO_3^{-} + 2\ OH^{-}$
15	1	$Al\ (s) \mid Al^{3+}\ (aq) \parallel Zn^{2+}\ (aq) \mid Zn\ (s)$
	2	Discussed in class
	3	Cr is anode; Fe is cathode; electrons flow right to left (anode to cathode) Overall equation: $Cr\ (s) + Fe^{3+}\ (aq) \rightarrow Cr^{3+}\ (aq) + Fe\ (s)$
17	1	$Zn\ (s)\ Zn^{2+}\ (aq) \parallel H^{+}\ (aq) \mid H_2\ (g) \mid Pt$
	2	$Cd\ (s) + 2\ H^{+}\ (aq) \rightarrow Cd^{2+}\ (aq) + H_2\ (g)$
21	1	Not spontaneous
	2	Spontaneous
	3	Al
	4	HNO_3
22	1	$E°_{cell} = +\ 0.26$ V
	2	$E°_{cell} = +\ 2.20$ V
23	1	Not spontaneous
	2	NO_3^{-} in acidic solution
27	1	$\Delta G° = 1.1x10^{5}$ J or 110 kJ
	2	$K = 1.6x10^{37}$
	3	$K = 8.6x10^{19}$

Page	***Example No.***	***Answer***
29	1	$E_{cell} = 1.22$ V
	2	$E_{cell} = 1.42$ V
	3	$E_{cell} = 1.08$ V
31	1	Anode: $2\,Cl^- \rightarrow Cl_2 + 2\,e^-$ Cathode: $Na^+ + e^- \rightarrow Na$
	2	Anode: $2\,Br^- \rightarrow Br_2 + 2\,e^-$ Cathode: Al3+ + 3 e– → Al (Al has a larger reduction potential value compared to Mg, therefore it is reduced)