

Oxidation and Reduction Reactions

How to determine oxidation # of atoms:

- 1.) An unbonded atom = 0
- 2.) Monatomic ions = its normal charge due to its group
- 3.) If atoms are in a polyatomic ion or compound:
 - a.) Fluorine present = it has priority = it is -1
 - b.) Oxygen is normally -2
 - c.) Hydrogen = +1
 - d.) The summed charges of the atoms needs to = total charge of ion or compound

Details about Redox reactions:

Electrons are transferred to:

- 1.) form ions
- 2.) rearrange atoms

Oxidation = increase in oxidation state (become more +)

Reduction = decrease in oxidation state (become more -)

OIL RIG

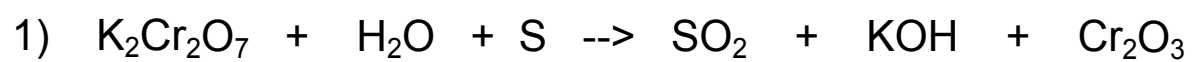
Oxidizing agent (OA) - electron acceptor (gets reduced)

Reducing agent (RA) - electron donor (gets oxidized)

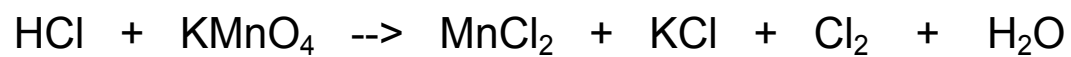
Balancing:

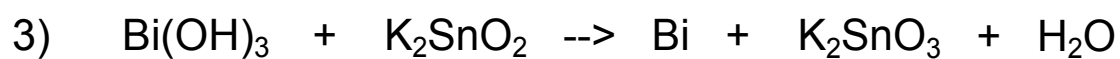
1) Oxidation Number Method:

- a) Look for elements in their natural states
- b) Look for transition metals along with Pb, Bi, Sn, and Sb
- c) Halogens can gain and lose electrons in the same reaction
- d) Determine the charge of a single atom (denominator)
- e) Determine the total gain or loss from numerator and subscripts
- f) Remember Step #2
 - balance elements changing charge
 - change total if you need to add a coefficient
- g) Brackets go from element to element NOT compound to compound
- h) Remember rules for assigning charged
- i) Oxidizing agent (the whole reactant) contains the element that gains electrons

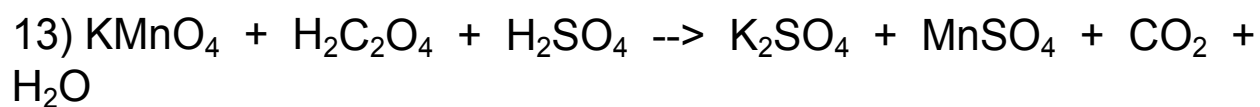
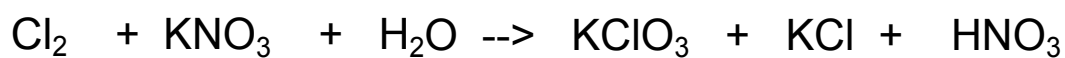


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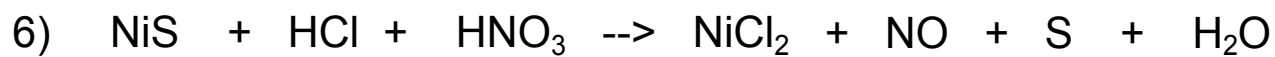
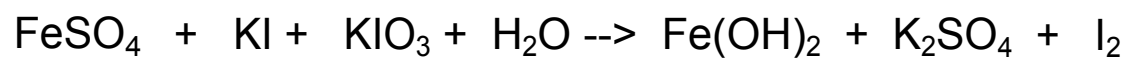


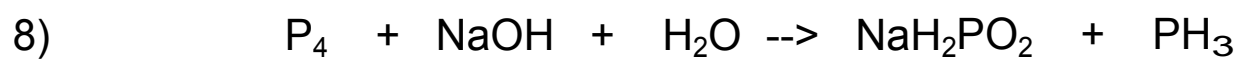


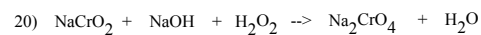
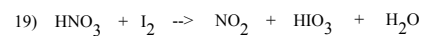
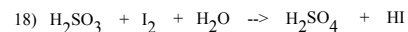
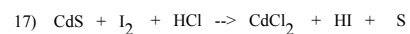
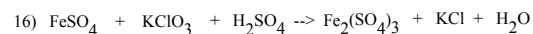
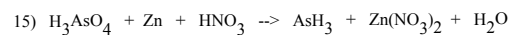
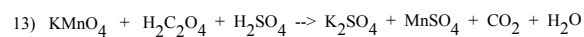
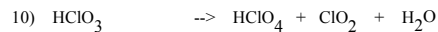
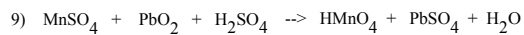
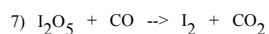
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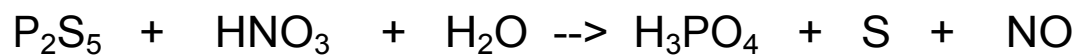
5)







More oxidation number balancing:



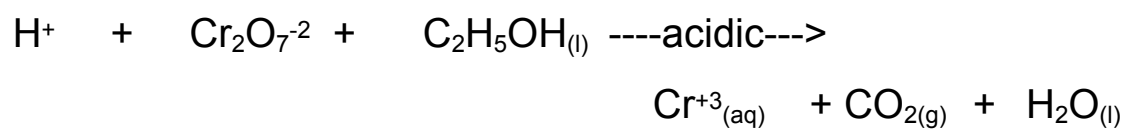
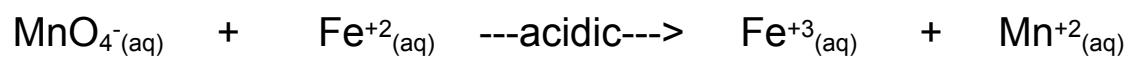
HALF-REACTION - Another way to balance:

- 1) Look whether reaction is in an acid or base solution
- 2) Divide into 2 half-reactions: reduction - gain of electrons
oxidation - loss of electrons
- 3) Make sure charges are shown throughout steps.
- 4) Balance elements first other than H and O
- 5) Balance oxygens with water
- 6) Balance hydrogens with H^+
- 7) a) Add electron(s) to side needing negative charges so that charges are the same on both sides.
- 8) If necessary, balance electrons by multiplying whole equation(s) by a number(s)
- 9) Remember to distribute that number throughout the half-reaction
- 10) Add equations
- 11) Combine H^+ and H_2O if necessary.
- 12) If necessary, reduce coefficients

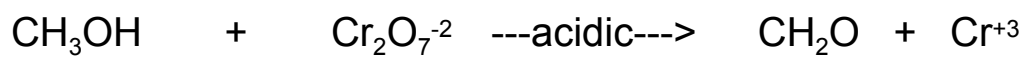
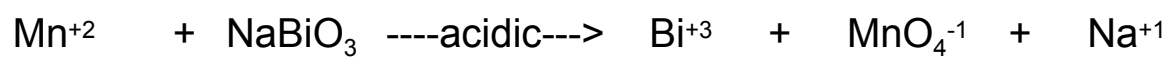
BASE:

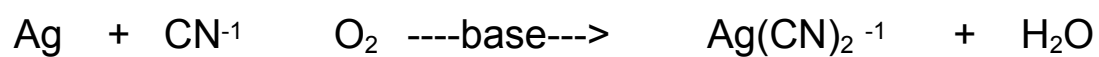
- 1) Follow steps 1-7
- 7) b) Add the same number of OH^- as H^+ to **BOTH** sides
- c) Combine the H^+ and OH^- and make the correct number of water(s)
- d) Do this to both half-reactions
- 8) Do Steps 8, 9, 10
- 11) Combine OH^- and H_2O if necessary.
- 12) If necessary, reduce coefficients

1/2 Reaction Examples:

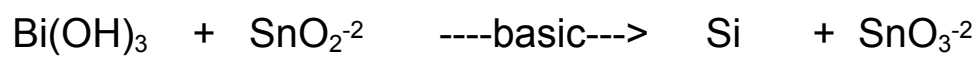




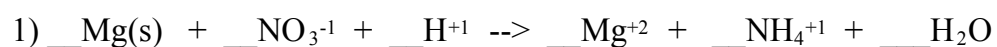




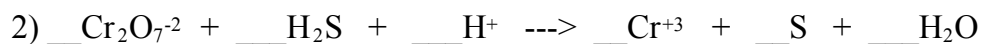




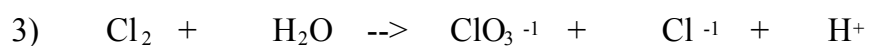
AP TEST EXAMPLES:



When the skeleton equation above is balanced and all coefficients reduced to their lowest whole-number terms, what is the coefficient of H^+ ?

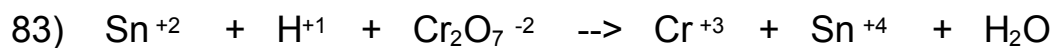
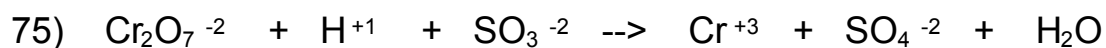
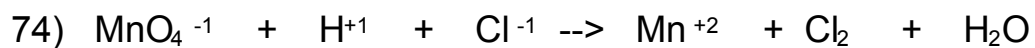


When the equation above is correctly balanced and all coefficients are reduced to their lowest whole-number terms, what is the coefficient of H^+ ?



When the equation is correctly balanced what is the sum of the coefficients?

More AP TEST EXAMPLES



Galvanic Cells (also called voltaic cells):

- 1) Break given rxn into 1/2 rxns and balance
- 2) Each 1/2 reaction goes in a cell (beaker)
- 3) Electrons flow FROM the RA to the OA (OA pulls e- through wire)
 - That means they flow out of the cell undergoing oxidation to the cell undergoing reduction
- 4) Must use a salt bridge (lets the (-) charge equalize)

SALT BRIDGE = tube of electrolytes, e- flow back to RA cell

- 5) Wire allows e- to flow
- 6) Who is in what compartment?

Anode = where oxidation occurs (RA)

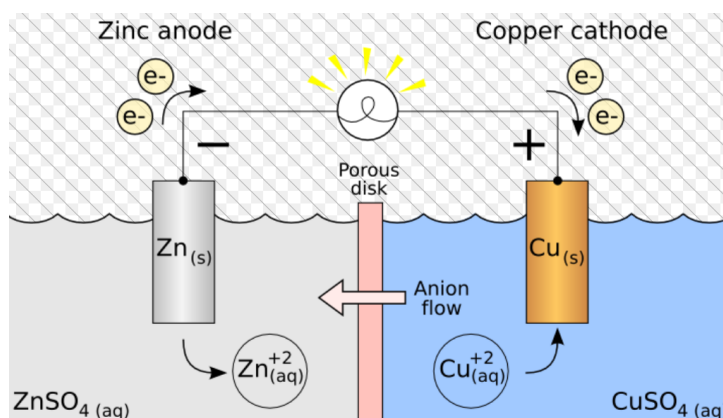
An OX

Cathode = where reduction occurs (OA)

Red CAT

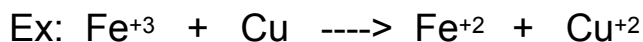
<http://www.youtube.com/watch?v=0oSqPDD2rMA>

Flow is from A (-) ----> C (+)

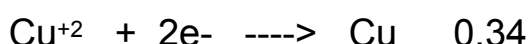
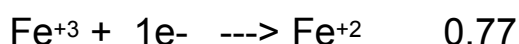


Standard Reduction Potentials (Using and Finding):

- 1) Numerical values for all elements at standard state (1 atm and 25 C) are based on Hydrogen (0 V)
- 2) Use the chart of Standard Reduction Potentials (pg 845 or appendix A5.5) to determine the "potential" per cell



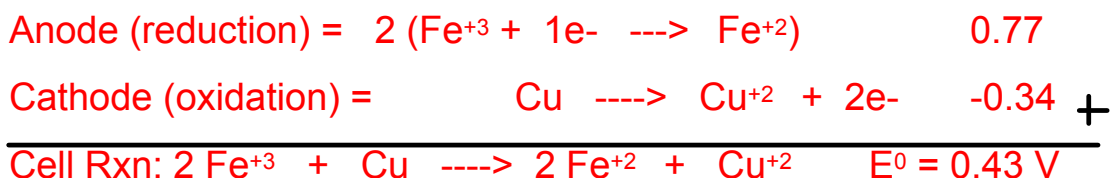
A) Look up the values on pg 845



B) - Arrange equations so the Rxn with Larger Positive Reduction Potential runs as reduction

-Then Reverse the other reaction (it will undergo oxidation, charge of cell potential becomes opposite (+ to -) or (- to +))

C) If electron count doesn't match, multiply by a factor to get each reaction to have same e- count (BUT THIS DOESN'T CHANGE THE REDUCTION POTENTIAL)



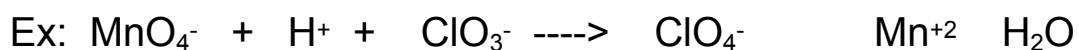
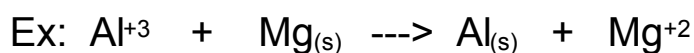
D) Then Add the values to find the Cell Potential, and add the rxns, cancelling what cancels

Some More practice finding Net Cell potential and showing a balanced equation:

More stuff to know:

- 1) Values are for REDUCTION (Flip less + value to become oxidation)
- 2) You need a (+) E_{cell} , or the rxn won't go

More Practice:



What do the values of Standard Reduction Potential Mean?

- 1) Compound with Larger (+) number will be reduced (act as OA)
= cathode
- 2) Other reaction (lower value) will undergo oxidation (act as RA)
= anode
- 3) The Larger the (+) value the stronger the OA it is (gets reduced)
The Smaller the value, the stronger the RA it is (gets oxidized)
- 4) The ACTIVITY SERIES is based on these standard reduction potentials

QUESTION:

1) CONSIDER THE FOLLOWING:

Na^{+1} , Cl^{-1} , Ag^{+1} , Ag, Zn^{+2} , Zn, Pb

- a) Which is the strongest oxidizing agent?
- b) Which is the strongest reducing agent?
- c) Which species can be reduced by Al(s)?

2) PICK A REAGENT THAT IS CAPABLE OF:

- a) Oxidize Br^{-} to Br_2 but not oxidize Cl^{-} to Cl_2 .
- b) Oxidize Mn to Mn^{+2} but not oxidize Ni to Ni^{+2} .

From the following pairs of substances, choose the one that is the stronger reducing agent:

- A) Fe or Mg
- B) Ca or Al

Determine whether each of the following substances serve as an oxidizing agent or a reducing agent:

- A) $\text{Cl}_2(\text{g})$
- B) $\text{Ba}(\text{s})$
- C) $\text{MnO}_4^{-1}(\text{aq})$
- D) $\text{Zn}(\text{s})$

What electrode do I use?

- 1) If the ions in solution have a solid metal of their type (that conducts electricity) - use it (Ex: Fe^{+3} would have a $\text{Fe}_{(s)}$ electrode)
- 2) If they don't have a metal to use- use an inert electrode

Examples of other "inert electrodes" = Pt, H_2

Line Notation Use: Shows details of galvanic cell in just one line

Anode (left) Rxn happening || Rxn happening (right) Cathode

- a) Phase changes are separated by a single line for each individual 1/2 reaction
- $$\text{Mg}_{(s)} \mid \text{Mg}^{+2}_{(aq)}$$

If electrode used is not the metal seen in the rxn, list the electrode

Ex: Show the line notation for $\text{Al}^{+3} + \text{Mg}_{(s)} \rightarrow \text{Al}_{(s)} + \text{Mg}^{+2}$

(Hint: We already did this cell potential and balancing)

Importance of Molarity concentration in a cell:

- 1) When we do "cells under standard conditions, the solutions are at 1M" and the values for E^0 are for 1M solutions
- 2) When Molarity is changed, the cell potential also changes
- 3) Use the Nernst Equation to find the E for the cell when not at standard conditions

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

(values in volts at 25°C)

E = new cell potential at new concentrations

E^0 = Cell potential at standard conditions

n = moles e⁻ exchanged between balanced anode and cathode rxn

Q = equilibrium value, easily found by:

$$Q = \frac{[\text{Molarity of Product side ION}]^x}{[\text{Molarity of Reactant side ION}]^y}$$

(x and y = coefficient in front of ion in eqn)

Example: Find the new cell potential for the following reaction if the

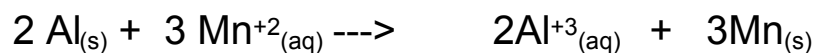
$[\text{Mn}^{+2}] = 0.50 \text{ M}$ and the $[\text{Al}^{+3}] = 1.50 \text{ M}$



Some general "qualitative" things about concentration and equilibrium:

- 1) Increasing conc. of reactant only = drives rxn toward product
(shifts equilibrium to product side)
- 2) Increasing conc. of product only = causes less product to form
(shifts equilibrium to reactant side)

Ex:



What if $[\text{Al}^{+3}] = 2.0 \text{ M}$ and $[\text{Mn}^{+2}] = 1.0 \text{ M}$

What if $[\text{Al}^{+3}] = 1.0 \text{ M}$ and $[\text{Mn}^{+2}] = 3.0 \text{ M}$

A 1M solution of $\text{Cu}(\text{NO}_3)_2$ is placed in a beaker with a strip of Cu metal. A 1M solution of SnSO_4 is placed in the second beaker with a strip of Sn metal. The two beakers are connected by a salt bridge, and the two metal electrodes are linked by wires to a voltmeter.

- A) Which electrode serves as the anode?
- B) Which electrode loses mass?
- C) What is the voltage(EMF) of the cell at standard conditions?
- D) Which directions do the cations from the salt bridge migrate?
- E) Which electrode could be replaced by an inert material?

A student places a copper electrode in a 1M solution of CuSO_4 and in another beaker places a silver electrode in a 1M solution of AgNO_3 . A salt bridge composed of Na_2SO_4 connects the two beakers.

- A) Draw a diagram of this cell
- B) Determine the E° .
- C) Describe what is happening at the cathode(Include any equations that may be happening)
- D) Describe what is happening at the anode(Include any equations that may be happening)
- E) Write the overall cell equation.
- F) Write the standard cell line notation.
- G) To which solution do the Na^{+1} ions migrate?
- H) From which solution to what solution do the electrons flow?
- I) Which electrode could be replaced by an inert material?
- J) Give the concentrations of the silver nitrate and copper(II) sulfate solutions that would be needed to generate E° .

Practice with Galvanic cells

- 1) Draw an electrochemical cell (galvanic) with a piece of silver in a silver nitrate solution in one part of the cell and a piece of zinc in a zinc nitrate solution in the other part.
- 2) Write a balanced equation for the spontaneous reaction that takes place in the cell.
- 3) Calculate the standard cell potential, E° , for the reaction in part (1).
- 4) In the diagram drawn, label the anode and the cathode
- 5) Give the concentrations of the silver nitrate and zinc nitrate solutions that would be needed to generate E°
- 6) Indicate the direction of electron flow.
- 7) Indicate the directional flow of the anions and cations from the salt bridge.
- 8) Which electrode could be replaced by an inert electrode?
- 9) Draw the line notation for the cell.

More Galvanic cell practice:

- 1) Draw an electrochemical cell (galvanic) with a piece of graphite in a tin(II) and tin(IV) nitrate solutions in one part of the cell and a piece of copper in a copper(II) nitrate solution in the other part.
- 2) Write a balanced equation for the spontaneous reaction that takes place in the cell.
- 3) Calculate the standard cell potential, E° , for the reaction in part (1).
- 4) In the diagram drawn, label the anode and the cathode
- 5) Give the concentrations of the tin nitrate solutions and copper(II) nitrate solution that would be needed to generate E°
- 6) Indicate the direction of electron flow.
- 7) Indicate the directional flow of the anions and cations from the salt bridge.
- 8) Which electrode could be replaced by an inert electrode?
- 9) Draw the line notation for the cell.

(B) Four voltaic cells are set up. In each, one half-cell contains the standard hydrogen electrode. The second half-cell is one of the following:

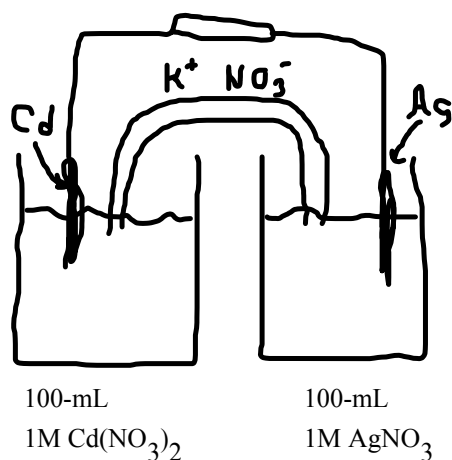
- 1) $\text{Cr}^{3+}(\text{aq}, 1\text{M}) \mid \text{Cr}(\text{s})$
- 2) $\text{Fe}^{2+}(\text{aq}, 1\text{M}) \mid \text{Fe}(\text{s})$
- 3) $\text{Cu}^{2+}(\text{aq}, 1\text{M}) \mid \text{Cu}(\text{s})$
- 4) $\text{Mg}^{2+}(\text{aq}, 1\text{M}) \mid \text{Mg}(\text{s})$

- a) In which of the voltaic cells is the hydrogen electrode the cathode?
- b) Which voltaic cell produces the highest voltage?
- c) Which voltaic cell produces the lowest voltage?

(C) The following half-cells are available:

- 1) $\text{Ag}^{+}(\text{aq}, 1\text{M}) \mid \text{Ag}(\text{s})$
- 2) $\text{Zn}^{2+}(\text{aq}, 1\text{M}) \mid \text{Zn}(\text{s})$
- 3) $\text{Cu}^{2+}(\text{aq}, 1\text{M}) \mid \text{Cu}(\text{s})$
- 4) $\text{Co}^{2+}(\text{aq}, 1\text{M}) \mid \text{Co}(\text{s})$

- a) i) In which of the voltaic cells is the copper electrode the cathode?
ii) In which of the voltaic cells is the cobalt electrode the anode?
- b) i) Which combination of half-cells generates the highest voltage?
ii) Which combination of half-cells generates the lowest voltage?



A practice AP Problem:

A) Write the balanced net-ionic equation for the spontaneous reaction that occurs as the cell operates, and determine the cell voltage.

B) In which direction do anions flow in the salt bridge as the cell operates? Justify your answer.

C) If 10-mL of 3M AgNO_3 solution is added to the half-cell on the right, what will happen to the cell voltage? Explain.

D) If 1.0-g of solid NaCl is added to each half cell, what will happen to the cell voltage? Explain.

E) If 20-mL of distilled water is added to both half-cells, the voltage decreases. Explain.

A Practice AP Problem:

Answer parts (a) through (e) below, which relate to reactions involving silver ion, Ag^+

The reaction between silver ion and solid zinc is represented by the following reaction:

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

- A) A 1.50-g sample of Zn is combined with 250.-mL of 0.110M AgNO_3 at 25° C.
- Identify the limiting reactant. Show calculations to support your answer.
 - On the basis of the limiting reactant that you identified in part(i), determine the value of $[\text{Zn}^{2+}]$ after the reaction is complete. Assume that volume change is negligible.

- B) Determine the value of the standard potential, E° , for a galvanic cell based on the reaction between $\text{AgNO}_3(\text{aq})$ and solid Zn at 25° C.

Another galvanic cell is based on the reaction between $\text{Ag}^+(\text{aq})$ and $\text{Cu}(\text{s})$, represented by the equation:

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

- C) Determine the value of the standard free-energy change, ΔG° , for the reaction between $\text{Ag}^+(\text{aq})$ and $\text{Cu}(\text{s})$ at 25° C.

- D) The cell is constructed so that $[\text{Cu}^{2+}]$ is at 0.045M and $[\text{Ag}^+]$ is 0.010M. Calculate the value of the cell potential, E , for the cell.

- E) Under the conditions specified in part (D), is the cell spontaneous? Justify your answer.

Another AP Practice Problem: (a little harder)

The compound NaI dissolves in pure water according to the equation

$\text{NaI(a)} \rightarrow \text{Na}^+(\text{aq}) + \text{I}^-(\text{aq})$. Some of the information in the table of standard reduction potentials given below may be useful in answering the questions that

follow.	$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O(l)}$	1.23V
	$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-$	0.53V
	$2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$	- 0.83V
	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na(s)}$	- 2.71V

A) an electric current is applied to a 1.0M NaI solution.

- Write the balanced oxidation half-reaction for the reaction that takes place.
- Write the balanced reduction half-reaction that takes place.
- Which reaction takes place at the anode, the oxidation reaction or the reduction reaction.
- All electrolysis reactions have the same sign for ΔG° . Is the sign positive or negative? Justify your answer.

Determining Cell Potential, Free Energy, and Work:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

n = moles of e^- exchanged

F = Faraday's constant (96,485 C/mol e^-) (C = coulombs)

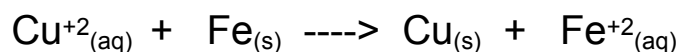
E° = Potential of cell at standard conditions for rxn

$$w = -qE$$

w = work (Joules)

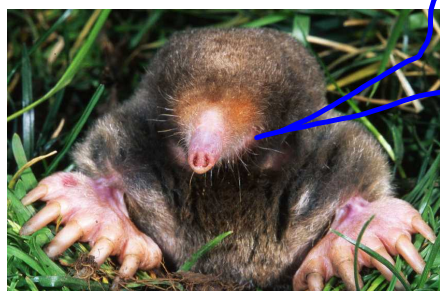
$q = n \cdot F$ (n = moles of e^- and F = Faraday's constant)

Ex: Determine ΔG° for the following reaction:

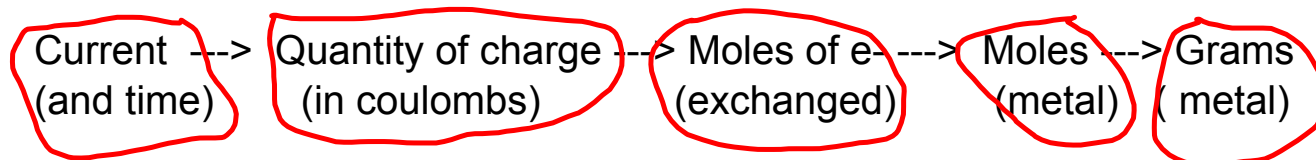


Electrolysis (is different than Galvanic Cells)

- 1) Voltage source is **applied**, not given off
- 2) Used to CHARGE a battery, plate metal
- 4) Net $E_{\text{cell}} < 0$ (meaning $E = -$) for rxn to be spontaneous
- 3) Steps to solve an electrolysis problem (Really it is just another attachment to our Stoichiometry mole map)



"You can never forget about me!!!"

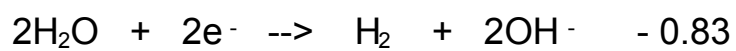
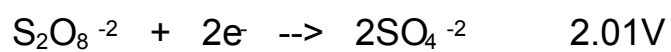


Units to know:

1 amp = 1 coulomb (C) per second (1 amp = 1C/s)

1 mole e^- = 96,485 C

coulombs of charge passed into a solution = amps * seconds

Water Electrolysis:

Electrolysis of Sodium and chloride ion solution:

Electrolysis of Aqueous Potassium Iodide:

Sketch a cell for the electrolysis of aqueous CuF_2 using inert electrodes. Give electrode reactions, and label the anode and cathode. Calculate the minimum applied voltage required for electrolysis to occur, assuming standard state conditions. Also give the overall reaction.

Sketch a cell for the electrolysis of aqueous NaBr using inert electrodes. Indicate the directions in which the ions move. Give the electrode reactions, and label the anode and cathode. Calculate the minimum applied voltage required for electrolysis to occur, assuming standard state conditions.

Calculate the mass of aluminum that could be obtained by the electrolysis of AlCl_3 using a current of 10.0-A for one hour.

What amperage is required to plate out 0.250-mol Cr from $\text{Cr}(\text{NO}_3)_3$ solution in a period of 8.00-hr?

How many minutes are needed to plate out 10.00-g of Mg from molten MgCl_2 using a 3.50-A current?

Which of the following metals will not react with HCl?

Mg, Ag, Zn, Fe, Au

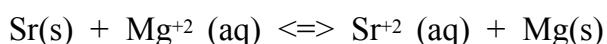
Should an object to be electroplated with a metal be made the anode or the cathode in an electrolytic cell? Explain.

What is the electric current , in amp, if 0.212-g Ag is deposited at the cathode in 1435-s in the electrolysis of silver nitrate.

The electrolysis of 0.100L of 0.785M AgNO_3 using platinum electrodes is carried out with a current of 1.75A. What is the molarity of silver nitrate 25-min. after the electrolysis began.

The rest of the problems in this file will be revisited after "equilibrium chapter is covered"

To cover after K values are understood (equilibrium chapter)



Consider the reaction represented above that occurs at 25° C. All reactants and products are in their standard states. The value of the equilibrium constant for the reaction is 4.2×10^{17} at 25° C.

A) Predict the sign of the standard cell potential, E° , for the cell based on the reaction. Explain your prediction.

B) Identify the oxidizing agent for the spontaneous reaction.

C) If the reaction is carried out at 60° C instead of 25° C, how would the cell potential change. Justify your answer.

D) How would the cell potential change if the reaction were carried out at 25° C with a 1.0M solution of $\text{Mg}(\text{NO}_3)_2$ and a 0.10M solution of $\text{Sr}(\text{NO}_3)_2$? Explain.

E) When the cell in (D) reaches equilibrium, what is the cell potential?

(3)

Answer the following questions that relate to electrochemical reactions:

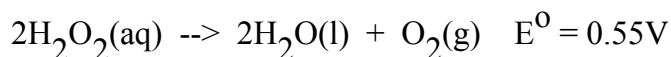
A) Under standard conditions at 25°C, Zn(s) reacts with $\text{Co}^{+2}(\text{aq})$ to produce Co(s).

i) Write a balanced equation for the oxidation half-reaction.

ii) Write the balanced net-ionic equation for the overall reaction.

iii) Calculate the standard potential, E^0 , for the overall reaction at 25°C.

B) At 25°C, H_2O_2 decomposes according to the following equation.



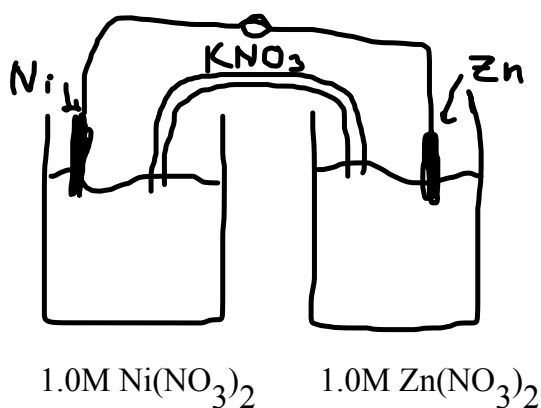
i) Determine the value of the standard free energy change, ΔG^0 , for the reaction at 25°C.

ii) Determine the value of the equilibrium constant, K_{eq} , for the reaction at 25°C.

iii) The standard reduction potential, E^0 , for the half-reaction $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$ has a value of 1.23V. Using this information in addition to the information given above, determine the value of the standard reduction

potential, E^0 , for the half-reaction: $\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2(\text{aq})$

C) In an electrolytic cell, Cu(s) is produced by the electrolysis of $\text{CuSO}_4(\text{aq})$. Calculate the maximum mass of Cu(s) that can deposited by a direct current of 100 amperes passed through 5.00-L of 2.00M $\text{CuSO}_4(\text{aq})$ for a period of 1.00 hour.



Answer the following questions that refer to the galvanic cell shown in the diagram.

A) Identify the anode of the cell and write the half-reaction that occurs there.

B) Write the net ionic equation for the overall reaction that occurs as the cell operates and calculate the value of the standard cell potential, E° .

C) Indicate how the value of E_{cell} would be affected if the concentration of $\text{Ni}(\text{NO}_3)_2$ (aq) was changed from 1.0M to 0.10M and the concentration of $\text{Zn}(\text{NO}_3)_2$ (aq) remained at 1.0M. Justify your answer.

D) Specify whether the value of K_{eq} for the cell is less than 1, greater than one, or equal to 1. Justify your answer.

Sketch a cell for the electrolysis of molten NaBr using inert electrodes. Indicate the directions in which the ions move. Give the electrode reactions, and label the anode and cathode. Calculate the minimum applied voltage required for electrolysis to occur, assuming standard state conditions.

Sketch a cell for the electrolysis of aqueous CuBr_2 using inert electrodes. Indicate the directions in which the ions move. Give the electrode reactions, and label the anode and cathode. Calculate the minimum applied voltage required for electrolysis to occur, assuming standard state conditions.

- 1) a) What are the expected half-reactions at each electrode upon hydrolysis of molten CuCl_2 using inert electrodes.
- b) What are the expected half-reactions upon electrolyzing aqueous CuCl_2 ?
- c) Sketch a cell for the reaction in PART b . Indicate the directions in which the ions move. Give the electrode reactions, and label the anode and cathode, indicating which is connected to which terminal of the voltage source.

