Learning Outcomes

- Calculate amounts of reactants and products using stoichiometry and molarity
- Titrate to equivalence point
- Recognize, classify, write, balance, and predict product-favored redox reactions

Use molarity with stoichiometry

Example 1: What volume of 2.50 M HCl converts 10.0g of Zn to H_2 gas?

Step 1: Write the balanced equation and organize the data under the chemical reaction
Step 2: Calculate amount of Zn in mol using the molar mass of zinc
Step 3: Use the stoichiometric factor to convert to mol of HCl
Step 4: Calculate volume of HCl using the molarity

Step 1:	Zn(s)	+ 2 HCl(aq) -->	$ZnCl_2$(aq) + H_2(g)
V (L)		?	
M (mol/L)		2.50	
m (g)	10.0		
mol	____	____	

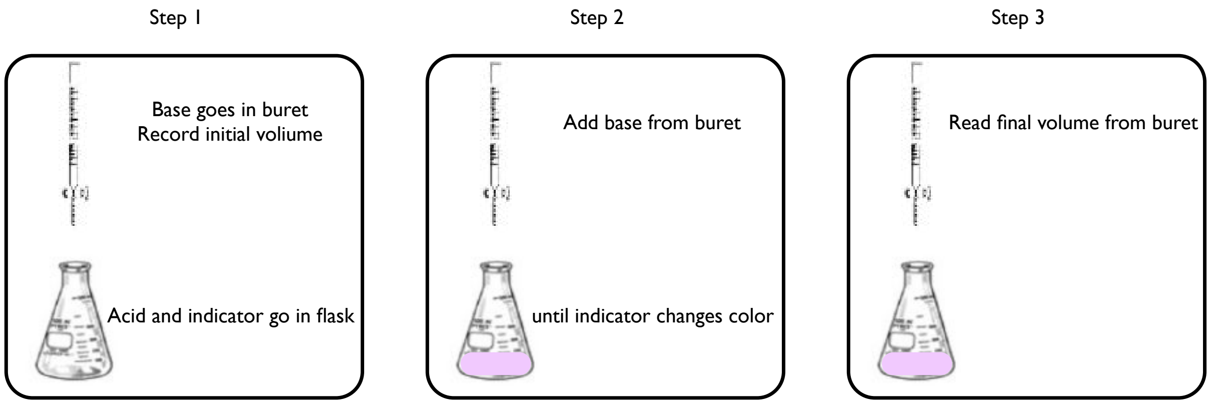
10.0 g Zn	1 mol Zn	2 mol HCl	1 L
	65.39 g Zn	1 mol Zn	2.50 mol HCl

Step 2: 0.15293 mol Zn (3SD)
Step 3: 0.30586 mol HCl (3SD)
Step 4: 0.12234 L of 2.50M HCl solution (3SD)
V=0.122L

Titration

With titration, one combines two reactants to reach a stoichiometric proportion or endpoint. The endpoint is often visualized by adding an indicator. At the endpoint, one can analyze an analyte (moles, grams, percentage, or concentration). Titration Works for any reaction type. The calculations for titration are similar to other stoichiometry calculations.

The reaction type that we will study is the titration of an acid by a base guided by an indicator that changes color at the endpoint. The picture below shows the basic steps involved in a titration, where an indicator changes color at the equivalence point. In the example that follows, the acid will be a known amount and the concentration of the base will be determined. (Either the acid or the base can be determined/analyzed by titration.)



What is the concentration of NaOH given that 1.103 g of $H_2C_2O_4$ (oxalic acid) requires 35.65 mL of NaOH to titrate to an equivalence point? The balanced chemical reaction is:
$2NaOH(aq) + H_2C_2O_4(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$

Step 1: Calculate amount of $H_2C_2O_4$ using the molar mass (90.034g/mol)
Step 2: Calculate amount of NaOH needed using the stoichiometry of reaction
Step 3: Calculate molar concentration of NaOH using the volume of NaOH.

	$2NaOH(aq)$	$H_2C_2O_4(aq)$	$Na_2C_2O_4(aq)$	$2H_2O(l)$
m (g)		1.103		
V (L)	0.03565			
mol	______	_______		
M(mol/L)	______			

1.103 g $H_2C_2O_4$	1 mol $H_2C_2O_4$	2 mol NaOH	1
	90.034 g $H_2C_2O_4$	1 mol $H_2C_2O_4$	0.03565 L

Step 1: 0.1225093mol $H_2C_2O_4$ (4SD)
Step 2: 0.02450185mol NaOH (4SD)
Step 3: 0.687289M NaOH (4SD)
M=0.6873M NaOH

89.813g of orange requires 43.55mL of 0.6873M NaOH for titration. What is the mass percent of citric acid in the orange? The chemical reaction is:

	$H_3C_6H_5O_7(aq)$	$3NaOH(aq)$	$Na_3C_6H_5O_7(aq)$	$3H_2O(l)$
V (L)		0.04355		
M(mol/L)		0.6873		
mol	_______	______		
g	_______			

Note: the orange contains citric acid, but the 89.813g of citric acid is not pure citric acid so it does not appear under citric acid in the chemical reaction. We will use the mass of orange to get mass percent.

Step 1: Calculate amount of NaOH used using the molarity of NaOH
Step 2: Calculate amount of acid using stoichiometry.
Step 3: Calculate mass of acid titrated using the molar mass of the acid (192.123).
Step 4: Calculate percent by mass of citric acid in the orange.

0.04355 L	0.6873 mol NaOH	1 mol $H_3C_6H_5O_7$	192.123 g $H_3C_6H_5O_7$
	1 L	3 mol NaOH	1 mol $H_3C_6H_5O_7$

Step 1: 0.0299319mol NaOH (4SD)
Step 2: 0.0099773mol $H_3C_6H_5O_7$ (4SD)
Step 3: 1.9168698g $H_3C_6H_5O_7$ (4SD)
Step 4: 1.9168698g $H_3C_6H_5O_7$/89.813g orange sample * 100% = 2.1342899% (4SD)
Mass% $H_3C_6H_5O_7$ = 2.134%

Classifying, Writing, and Balancing Redox Reactions
We previously classified, wrote, and balanced precipitation, acid-base, and gas-forming reactions. Redox reactions have electron transfer, and that is what sets them apart from the other reaction types. With redox, one atom loses one or more electrons electron, so the charge (or oxidation number) will increase. Another atom gains one or more electrons, so the oxidation number will decrease. The term "redox" comes from the terms **red**uction and **ox**idation. If a substance gets oxidized (or loses electrons), then another substance gets reduced (or gains electrons). Phrases that may help you to remember these facts are LEO goes GER (Loss electrons oxidation / Gain electrons reduction) or OIL RIG (Oxidation is loss / Reduction is gain). Otherwise, you can remember that oxidation results in an increase in oxidation number (or charge) across a reaction arrow, while reduction results in a decrease.

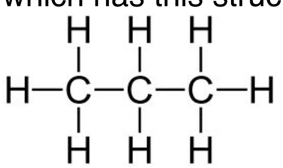
Redox reactions are commercially important. Batteries, fuels, metals, and corrosion are redox reactions. Living systems are based on redox reactions.

This set of rules can be used to determine oxidation numbers for atoms or bound atoms. An oxidation number is the charge that an atom (or bound atom) appears to have when counted according to this set of rules.

1. Each atom in a free element has an oxidation number of zero
   Examples: Cu O_2 Cl_2 P_4 S_8 C_{60}
2. In monatomic ions, the oxidation number equals the charge on the ion.
   Examples: -1 for F^- +2 for Ca^{2+}
3. In compounds, assign O an oxidation number of –2
   (except in peroxides like H_2O_2 where O is -1)
4. In compounds, assign H an oxidation number of +1
   (except in hydrides, such as NaH, where H is -1)
5. The algebraic sum of oxidation numbers equals zero for a compound and the charge for an ion.

(Note that electronegativity can be used to assign oxidation numbers when the above rules are not sufficient, but this rule is skipped for now.)

Use the rules for oxidation number to practice assigning oxidation numbers for these examples: P in PH_3, Br in BrO_3^-, S in H_2SO_4, Cr in CrO_4^{2-}, Cr in $AuCr_2O_7$, and C in C_3H_8.
Answers: For PH_3, assign H=+1. The three bound H atoms give a total of +3. The algebraic sum of P + 3 = 0, giving P= –3. For BrO_3^-, assign O=-2. The three bound O atoms give a total of -6. The algebraic sum of Br + -6 = -1, giving Br=+5. For H_2SO_4, assign H=+1 and O=-2. The two bound hydrogen atoms give +2, while the four bound oxygen atoms give -8.The algebraic sum of +2 + S + -8 = 0, giving S=+6. For CrO_4^{2-}, assign O=-2. The four bound O atoms give -8. The algebraic sum of Cr + -8 = -2, giving Cr=+6. For $AuCr_2O_7$, name the compound. It is gold(II) dichromate. The oxidation number of the gold cation can be assigned using rules previously taught for writing and naming compounds. Assign the bound oxygen =-2. The seven bound oxygen atoms give a total of -14. The algebraic sum of 2 + 2Cr -14 = 0, giving 2Cr = 12 (and Cr=+6). For C_3H_8, assign H=+1. This gives +8 for the 8 bound H atoms. The algebraic sum of 3C + 8 = 0, giving C=–8/3. The oxidation number should be an integer. C_3H_8 is propane, which has this structure:



If you determine the oxidation number at each carbon, the first and third bound C are –3, while the middle bound C is –2. The average of these comes to –8/3.

In this redox reaction, $Cu(s) + 2\,Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)$, copper metal is oxidized because it goes from a oxidation number (or charge) of zero on the left to +2 on the right. Silver ion is reduced from a +1 oxidation state on the left to a 0 oxidation state on the right.

	Cu(s)	+ 2 $Ag^+(aq)$	→ $Cu^{2+}(aq)$	+ 2 Ag(s)
Oxidation Number	0	+1	+2	0

Cu(s) was oxidized because its oxidation number increased (or it lost electrons). Ag^+ was reduced because its oxidation number decreased (or it gained electrons). When we use the term agent, such as oxidizing agent or reducing agent, it means the effect one chemical has on the other. As a result, copper, Cu(s), is the reducing agent because it reduced the silver ion, Ag^+. Silver ion, Ag^+, is the oxidizing agent because it oxidized copper metal, Cu(s). Notice that all of these terms referred to the reactants of a redox reaction.

Redox reactions require special rules to balance. These rules are given below.
Step 1: Split the reaction into half-reactions, one for oxidation and the other for reduction.

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

Step 2: Balance the half reactions for mass (in aqueous, acidic solution, you can add H_2O to balance O and H^+ to balance H). The reaction is already balanced by mass so none of these steps is needed.

Step 3: Balance the half-reactions for charge by adding electrons.

Oxidation $\quad Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Reduction $\quad Ag^+(aq) + e^- \rightarrow Ag(s)$

Note that the oxidation adds electrons to the right side of the arrow (a loss of electrons by the reactant), while the reduction adds electrons to the left side of the arrow (a gain or electrons by the reactant).

Step 4: Multiply the half-reactions by factors so that the electrons cancel. Use the concept of least-common multiple.

Oxidation $\quad Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Reduction $\quad 2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

Step 5: Add the half-reactions (and simplify) to give the balanced redox reaction:

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

Step 6: If you need a redox reaction balanced in base (instead of acid solution), add OH^- to both sides to neutralize all H^+ to form water, then cancel out species that are the same on both sides. (No H^+ appears in the balanced reaction, so this step would not be needed).

Balance the following reaction in acid solution:

$$VO^{2+}(aq) + Al(s) \rightarrow V^{3+}(aq) + Al^{3+}(aq)$$

Step 1: Half reactions

Oxidation: $\quad Al(s) \rightarrow Al^{3+}(aq)$

Reduction: $\quad VO^{2+} \rightarrow V^{3+}(aq)$

Step 2: Balance for mass

Oxidation: $\quad Al(s) \rightarrow Al^{3+}(aq)$

Reduction: $\quad 2H^+(aq) + VO^{2+}(aq) \rightarrow V^{3+}(aq) + H_2O(l)$

Step 3: Balance for charge

Oxidation: $\quad Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

Reduction: $\quad e^- + 2H^+(aq) + VO^{2+}(aq) \rightarrow V^{3+}(aq) + H_2O(l)$

Step 4: Use least-common multiple between 3 and 1 to get electrons to cancel.

Oxidation: $\quad [Al(s) \rightarrow Al^{3+}(aq) + 3e^-] \times 1$

Reduction: $\quad [e^- + 2H^+(aq) + VO^{2+}(aq) \rightarrow V^{3+}(aq) + H_2O(l)] \times 3$

Step 5: Add half reactions to give the balanced redox reaction

$$Al(s) + 6H^+(aq) + 3VO^{2+}(aq) \rightarrow 3V^{3+}(aq) + 3H_2O(l) + Al^{3+}(aq)$$

Step 6: Not needed for balancing in acid.

Balance the above reaction in base.

Answer: It is easiest to start from Step 5 above, though you could repeat the process from the beginning.

$Al(s) + 6H^{+}(aq) + 3VO^{2+}(aq) \rightarrow 3V^{3+}(aq) + 3H_2O(l) + Al^{3+}(aq)$

Step 6: Add $6OH^{-}(aq)$ to both sides to form water, then simplify.

Add OH^{-}: $Al(s) + 6H^{+}(aq) + 6OH^{-}(aq) + 3VO^{2+}(aq) \rightarrow 3V^{3+}(aq) + 3H_2O(l) + 6OH^{-}(aq) + Al^{3+}(aq)$

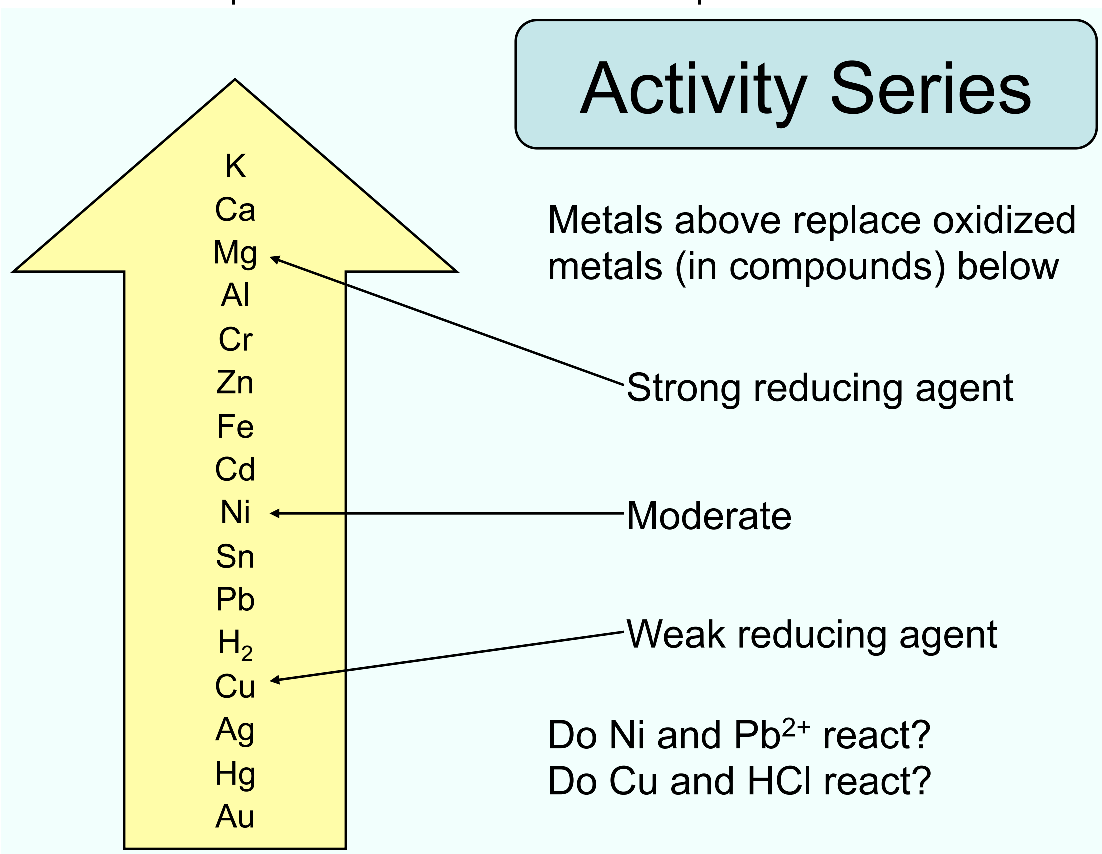
Form H_2O: $Al(s) + 6H_2O(l) + 3VO^{2+}(aq) \rightarrow 3V^{3+}(aq) + 3H_2O(l) + 6OH^{-}(aq) + Al^{3+}(aq)$

Simplify: $Al(s) + 3H_2O(l) + 3VO^{2+}(aq) \rightarrow 3V^{3+}(aq) + 6OH^{-}(aq) + Al^{3+}(aq)$

In addition to oxidation numbers (and LEO/GER), you can recognize an oxidation by an increase of oxygen or halogen or by a loss of hydrogen. Conversely, reduction is characterized by loss of oxygen or halogen or by a gain of hydrogen.

Activity Series and Product-Favored Redox Reactions

The activity series tells if a redox reaction is product favored as written. Metals above in the series will replaced oxidized metals from compounds below.



Ni and Pb^{2+} would react because Ni is above Pb (the metal is above the ion). Cu does not react with HCl because Cu is below H_2, (the metal is below the ion, H^{+}). No reaction occurs. Do Cu(s) and $Ag^{+}(aq)$ react. Yes, because copper metal is above silver ion. Also, strong reducing agents produce weak oxidizing agents. Mg^{2+} would be a weak oxidizing agent because Mg is a strong reducing agent. Conversely, weak reducing agents produce strong oxidizing agents. Cu^{2+} would be a strong oxidizing agent because Cu is a weak reducing agent.