Chapter 19-8-20

Oxidation and Reduction "Redox"

Rules for Assigning Oxidation Numbers

- 1. The CATION is listed first and has a positive oxidation number (charge)
- 2. The ANION is listed second and has a negative oxidation number (charge)
- 3. The oxidation # of an atom in an uncombined element = 0 - when an element is by itself or diatomic, it has a charge of 0 ex/ Mg _(s), $Cl_{2(g)}$, $O_{2(g)}$, Hg _(l) all have a charge of 0
- 4. If it is an ion, its ionic charge is its oxidation #.
 ex/ NaCl □ Na⁺ + Cl⁻

+1 -1

- 5. Many charges relate to their group #'s
 - a) elements in group 1 have an oxidation # =
 - b) elements in group 2 have an oxidation # = ·
 - c) Aluminum is always +3
 - d) Fluorine is always 1

- the other elements in group 17 are -1 when combined with a metal or hydrogen.

- e) Hydrogen is always +1 when combined with a non-metal it is -1 when combined with a group 1 metal (ex/ NaH)
- f) Oxygen is always -2 except when in a peroxide, it is -1 Ex/ H₂O₂ and +2 in OF₂
- 6. Oxidation #'s are per atom

 $-ex/MgCl_{2}Mg = +2$ and Cl = -1 and Cl = -1

7. For a compound, the sum of the oxidation #'s will add up to 0 - ex/ BaF₂ Ba = +2 and F = -1 and F = -1 (remember rule 6) 2 + -1 + -1 = 0 8. For a polyatomic ion, the sum of the oxidation #'s = the charge of the polyatomic ion

- ex/ SO,⁻²

O = -2 and there are 4 of them

to figure out the sulfur, we must use the total charge of the ion

Sulfur + 4 (oxygens) = -2

X + 4(-2) = -2

X = +6

Sulfur = +6

9. Compounds containing a polyatomic ion must have a total charge of 0 (the same as rule 7)

ex/ K_2CrO_4 Find the oxidation numbers of each element K = +1 (see rule 5a)

since we have 2 K ions, the total charge of the K's is +2

O = -2 (see rule 5f)

since we have 4 0 ions, the total charge of the 0's is -8 To figure out the Cr:

 $(2 \times K) + Cr + (4 \times O) = 0$ (see rule 7)

(2 x + 1) + Cr + (4 x - 2) = 0

Cr = +6

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What is the oxidation #s for each element in the compound

K_2SO_4?

K is in group 1, therefore = +1

O is always -2 (except in H_2O_2

To find S, the sum of the oxidation #s must equal 0

2 (+1) + X + 4 (-2) = 0

2 + X + -8 = 0

-6 + X = 0

X = 6 \square S is +6
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Find the oxidation #'s for each element in the compound $H_2S_2O_7$ H is always +1 when bonded to a non-metal O is always -2 (except in H_2O_2) To find S, the sum of the oxidation #s must equal 0 2 (+1) + 2X + 7 (-2) = 0 2 + 2X + -14 = 0 -12 + 2X = 0 2X = 12 X = 6 \square S is +6

LEO the LEPer says GER to GENnifer L = lose L = lose E = electrons E = electrons O = Oxidation P = Positive

G = gainG = gainE = electronsE = electronsR = ReductionN = NegativeCoes town

These are important concepts!!!

When an element undergoes OXIDATION, the oxidation number increases
It gets more POSITIVE (goes up)

When an element undergoes REDUCTION, the oxidation number decreases I it gets more NEGATIVE (goes down)

OXIDIZING AGENT – causes something to be oxidized - It gets REDUCED

<u>REDUCING AGENT</u> – causes something to be reduced - It gets OXIDIZED

The middle charge of a transition metal can be both a reducing agent and an oxidizing agent because its charge can go up or down.

ex/ Cu^{+1} can go to either $Cu_{(s)}$ or Cu^{+2}

Determining what gets: oxidized, reduced, the oxidizing agent & the reducing agent

Ex/ $Zn_{(s)}$ + $CuCl_{2(aq)}$ \Box $ZnCl_{2(aq)}$ + $Cu_{(s)}$

Step 1) Write down the oxidation numbers for each element

- Step 2) Connect the elements on each side of the Rxn. That change
- Step 3) What gets more negative is what gets reduced and is the oxidizing agent. ALWAYS USE THE REACTANT
- Step 4) What gets more positive is what gets oxidized and is the reducing agent. ALWAYS USE THE REACTANT
- A) What gets reduced? Cu⁺² Cu⁰ ans. Cu⁺²
- **B)** What gets oxidized? $Zn^0 \square Zn^{+2}$ ans. Zn^0
- C) What is the reducing agent? Zn⁰ ans. Zn⁰
- D) What is the oxidizing agent? Cu⁺² ans. Cu⁺²

Ex/ for the following Rxn:

 $C_{(S)} + Cl_{2(g)} \square CCl_{4(I)}$

- A) What gets reduced?
- **B) What gets oxidized?**
- **C)** What is the reducing agent?
- **D)** What is the oxidizing agent?

Ex/ for the following Rxn:

 $MgO \square Mg + O_2$

- A) What gets reduced?
- **B) What gets oxidized?**
- **C)** What is the reducing agent?
- D) What is the oxidizing agent?



Table J Activity Series**				
Most	Metals	Nonmetals	Most	
	Li	F ₂ Mos	easily	And the second
	\mathbf{Rb}	Cl ₂ redu	ced	
	к	Br_2		
	\mathbf{Cs}	I ₂		
	Ba	Most opsily		
	\mathbf{Sr}			
	\mathbf{Ca}	oxiaizea		
	Na			
	Mg			
	Al			
	Ti			Table J is
	Mn			hased on
	Zn			
	\mathbf{Cr}			the
	Fe			oxidation
	Co			of
	Ni			Hydrogen
	\mathbf{Sn}			qas = 0
	\mathbf{Pb}			
	**H2			
	Cu			
	Ag			
I	Au		↓	
Least			Least	

Most easily oxidized

Most easily reduced

**Activity Series based on hydrogen standard

Using Table J

Table J is used to determine if a Rxn will occur spontaneous

For Metals: A Rxn will be spontaneous if the substance to be oxidized is above the substance to be reduced.

Ex/ Will the reaction Cu^{+2} + K \square Cu + K^+ be spontaneous?

 $Cu^{+2} \square$ Cu is reduction and K \square K⁺ is oxidation

Since K is oxidized and above Cu on the table the Rxn <u>will be</u> <u>spontaneous</u>.

Ex/Will the reaction $Li^+ + AI \square Li + AI^{+3}$ be spontaneous?

Li⁺ is reduction Al is oxidation

Since AI is getting oxidized and is below Li on the table, the Rxn is non-spontaneous.

Half-Reactions

- A half reaction is used to show either a reduction reaction oxidation reaction.
- If the electrons are on the reactant side, it is a reduction $\frac{1}{2}$ rxn
- If the electrons are on the product side, it is an oxidation $\frac{1}{2}$ rxn
- (You must still check the charges to make sure they are going up for an oxidation rxn or down for a reduction rxn. This is how I will try to fool you on a test)

Reduction $\frac{1}{2}$ Rxns gain electrons (on the reactant side)

 $F_{2(g)} + 2e^{-} = 2F^{-}$ $Sn^{+2} + 2e^{-} = Sn_{(s)}$

Oxidation 1/2 Rxns lose electrons (on the product side)

2 $F^{-} \square F_{2(g)^{+}}$ **2** e^{-} **5** $n_{(s)} \square Sn^{+2}$ **+ 2** e^{-}

Most easily reduced

To get an oxidation 1/2 **Rxn**, you must write the reverse **Rxn** and change the sign of the E⁰ value

Products are Most easily oxidized

STANDARD ELECTRODE POTENTIALS				
Ionic Concentrations 1 M Water At 298 K, 1 atn				
Half-Reaction	$E^{\prime\prime}$			
	(volts)			
$F_2(g) + 2e^- \rightarrow 2F^-$	+2.87			
$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51			
$Au^{3^+} + 3e^- \rightarrow Au(s)$	+1.50			
$Cl_2(g) + 2e - 2Cl$	+1.36			
$14H^+ + Cr_2O_2^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.23			
$4H^+ + O_2(g) + 4e^- \rightarrow 2H_2O$	+1.23			
$4H^+ + MnO_7(s) + 2e \rightarrow Mn^{2+} + 2H_2O$	+1.22			
$Br_2(\ell) + 2e^- \rightarrow 2Br^-$	+1.09			
$Hg^{2-} + 2e^- \rightarrow Hg(\ell)$	+0.85			
$Ag^+ + e^ Ag(s)$	+0.80			
$Hg_2^{2^+} + 2c^- \rightarrow 2Hg(\ell)$	+0.80			
Fe^{3+} + $e^ \rightarrow$ Fe^{2+}	+0.77			
$I_2(s) + 2e^- \rightarrow 2I^-$	+0.54			
$Cu^+ + c^- \rightarrow Cu(s)$	+0.52			
$Cu^{2+} + 2e^ Cu(s)$	+0.34			
$4H^+ + SO_4^{2-} + 2e^ SO_2(aq) + 2H_2O$	+0.17			
Sn^{4} + 2c ⁻ \rightarrow Sn^{2+}	+0.15			
$2H^- + 2e \rightarrow H_2(g)$	0.00			
$Pb^{2-} + 2e^{-} \rightarrow Pb(s)$	-0.13			
$\operatorname{Sn}^{2^{-}} + 2e^{-} \rightarrow \operatorname{Sn}(s)$	-0.14			
$Ni^{2+} + 2e^- \rightarrow Ni(s)$	-0.26			
$Co^{2-} + 2e^{-} \rightarrow Co(s)$	-0.28			
$Fe^{2-} + 2e^{-} \rightarrow Fe(s)$	-0.45			
$Cr^{3-} + 3e \rightarrow Cr(s)$	-0.74			
$Zn^{2+} + 2e^- \rightarrow Zn(s)$	-0.76			
$2H_2O + 2e^ 2OH^- + H_2(g)$	-0.83			
$Mn^{2+} + 2e^{-} \rightarrow Mn(s)$	-1.19			
$Al^{3+} + 3e^- \rightarrow Al(s)$	-1.66			
$Mg^{2+} + 2e^- \rightarrow Mg(s)$	-2.37			
$Na^+ + e^- \rightarrow Na(s)$	-2.71			
$Ca^{2+} + 2e^{-} \rightarrow Ca(s)$	-2.87			
$\mathrm{Sr}^{2+} + 2\mathrm{e}^{-} \rightarrow \mathrm{Sr}(\mathrm{s})$	-2.89			
$Ba^{2+} + 2e^- \rightarrow Ba(s)$	-2.91			
$Cs^+ + e^- \rightarrow Cs(s)$	-2.92			
$K^+ + e^- \rightarrow K(s)$	-2.93			
$Rb^+ + e^- \rightarrow Rb(s)$	-2.98			
$Li^+ + e^- \rightarrow Li(s)$	-3.04			



Every ½ Rxn in this table is a reduction ¹/₂ **Rxn**

Using the Half-Reaction Table

Every Rxn on the table is REDUCTION. The most easily reduced are at the top, the least easily reduced are at the bottom.

 F_2 is the most easily reduced element on the table

To find if a Rxn is spontaneous, the element you want to be reduced must be above the element you want to be oxidized.

The element that gets oxidized will be on the product side of the half reaction

The most easily oxidized are at the bottom of the table on the right hand side (product side) Li_(s) is the most easily oxidized element on the table Rules for Spontaneous Rxns and the 1/2 Rxn Table

Substances to the left and those below them on the right is spontaneously with each other.

Anything on the left side will react spontaneously with anything below and to the right.

F₂ reacts spontaneously with Cl⁻

Anything on the right side will react spontaneously with anything on the left and above it.

CI⁻ reacts spontaneously with F₂

Ex/ Is F_2 + CuCl₂ \Box CuF₂ + Cl₂ spontaneous?

Assign oxidation #'s to determine what gets reduced and

Write the ½ Rxns. If the reduction ½ rxn is above the oxidization rxn, the Overall Reaction will be spontaneous.

 F_2 gets reducedCI⁻ gets oxidized (flip the $\frac{1}{2}$ Rxn $F_2 + 2 e^- \Box 2 F^ 2 CI^- \Box CI_2 + 2 e^-$

Since F_2 is reduced and is above CI_2 , the rxn is spontaneous.

Ex/ According to The ½ Rxn table, which metal will react spontaneously with Ag⁺ but not with Zn⁺²?

1) Cu 2) Au 3) Al 4) Mg

(1) Cu is the only choice between Ag⁺ and Zn⁺² On the ¹/₂ Rxn table, it is below Ag⁺ and above Zn⁺². On Table J, it is below Zn and above Ag According to Table J, which rxn will take place spontaneously?

- **1.** Ni⁺² + Pb 🗆 Ni + Pb⁺²
- 2. Au⁺³ + Al □ Au + Al⁺³
- 3. $Sr^{+2} + Sn \square Sr + Sn^{+2}$
- **4.** Fe⁺² + Cu □ Fe + Cu⁺²



- Start by finding what gets oxidized and what gets reduced, then use the table
- Using table J, what gets oxidized should be above what gets reduced
- Using the $\frac{1}{2}$ Rxn table, what gets reduced should be above and on the left (reactant side) and what gets oxidized should be below and on the right (product side)

Calculating Spontaneous Rxns using Cell Potential

According to the ¹/₂ Rxn Table, which rxn will take place spontaneously?

1. $Ni^{+2} + Pb \square Ni + Pb^{+2}$ 2. $Au^{+3} + Al \square Au + Al^{+3}$ 3. $Sr^{+2} + Sn \square Sr + Sn^{+2}$ 4. $Fe^{+2} + Cu \square Fe + Cu^{+2}$

This same problem can be calculated using the Cell Potential (E⁰) Steps:

1. Write the Oxidation and Reduction 1/2 Rxns

2. Write down their E^0 value from the table, remember, you must change the sign of the E^0 for the oxidation Rxn

3. Add up the E⁰ values

A positive E^0 = spontaneous (remember, a $-\Delta G$ = spontaneous) A negative E^0 = non-spontaneous (remember, a + ΔG = non-spon)

Electrochemical Cells

The theory behind an electrochemical cell

- **1.** Redox Rxns are the loss and gain of e-'s.
- 2. Metals are a "mobile sea of e-'s" 🗆 e-'s can move in a meta
- **3. Therefore, metals will conduct electricity.**
- 4. When an ionic compound is dissolved in water, it becomes an electrolyte (electrolytes conduct electricity)

<u>Electrochemical Cells</u> - devices that use Redox Rxns to produce electricity

e's enter and exit electrochemical cells from electrodes

<u>Electrodes</u> – made of electrical conductors ex/ Metals or graphite ex/ Cu_(s) or Zn_(s)

The RED CAT and AN OX

Oxidation and Reduction Occur at these electrodes

- In a cell, there are 2 electrodes:
 - 1. <u>Cathode</u>
 - 2. Anode
- <u>**Reduction**</u> occurs at the <u>Cathode</u> = RED CAT
- **Oxidation** occurs at the <u>Anode</u> = AN OX



TYPES OF CELLS

- 1. <u>Electrochemical (Voltaic) (Galvanic) Cells</u> Produce electricity using a spontaneous Rxn ex/ Batteries
- 2. <u>Electrolytic Cells</u> use electricity to make a non-spon Rxn happen. ex/ Electroplating jewelry, purifying metals

Electrochemical Cells

Contents:

2 half cells, each one contains an electrode (metal solution of the metal's ions.

The Cathode is positive The Anode is negative

The electrodes are connected by a wire attached to a volt meter.

Electrons pass through the wire from the anode to the cathode!

1 salt bridge – The salt bridge connects the half cells

The purpose of the salt bridge is to allow ions to flow between the half cells.

The ions also flow from the anode side to the cathode side NO SALT BRIDGE = NO WORK We can calculate the voltage produced using the $\frac{1}{2}$ Rxns table (N)

The voltage produced depends on 3 things

- 1. [] of the solutions
- 2. types of electrodes
- 3. pressure if gasses are involved.



The voltages in the $\frac{1}{2}$ Rxn tables are calculated at standard conditions of 1 M solutions and at 1 atm pressure.

Calculating Cell Potential

In order to calculate cell potentials it helps to:

- **1. Draw a picture**
- **2. Write the two \frac{1}{2} Rxns**
- 3. Flip the oxidation Rxn and Change the sign
- 4. $E^0_{total} = E^0_{Reduction} + E^0_{Oxidation}$

An electrochemical cell looks like this



- Ex/ If I connect a half cell of Ni(NO₃)₂ w/ a Nickel electrode to a half cell consisting of a Silver electrode in a AgNO₃ solution with a salt bridge:
- **1. What gets oxidized?**
- 2. What gets reduced?
- 3. Which electrode is the anode?
- 4. Which electrode is the cathode?
- 5. Which electrode is the + electrode?
- 6. Which electrode is the electrode?
- 7. Which electrode gains mass?
- 8. Which electrode loses mass?
- 9. The electrons flow from ____
- 10. The ions flow from _____
- **11. What is the cell potential?**



to

to



- Ex/ If I connect a half cell of CuSO₄ w/ a Copper electrode to a half cell consisting of an Iron electrode in a FeSO, solution with a salt bridge:
- **1. What gets oxidized?**
- 2. What gets reduced?
- **3.** Which electrode is the anode?
- 4. Which electrode is the cathode?
- 5. Which electrode is the + electrode?
- 6. Which electrode is the electrode?
- 7. Which electrode gains mass?
- 8. Which electrode loses mass?
- 9. The electrons flow from _____
- **10.** The ions flow from _
- **11. What is the cell potential?**







Electrolytic Cells (Electrolysis)

Electrolytic Cells use electricity to force a non-spontaneous Rxn to happen.

This means that the E^0 will always be negative.

What gets Oxidized will be the Rxn on top of the ½ Rxn chart and must be flipped.

What gets Reduced will be below and will be written as is.

HOW TO RECOGNIZE AN ELECTROLYTIC CELL:



- 2. The electrodes are hooked to a battery or a power source.
- **3.** Often, there is a fork or a spoon.

In an electrolytic cell:

THE ANODE IS +

<u>THE CATHODE IS -</u>

Uses of electrolysis:

- **1.** To electroplate jewelry or eating utensils.
- 2. Breaking a compound into its elements
- **3. Rechargeable Batteries**
- 4. Car Batteries (Lead Storage Battery)

Ex/ Electrolysis of Water

cathode: $4 H_2 O + 4 e^{-} \Box 2 H_2 + 4 OH^{-}$ anode: $2 H_2 O \Box O_2 + 4 H^{\pm} + 4 e^{\pm}$ overall Rxn: $6 H_2 O \Box 2 H_2 + O_2 + 4 H_2 O$ $2 H_2 O \Box 2 H_2 + O_2$ (the waters cancel out)





Ex/ Electrolysis of KI_(aq)

 cathode:
 $2 H_2 O_{(1)} + 2 e^- \Box H_{2(g)} + 2 O H_{(aq)}^-$

 Anode:
 $2 I_{(aq)}^2 \Box I_{2(I)} + 2 e^-$

 Overall ionic equation:
 $2 I_{(aq)}^2 + 2 H_2 O_{(1)} \Box H_{2(g)} + 2 O H^{-(aq)} + I_{2(I)}^-$

 Including spectator ions:
 $2 KI_{(aq)} + 2 H_2 O_{(I)} \Box H_{2(g)} + 2 KO H_{(aq)} + I_{2(I)}^-$

Electrolysis of Moltan NaCl:

 Cathode:
 $2 \operatorname{Na}_{(l)}^+ + 2 \operatorname{e}^- \Box 2 \operatorname{Na}_{(l)}$

 Anode:
 $2 \operatorname{Cl}_{(l)}^- \Box \operatorname{Cl}_{2(g)}^- + 2 \operatorname{e}^-$

 Overall:
 $2 \operatorname{NaCl}_{(l)} \Box 2 \operatorname{Na}_{(l)}^- + \operatorname{Cl}_{2(g)}^-$

Lead Storage Battery (Car Battery)



Anode: $Pb_{(s)} + SO_4^{-2} \square PbSO_4_{(s)} + 2e^{-1}$ Cathode: $PbO_{2(s)} + 4H^+_{(aq)} + SO_4^{-2}_{(aq)} + 2e^{-1} \square PbSO_4_{(s)} + 2H_2O_{(l)}$

Overall Rxn when discharged (Used to start the car):

$$Pb_{(s)} + PbO_{2(s)} + 2 H_2SO_{4(aq)} \square 2 PbSO_{4(s)} + 2 H_2O_{(l)}$$

Overall Rxn when the battery is recharging (engine is running):

2 PbSO_{4 (s)} + 2 H₂O_(l)
$$\Box$$
 Pb_(s) + PbO_{2 (s)} + 2 H₂SO_{4 (aq)}

Electroplating

The object to be plated must be at the cathode (jewelry or

The metal you want to plate with (ex/ Ag or Au) will be the anode and must be in a solution of the same ions (ex/ Ag ⁺ or Au ⁺³)



Balancing Redox Rxns

The Law of Conservation of Matter states that Matter can not be created or destroyed.

Therefore, # of e^{-t} s lost must equal # of e^{-t} s gained.

Using 1/2 Rxns: multiply all of the coefficients so that the electrons on both sides become equal

 $Ex/F_2 + 2 e^{-} 2 F^{-}$ $Ag - Ag^{+} + e^{-}$

We are gaining 2 electrons but only losing 1 electron. This is a bad thing

We try to find a common denominator for the electrons and multiply accordingly.

Common denominator is 2, so we must multiply the Ag Rxn's coefficients by 2 $F_{2} + 2 e^{-} \square 2 F^{-}$ $2(Ag \square Ag^{+} + e^{-})$

 $F_{2} + 2 e^{-} \square 2 F^{-}$ $2Ag \square 2Ag^{\pm} + 2e^{\pm}$ $F_{2} + 2 Ag \square 2 Ag^{\pm} + 2 F^{-}$



Ex/ Balance the Redox $\frac{1}{2}$ Rxns and write the complete balanced Rxn Fe \square Fe $^{+3}$ + 3 e⁻ <u>Cu⁺² + 2e⁻</u> \square Cu

2(Fe \square Fe ⁺³ + 3 e⁻) 3(<u>Cu⁺² + 2e⁻</u> \square Cu) 2 Fe + 3 Cu⁺² \square 2 Fe⁺³ + 3 Cu