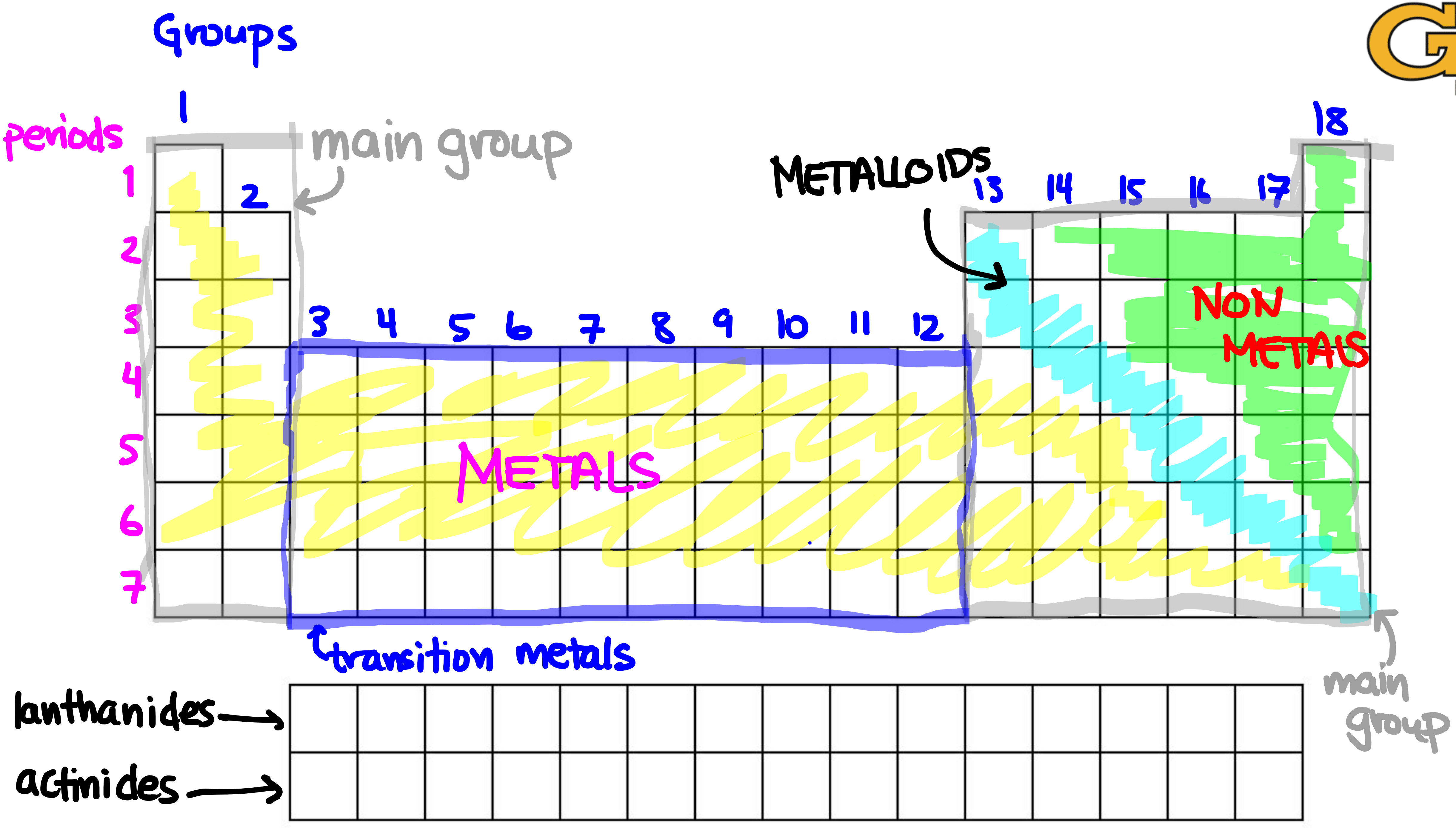
3. A Compounds and the Mole I

First-year Chemistry Program



Groups
periods
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
main group
METALLOIDS
NON METALS
METALS
transition metals
lanthanides
actinides
main group

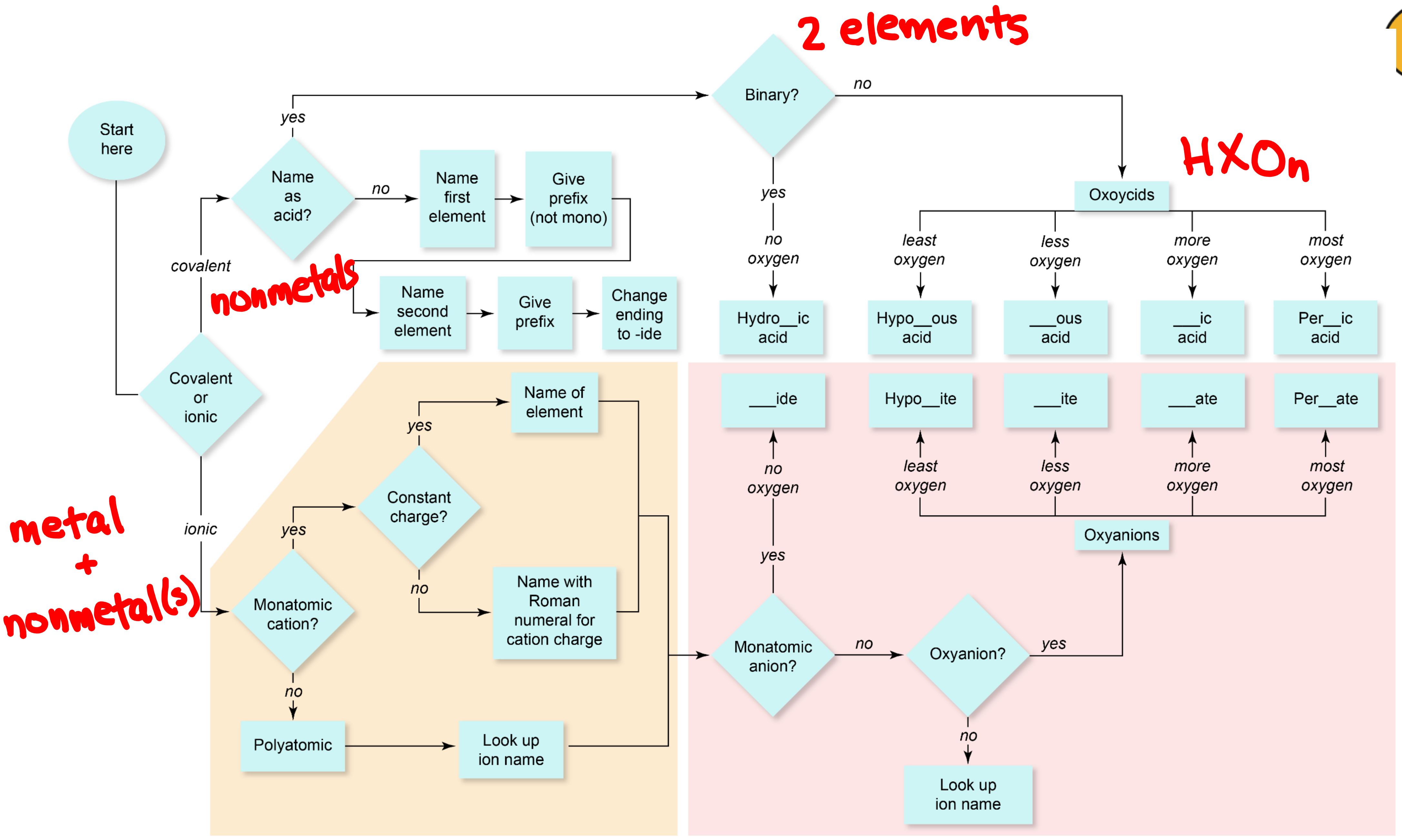
Objectives

- At the end of this chapter you should be able to:
  - Interpret chemical formulas.
  - Write chemical formulas to represent simple inorganic chemical compounds.
  - Name simple inorganic chemical compounds

F

  - Calculate the number of moles from the number of particles and vice versa.
  - Calculate the mass of 1 mol of a substance based on its chemical formula and atomic masses from the periodic table. molar mass
  - Calculate the percent composition by mass of a compound based on its chemical formula and atomic masses from the periodic table.
  - Determine the empirical and molecular formulas of a compound from percent composition or other mass-ratio data.
  - Determine the empirical formula for a compound based on data from a combustion analysis, in which the carbon in the compound is converted to carbon dioxide and the hydrogen is converted to water.

M



Name cation first.

Then name anion.

Check out the links below to practice naming ionic compounds given formulas and generating the formulas of ionic compounds from their names. How many correct answers can you get in 3 minutes?

Practice generating names from formulas at this link. Don't forget to include Roman numerals with the names of cations where multiple oxidation states are possible. Post your score after 3 minutes in Teams!

$Co(ClO_2)_3$

Co^{3+} ClO_2^-

cobalt(III) chlorite

transition metal w/ multiple oxidation states

Check out the links below to practice naming ionic compounds given formulas and generating the formulas of ionic compounds from their names. How many correct answers can you get in 3 minutes?

Practice generating formulas from names [at this link](). Don't worry about subscripts when typing in formulas. Post your score after 3 minutes in Teams!

sodium bromate

Na^+ BrO_3^-

$NaBrO_3$

OR

$Na(BrO_3)$

$2H^+$

"dihydrogen phosphate"

PO_4^{3-}

$H_2PO_4^-$

$Mg(H_2PO_4)_2$

In this series of problems we will examine a few structures on the Crystallography Open Database (COD).

Visit this link and examine the three-dimensional structure that appears. Hover your mouse over each atom to see its chemical symbol. This structure contains both ionic and covalent bonds. List the different types of covalent bonds in the structure (e.g., C–C). Then, find the lone cation in the structure and determine its charge.

covalent

C–H

C–Si

Si–N

O–N

C–N

C–C

ionic

$Mg^{2+} \cdots {}^{-}OR$

metal

$\vdots$

${}^{-}NR_2$

nonmetal

In this series of problems we will examine a few structures on the Crystallography Open Database (COD).

Visit [this link]() and examine the three-dimensional structure that appears. Examine the AlF_5 molecules. What is the net charge on each molecule? How do you know? What is the net charge on the $HN(CH_2CH_2NH_3)_3$ molecule?

AlF_5

Al^{3+} $\quad 5\,F^-$ $\Rightarrow$ net charge $= -2$

Structure contains two AlF_5^{2-}. So, for overall neutrality, the net charge on $HN(CH_2CH_2NH_3)_3 = +4$.

In this series of problems we will examine a few structures on the Crystallography Open Database (COD).

Visit this link and examine the three-dimensional structure that appears. The title of the paper reporting this structure mentions a "heavy alkaline earth" metal. What is the identity of this metal and what is its charge in the structure? What other charged atoms are in the structure?

Sr = strontium

charge is +2 (Sr^{2+}) because it's a group 2 metal.

Note also the two ^{-}OR groups balancing this charge.

Classify each of the following acids as a binary acid or an oxyacid and determine its name. As you generate the name, document your thought process in as much detail as you can.

HI binary acid

(hydrogen iodide)

$H^+ \; I^-$ → iodide → hydroiodic acid

$HBrO_4$ oxoacid

$H^+ \; BrO_4^-$ → perbromate → perbromic acid

HBr binary

hydrobromic acid ($H^+ \; Br^-$)

Classify each of the following acids as a binary acid or an oxyacid and determine its name. As you generate the name, document your thought process in as much detail as you can.

H_2S binary (hydrogen sulfide)

$2H^+ \quad S^{2-} \rightarrow$ sulfide $\rightarrow$ hydrosulfic acid

H_3PO_3 oxoacid

$\hookrightarrow 3\,H^+ \quad PO_3^{3-} \rightarrow$ phosph<u>ite</u> $\rightarrow$ phosphor<u>ous</u> acid

Each of the following compounds can be used as a source of phosphorus in the synthesis of H_3PO_3. Determine whether each is an ionic or covalent compound and name them. Separate the ionic compounds into their component ions.

K_2HPO_3 ionic

$\rightarrow 2K^+ \quad HPO_3^{2-}$ potassium hydrogen phosphite

PCl_3 covalent

phosphorus trichloride

P_4O_6 covalent

tetraphosphorus hexoxide

The anion BF_4^- has acts in many ways like an oversized halide anion. The conjugate acid of this anion, HBF_4, is of interest as a strong acid (similar to HCl, etc.).

The name of BF_4^- is "tetrafluoroborate." From this information, generate a name for the acid HBF_4.

-ic acid

tetrafluoroboric acid

The anion BF_4^- has acts in many ways like an oversized halide anion. The conjugate acid of this anion, HBF_4, is of interest as a strong acid (similar to HCl, etc.).

Pure HBF_4 decomposes to form HF and BF_3. Provide chemical names for each of the products of this reaction.

$HF \longrightarrow H^+ \quad F^- \longrightarrow$ fluoride $\longrightarrow$ hydrofluoric acid

binary acid

BF_3
covalent $\Big\}$ boron trifluoride

- Lab stuff
  - ↳ Lab coat (B&N)
  - ↳ Safety glasses (CULC 578)
  - ↳ Notebook pages
  - ↳ Intro quiz
  - ↳ Lab Safety 101

3.B Compounds and the Mole II

First-year Chemistry Program

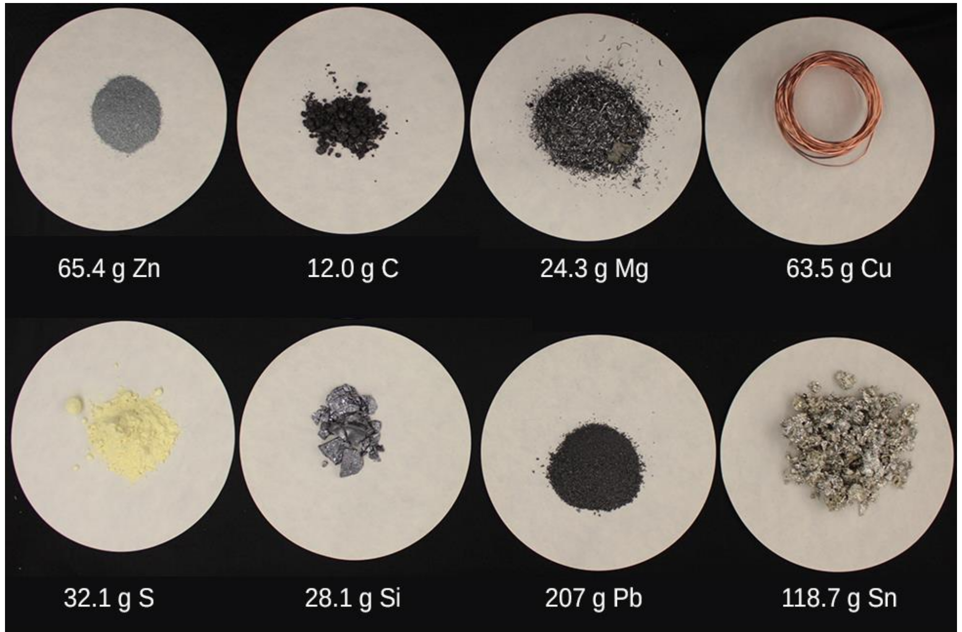
Moles of compound → Chemical formula → Moles of atoms → Avogadro's number → Number of atoms

data

molar mass

N_A

6.022×10^{23}



The fact that a mole corresponds to 6.022×10^{23} (Avogadro's number, N_A) objects is fairly well known. But where does this number come from? Through the following series of problems, we'll come to understand the mole better as a concept.

By definition, one carbon-12 atom has a mass of 12.00 atomic mass units (12.00 u). Using Wolfram Alpha, calculate the mass of Avogadro's number of carbon-12 atoms. "in grams"
(Wolfram Alpha is an intelligent calculator. You can type in "Avogadro's number" and it will understand what you mean quantitatively.)

N_A of ^{12}C atoms: 12.0 g

Repeat the calculation for Avogadro's number of oxygen-16 atoms (15.99 u) and bromine-79 atoms (78.92 u). Do you notice a pattern in the masses of N_A atoms?

N_A of ^{16}O atoms: 15.99 g

N_A of ^{79}Br atoms: 78.92 g

The fact that a mole corresponds to 6.022×10^{23} (Avogadro's number, N_A) objects is fairly well known. But where does this number come from? Through the following series of problems, we'll come to understand the mole better as a concept.

The pattern you're seeing is general for atoms and molecules. State the pattern as a general rule that relates mass on the atomic or molecular scale to mass on the scale of 1 mole.

The mass of an atom or molecule in atomic mass units (u) is equal to the mass of a mole of those atoms or molecules in grams (g). *Or,* the mass of a mole of a substance in grams is equal to the mass of a single atom or molecule in atomic mass units.

$$\boxed{1\,u \times N_A = 1\,g}$$

defined as $N_A = 1\,g/1\,u$

In the video on Mass Vocabulary, Dr. Shepler distinguishes between the terms formula mass and molecular mass. While not profoundly different in practice, these terms refer to compounds that look very different on the sub-microscopic scale. For each compound below, indicate whether the term "formula mass" or "molecular mass" is more appropriate for describing the mass of the formula unit. Then, calculate that mass in atomic mass units (u).

molar mass

Covalent (molecular) vs. ionic compounds

40.1 47.9

$CaTiO_3$ ← nonmetal

metal

16.0

*ionic (formula mass)

$40.1 + 47.9 + 3(16.0) = 136.0$ g/mol

$C_{21}H_{23}NO_5$

369.4 g/mol

*molecular (molecular mass)

Al_2O_3

*ionic

101.96 g/mol

$Be_3Al_2(SiO_3)_6$

*ionic

537.5 g/mol

Desmopressin is a drug that promotes the re-uptake of water by cells, raising blood pressure and decreasing the frequency of urination (an *anti-diuretic*).

Desmopressin contains 51.67% C, 6.03% H, 18.34% N, 17.96% O, and 6.00% S by mass. Determine the empirical formula of desmopressin from this data.

$C_x H_y N_z O_w S_a$

moles!

$$51.67\text{ g C}\left(\frac{1\text{ mol}}{12.011\text{ g}}\right) = 4.30\text{ mol C}/0.187 = 23\text{ mol C}$$

$$6.03\text{ g H}\left(\frac{1\text{ mol}}{1.01\text{ g}}\right) = 5.97\text{ mol H}/0.187 = 32\text{ mol H}$$

$$18.34\text{ g N}\left(\frac{1\text{ mol}}{14.01\text{ g}}\right) = 1.31\text{ mol N}/0.187 = 7\text{ mol N}$$

$$17.96\text{ g O}\left(\frac{1\text{ mol}}{16.00\text{ g}}\right) = 1.12\text{ mol O}/0.187 = 6\text{ mol O}$$

$$6.00\text{ g S}\left(\frac{1\text{ mol}}{32.07\text{ g}}\right) = 0.187\text{ mol S}/0.187 = 1\text{ mol S}$$

empirical

$\boxed{C_{23}H_{32}N_7O_6S}$

534.6 g/mol

Desmopressin is a drug that promotes the re-uptake of water by cells, raising blood pressure and decreasing the frequency of urination (an *anti-diuretic*).

An independent experiment confirmed that a sample of 1.0692 g of desmopressin contains 1.000 mmol of desmopressin molecules. What is the molar mass of desmopressin? What is its molecular formula?

millimoles!

$$\frac{1.0692\text{ g}}{1.000\times10^{-3}\text{ mol}} = 1069.2\text{ g/mol}$$

$$\frac{1069.2\text{ g/mol}}{534\text{ g/mol}} = 2$$

molecular

$$\boxed{C_{46}H_{64}N_{14}O_{12}S_2}$$

multiply emp. formula by 2 = molecular formula

The combustion of an unknown hydrocarbon (a compound containing only carbon and hydrogen) produced 8.80 g of CO_2 and 4.50 g of H_2O. The molar mass of the compound, determined in a separate experiment, is 58.124 g/mol. What is the molecular formula of the compound?

$$C_xH_y + n\,O_2 \longrightarrow x\,CO_2 + (y/2)\,H_2O$$

$$8.80\text{ g }CO_2\left(\frac{1\text{ mol }CO_2}{44.0\text{ g}}\right)\left(\frac{1\text{ mol C}}{1\text{ mol }CO_2}\right) = 0.200\text{ mol C } (\times 5)$$

$$4.50\text{ g }H_2O\left(\frac{1\text{ mol }H_2O}{18.0\text{ g}}\right)\left(\frac{2\text{ mol H}}{1\text{ mol }H_2O}\right) = 0.500\text{ mol H } (\times 5)$$

$$\left\{\begin{array}{l}1\text{ mol C } (\times 2)\\ 2.5\text{ mol H } (\times 2)\end{array}\right.$$

~29 g/mol
C_2H_5
empirical

58.1 g/mol
C_4H_{10}
molecular

$C_4H_{10} \Longleftarrow C_2H_5$

4.A Chemical Reactions and Aqueous Solutions

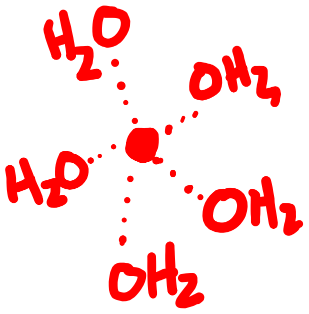
First-year Chemistry Program

Chemical Equations (4.1)

- ***Chemical equations***
  - Designed to represent the transformation of one or more chemical species into new substances.
- ***Reactants***
  - The starting components of a reaction
- ***Products***
  - The ending components.
- Chemical equations are always written:

Reactants → Products

• (aq)



Chemical Equations (4.1)

- A great deal of information can be gleaned from a chemical equation:

Information	Notation	Example
What happens?	Identity (names and/or formulas) of the reactants and products	Hydrogen (H_2) and oxygen (O_2) react to produce water (H_2O).
In what proportions?	Coefficients placed before the formulas	$2\ H_2 + O_2 \rightarrow 2\ H_2O$
In what physical states?	(s), (l), (g), (aq) included after the formulas	$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$
Under what conditions?	Special conditions written above or below the arrow	$\xrightarrow{Heat}$

Table 4.1

Chemical Equations (4.1)

- In a ***balanced chemical equation***, the number of atoms of *each element* on the left side of the balanced equation is *equal* to the number of atoms of *that element* on the right.

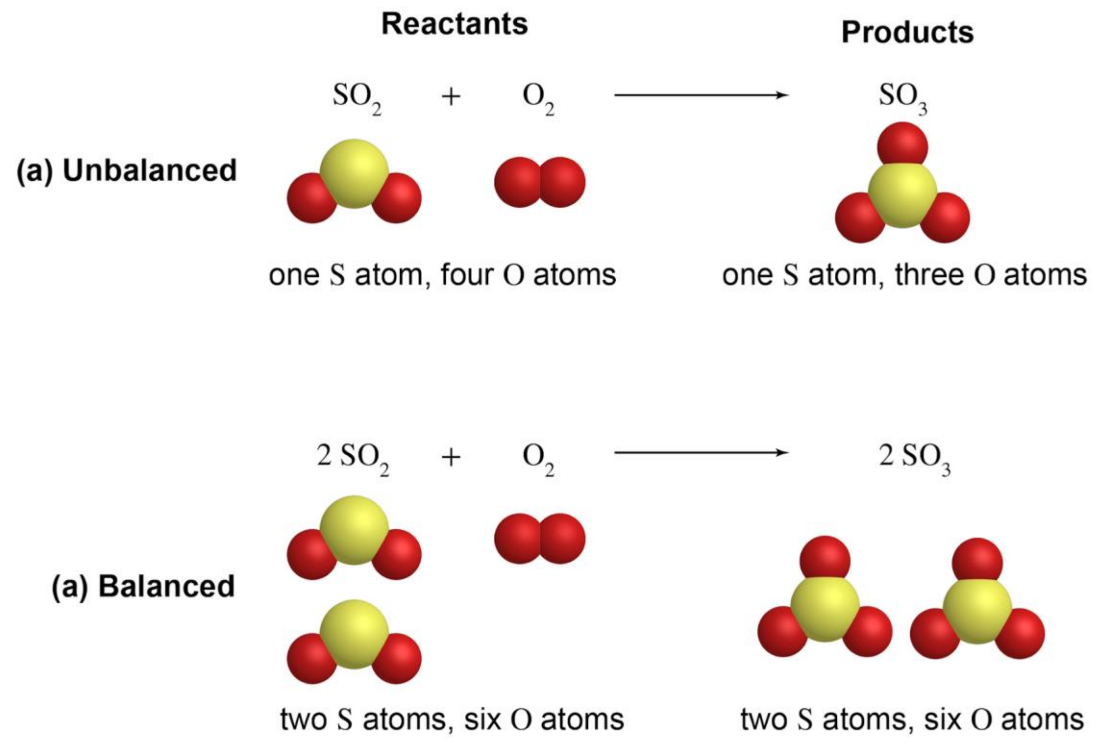


Figure 4.3

Types of Chemical Reactions (4.2)

- Summary of reaction types

Reaction Type	Generic Formula	Examples
Synthesis	A + B → AB	$2\ Fe(s) + 3\ O_2(g) \rightarrow Fe_2O_3(s)$
Decomposition	AB → A + B	$2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$ $KClO_3(s) \rightarrow KCl(s) + O_2(g)$
Single-Replacement	A + BC → AC + B	$Zn(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$
Double-Replacement	AB + CD → AD + CB	$2\ KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2\ KNO_3(aq)$ $HBr(aq) + KOH(aq) \rightarrow KBr(aq) + H_2O(l)$
Combustion	$C_xH_y + O_2 \rightarrow CO_2 + H_2O$	$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$

Table 4.2

Classify each of the reactions below using the reaction classes described in the Types of Chemical Reactions videos.

$$Si(s) + 2\ Cl_2(g) \rightarrow SiCl_4(l)$$

elements

compound

• 2 reactants

• 1 product

★Synthesis★

(Formation)

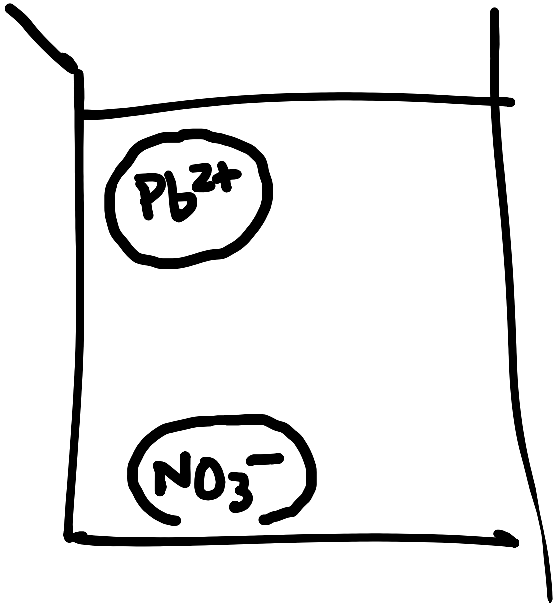
Classify each of the reactions below using the reaction classes described in the Types of Chemical Reactions videos.

$$\underbrace{2\ C_4H_{10}(g)}_{\text{hydrocarbon}} + \underbrace{13\ O_2(g)}_{\text{oxygen gas}} \rightarrow \underbrace{8\ CO_2(g) + 10\ H_2O(g)}_{\text{carbon dioxide, water}}$$

★ Combustion ★

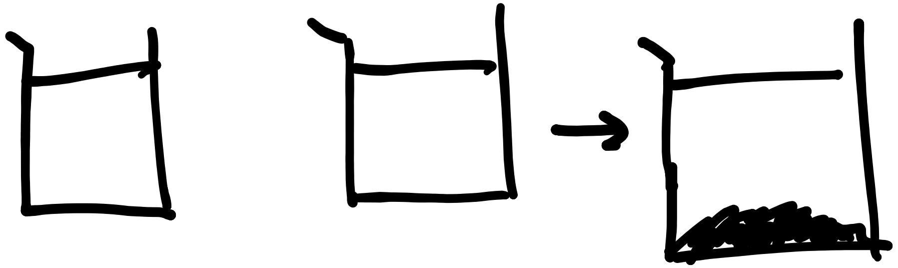
★Dissociation of Ionic Solutes★

$$Pb(NO_3)_2\,(aq) \xrightarrow{\text{dissociation}} Pb^{2+}(aq) + 2\,NO_3^-(aq)$$



Classify each of the reactions below using the reaction classes described in the [Types of Chemical Reactions] videos.

$Pb(NO_3)_2(aq) + 2\ KI(aq) \rightarrow PbI_2(s) + 2\ KNO_3(aq)$



Double replacement

What is the driving force in this reaction?

Formation of an insoluble precipitate

To better understand and predict how and why reactions happen, we often think about what's going on at the molecular or sub-microscopic level. For each of the reactions below, draw molecular-scale pictures of the reactants and products. Make an effort to balance the elements in both pictures.

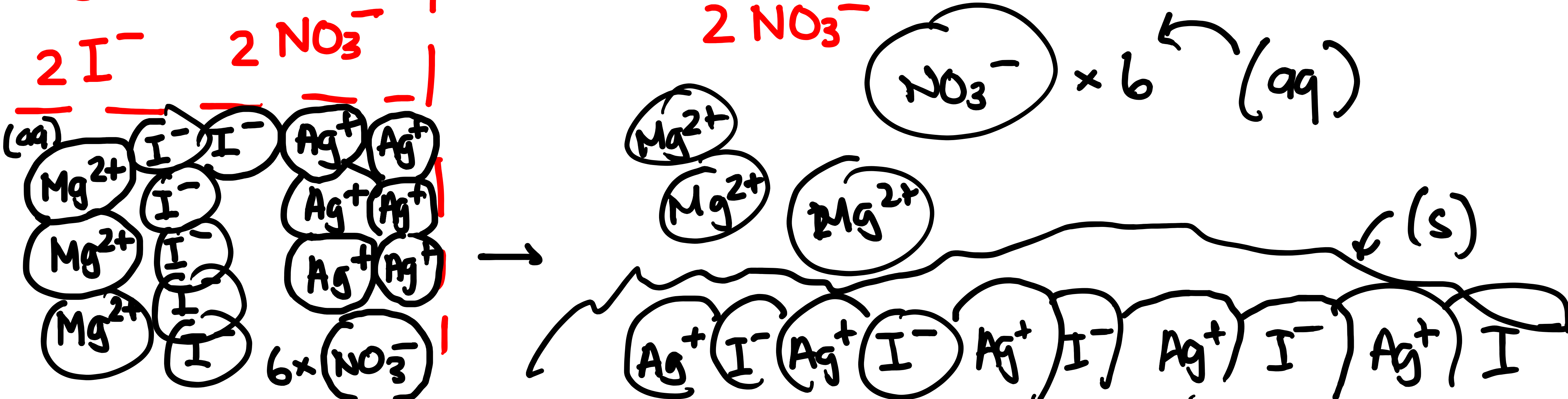
$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

To better understand and predict how and why reactions happen, we often think about what's going on at the molecular or sub-microscopic level. For each of the reactions below, draw molecular-scale pictures of the reactants and products. Make an effort to balance the elements in both pictures.

$MgI_2(aq) + 2\ AgNO_3(aq) \rightarrow 2\ AgI(s) + Mg(NO_3)_2(aq)$

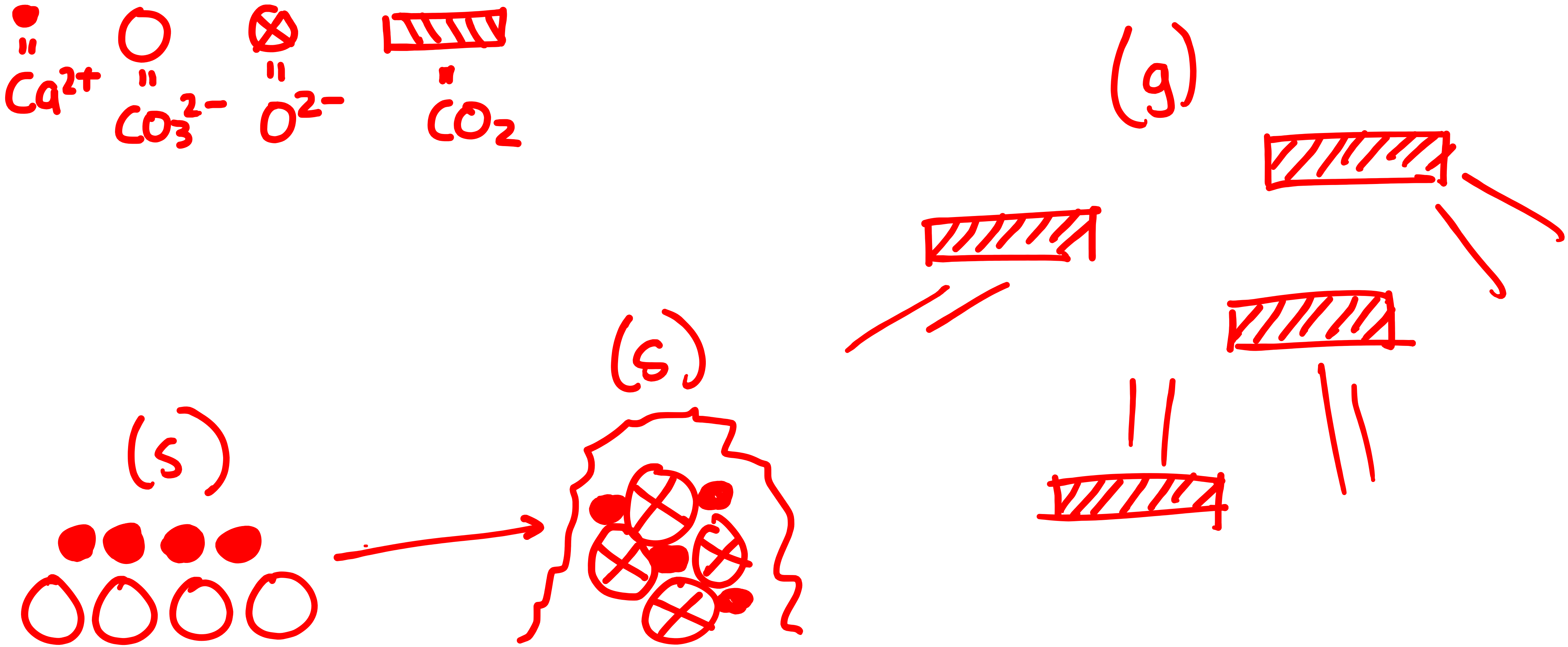
Mg^{2+} $2\ Ag^{+}$ $AgI(s)$ Mg^{2+}

$2\ I^{-}$ $2\ NO_3^{-}$ $2\ NO_3^{-}$



To better understand and predict how and why reactions happen, we often think about what's going on at the molecular or sub-microscopic level. For each of the reactions below, draw molecular-scale pictures of the reactants and products. Make an effort to balance the elements in both pictures.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$



When aqueous sodium carbonate (Na_2CO_3) is mixed with an aqueous solution of acetic acid ($HO_2C_2H_3$), a reaction occurs that produces carbon dioxide (CO_2), water (H_2O), and sodium acetate ($NaO_2C_2H_3$).

This reaction occurs in two stages: an initial formation of carbonic acid (H_2CO_3) followed by the conversion of carbonic acid to water and carbon dioxide. *Unbalanced* equations showing these processes are below.

Provide coefficients in both chemical equations so that the overall conversion of sodium carbonate to sodium acetate, water, and carbon dioxide is balanced.

$$\underline{\ 1\ }\ Na_2CO_3(aq) + \underline{\ 2\ }\ HO_2C_2H_3(aq) \rightarrow \underline{\ 2\ }\ NaO_2C_2H_3(aq) + \underline{\ 1\ }\ H_2CO_3(aq)$$

$$\underline{\ 1\ }\ H_2CO_3(aq) \rightarrow \underline{\ 1\ }\ H_2O(l) + \underline{\ 1\ }\ CO_2(g)$$

When aqueous sodium carbonate (Na_2CO_3) is mixed with an aqueous solution of acetic acid ($HO_2C_2H_3$), a reaction occurs that produces carbon dioxide (CO_2), water (H_2O), and sodium acetate ($NaO_2C_2H_3$).

This reaction occurs in two stages: an initial formation of carbonic acid (H_2CO_3) followed by the conversion of carbonic acid to water and carbon dioxide.

How would you classify the first reaction? What is its driving force?

replacement 1

$$1\ Na_2CO_3(aq) + 2\ HO_2C_2H_3(aq) \rightarrow 2\ NaO_2C_2H_3(aq) + 1\ H_2CO_3(aq)$$

replacement 2

Acid-base reaction

Driving force:

Neutralization

$(2H^+ + CO_3^{2-} \rightarrow H_2CO_3)$

Double replacement

When aqueous sodium carbonate (Na_2CO_3) is mixed with an aqueous solution of acetic acid ($HO_2C_2H_3$), a reaction occurs that produces carbon dioxide (CO_2), water (H_2O), and sodium acetate ($NaO_2C_2H_3$).

This reaction occurs in two stages: an initial formation of carbonic acid (H_2CO_3) followed by the conversion of carbonic acid to water and carbon dioxide.

How would you classify the second reaction?

$$\underbrace{1\ H_2CO_3(aq)}_{\text{1 reactant}} \rightarrow \underbrace{1\ H_2O(l) + 1\ CO_2(g)}_{\text{2 products}}$$

Decomposition

Melanoidins are complex structures formed when wet barley malt is heated in a kiln during the beermaking process. To model the formation of melanoidins, an α-hydroxy acetaldehyde ($C_2H_4O_2$) was combined with methylamine (CH_5N). The products were water (H_2O) and an organic compound with the formula $C_6H_{10}N_2$. Balance this chemical equation.

$$\underline{\ 2\ }\ C_2H_4O_2 + \underline{\ 2\ }\ CH_5N \longrightarrow \underline{\ 1\ }\ C_6H_{10}N_2 + \underline{\ 4\ }\ H_2O$$

4.B Chemical Reactions and Aqueous Solutions

First-year Chemistry Program

Compounds in Aqueous Solution (4.3)

- When ionic compounds dissolve, they ***dissociate*** or break apart into their constituent ions.
  - The associated reaction is called a ***dissociation reaction***.

$$NaCl(s) \longrightarrow Na^{+}(aq) + Cl^{-}(aq)$$

– Uneven distribution of electrons within the water molecule cause the O side to have a partial negative charge and the H side to have a partial positive charge.

– The result is ***hydrated ions.***

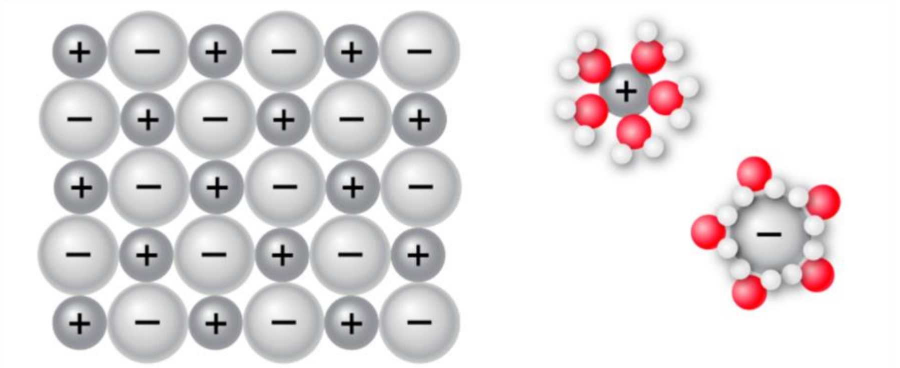


Figure 4.14 (a) Ionic lattice (b) Hydrated ions

Compounds in Aqueous Solution (4.3)

- There are only *seven* strong acids. ALL other acids are weak.

Table 4.3: Strong Acids

Acid Name	Formula	Ions in aqueous solution
Hydrochloric acid	HCl	H^+, Cl^-
Hydrobromic acid	HBr	H^+, Br^-
Hydroiodic acid	HI	H^+, I^-
Nitric acid	HNO_3	H^+, NO_3^-
Perchloric acid	$HClO_4$	H^+, ClO_4^-
Chloric acid*	$HClO_3$	H^+, ClO_3^-
Sulfuric acid**	H_2SO_4	H^+, HSO_4^-

*Considered weak in some sources.
**Only the first deprotonation is complete.

Compounds in Aqueous Solution (4.3)

- Only soluble hydroxide compounds are strong bases. ALL other bases are weak.
  - We will examine solubility rules in the next section.

Table not in text: Strong Bases

Base Name	Formula	Ions in aqueous solution
Lithium hydroxide	$LiOH$	Li^+, OH^-
Sodium hydroxide	$NaOH$	Na^+, OH^-
Potassium hydroxide	KOH	K^+, OH^-
Calcium hydroxide	$Ca(OH)_2$	Ca^{2+}, OH^-
Strontium hydroxide	$Sr(OH)_2$	Sr^{2+}, OH^-
Barium hydroxide	$Ba(OH)_2$	Ba^{2+}, OH^-

Compounds in Aqueous Solution (4.3)

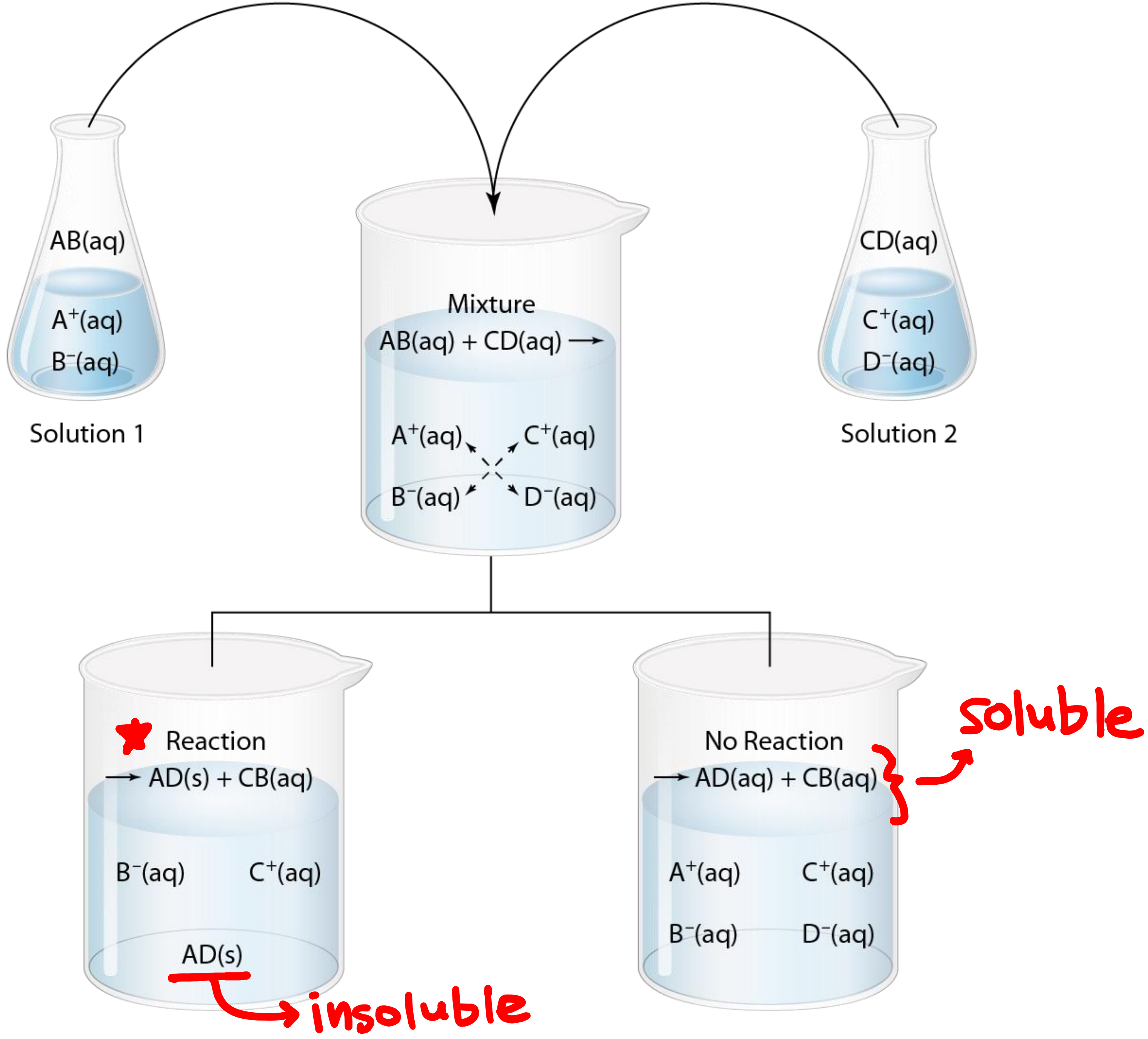
- Figure 4.16 gives you an opportunity to explore different compounds to determine if they are strong electrolytes, weak electrolytes, or nonelectrolytes.

Table 4.4: Electrolytic Properties of Various Types of Compounds

Solution Type	Compound Type	Examples
Strong electrolyte	Ionic (salts)	$NaCl(aq)$, $K_2SO_4(aq)$
	Ionic (strong bases)	$NaOH(aq)$, $KOH(aq)$
	Strong acid	$HCl(aq)$, $HNO_3(aq)$
Weak electrolyte	Weak acid	$HNO_2(aq)$, $H_3PO_4(aq)$
	Weak base	$NH_3(aq)$, $CH_3NH_2(aq)$
Nonelectrolyte	Molecular (most)	$C_6H_{12}O_6(aq)$ and other sugars

ionic, complete dissociation

molecular


AB(aq)
A+(aq)
B-(aq)
Solution 1
Mixture
AB(aq) + CD(aq) →
A+(aq)
C+(aq)
B-(aq)
D-(aq)
CD(aq)
C+(aq)
D-(aq)
Solution 2
Reaction
→ AD(s) + CB(aq)
B-(aq)
C+(aq)
AD(s)
insoluble
No Reaction
→ AD(aq) + CB(aq)
soluble
A+(aq)
C+(aq)
B-(aq)
D-(aq)

Precipitation Reactions (4.4)

- **Solubility Guidelines**

1. Compounds of group 1 elements (Li^+, Na^+, K^+, Rb^+, Cs^+, and Fr^+) and ammonium (NH_4^+) are soluble. MX is soluble. (M+)
2. Nitrates (NO_3^-), chlorates (ClO_3^-), perchlorates (ClO_4^-), and acetates ($C_2H_3O_2^-$) are soluble.
3. Chlorides (Cl^-), bromides (Br^-), and iodides (I^-) are soluble, except for those of Ag^+, Pb^{2+}, and Hg_2^{2+}.
4. Except for compounds of the cations in guideline 1, carbonates (CO_3^{2-}), sulfites (SO_3^{2-}), phosphates (PO_4^{3-}), and chromates (CrO_4^{2-}) are *in*soluble.
5. With the exception of guideline 1 and the barium ion (Ba^{2+}), hydroxides (OH^-) and sulfides (S^{2-}) are *in*soluble.
6. With the exception of guideline 2, silver (Ag^+), mercury (Hg_2^{2+}), and lead (Pb^{2+}) salts are *in*soluble.
7. With the exception of compounds of calcium (Ca^{2+}), strontium (Sr^{2+}), barium (Ba^{2+}), and the ions listed in guideline 6, all sulfates are soluble.

In the video [Compounds in Aqueous Solution], Dr. Shepler discusses the difference between *dissolution* and *dissociation*.

sucrose

Provide an example of a compound that does not undergo dissociation when dissolved in water. Write a balanced chemical equation with state indicators for the dissolution of this compound in water, looking up formulas where necessary.

$$C_{12}H_{22}O_{11}(s) \longrightarrow C_{12}H_{22}O_{11}(aq)$$

sucrose solid

aqueous sucrose

In the video [Compounds in Aqueous Solution], Dr. Shepler discusses the difference between *dissolution* and *dissociation*.

NaCl

Provide an example of a compound that does undergo dissociation when dissolved in water. Write separate balanced chemical equations for the dissolution and dissociation processes.

$NaCl(s) \longrightarrow NaCl(aq)$ · dissolution

$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$ · dissociation

In the video Compounds in Aqueous Solution, Dr. Shepler discusses the difference between *dissolution* and *dissociation*.

Examine molecular-level images of dissociating and non-dissociating solutes using the Sugar and Salt Solutions simulation.

see simulation!

Determine whether each of the following compounds is a strong or weak electrolyte. Provide a justification in each case.

$NaOH$ → strong electrolyte
ionic
strong base

$NiBr_2$ → strong electrolyte
ionic, soluble

H_2SO_4 → strong electrolyte
strong acid

$C_6H_{12}O_6$ → non-electrolyte
glucose
molecular, no dissociation to ions

$HO_2C_2H_3$ → weak electrolyte
weak acid

HCl → strong electrolyte
strong acid

The solubility rules are qualitative guidelines that enable us to predict whether a given ionic solid is soluble in water or not.

Use the solubility rules to construct six ionic compounds involving different ions (i.e., twelve distinct ions in all) that are soluble in water.

KNO_3	$Co(NO_3)_2$	NaOH	etc.…
K_2CO_3	NH_4F	FrBr	
$CsNO_3$	$MgCl_2$	PbS	

The solubility rules are qualitative guidelines that enable us to predict whether a given ionic solid is soluble in water or not.

Use the solubility rules to construct six ionic compounds involving different ions (i.e., twelve distinct ions in all) that are insoluble in water.

$CaSO_4$ $MgCO_3$ $AgBr$ etc....

$BaSO_4$ $AgCl$ $PbCl_2$

Lead(II) nitrate reacts with sodium chloride in aqueous solution to form a precipitate.

Write balanced molecular, ionic, and net ionic equations for this process with state indicators. Identify the spectator ions in the reaction.

$$Pb(NO_3)_2(aq) + 2\,NaCl(aq) \longrightarrow 2\,NaNO_3(aq) + PbCl_2(s)$$

molecular

spectators

ionic:

$$Pb^{2+}(aq) + 2\,NO_3^-(aq) + 2\,Na^+(aq) + 2\,Cl^-(aq) \longrightarrow PbCl_2(s) + 2\,Na^+(aq) + 2\,NO_3^-(aq)$$

net ionic:

$$Pb^{2+}(aq) + 2\,Cl^-(aq) \longrightarrow PbCl_2(s)$$

5.A Stoichiometry

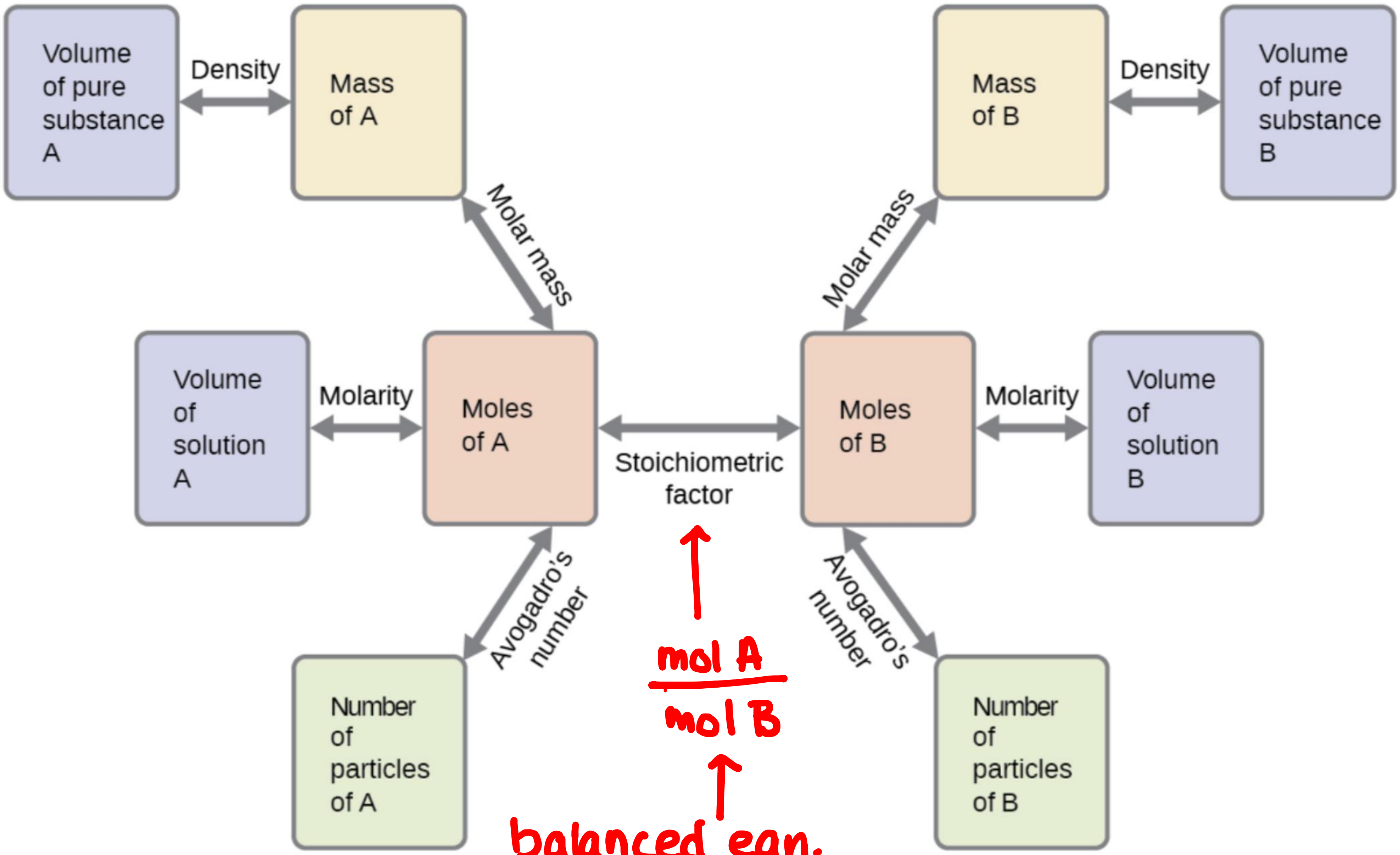
First-year Chemistry Program

Objectives

- At the end of this chapter you should be able to:
  - Calculate the number of moles of any substance involved in a chemical reaction from the number of moles of any other substance in the reaction.
  - Use the mass of one substance to determine the masses of other substances involved in a chemical reaction.
  - Calculate the quantities of substances produced in a reaction when quantities of more than one reactant are specified. (limiting reactant)
  - Express the quantity of product obtained from a reaction as a percentage of what the reaction is theoretically capable of producing. (yield)
  - Solve problems using molarity.

inputs

output



$\frac{\text{mol A}}{\text{mol B}}$

balanced eqn.

In several problems spread out over the next week, we'll explore the process of creating a desmopressin solution outlined in this video. We previously encountered the anti-diuretic drug desmopressin ($C_{46}H_{64}N_{14}O_{12}S_2$, 1069.2 g/mol) in Chapter 3.

molar mass

This compound is commonly treated with acetic acid ($HC_2H_3O_2$, 60.1 g/mol) to produce desmopressin acetate ($C_{48}H_{68}N_{14}O_{14}S_2$, 1129.3 g/mol). Desmopressin and acetic acid react in a 1:1 molar ratio.

molar mass

mole-mole ratio

How many moles of desmopressin are present in a 120. mg sample?

$$\text{mass D} \xrightarrow[\left(\div \frac{\text{mass}}{\text{mol}} D\right)]{\times \frac{\text{mol}}{\text{mass}} D} \text{mol D}$$

$$0.120\text{g}\left(\frac{1\text{ mol D}}{1069.2\text{g D}}\right) = 1.12\times10^{-4}\text{ mol D}$$

$$= 112\ \mu\text{mol}$$

$$(1\ \mu\text{mol} = 10^{-6}\text{ mol})$$

In several problems spread out over the next week, we'll explore the process of creating a desmopressin solution outlined in [this video](). We previously encountered the anti-diuretic drug desmopressin ($C_{46}H_{64}N_{14}O_{12}S_2$, 1069.2 g/mol) in Chapter 3.

This compound is commonly treated with acetic acid ($HC_2H_3O_2$, 60.1 g/mol) to produce desmopressin acetate ($C_{48}H_{68}N_{14}O_{14}S_2$, 1129.3 g/mol). Desmopressin and acetic acid react in a 1:1 molar ratio.

$$1D + 1A \longrightarrow 1DA$$

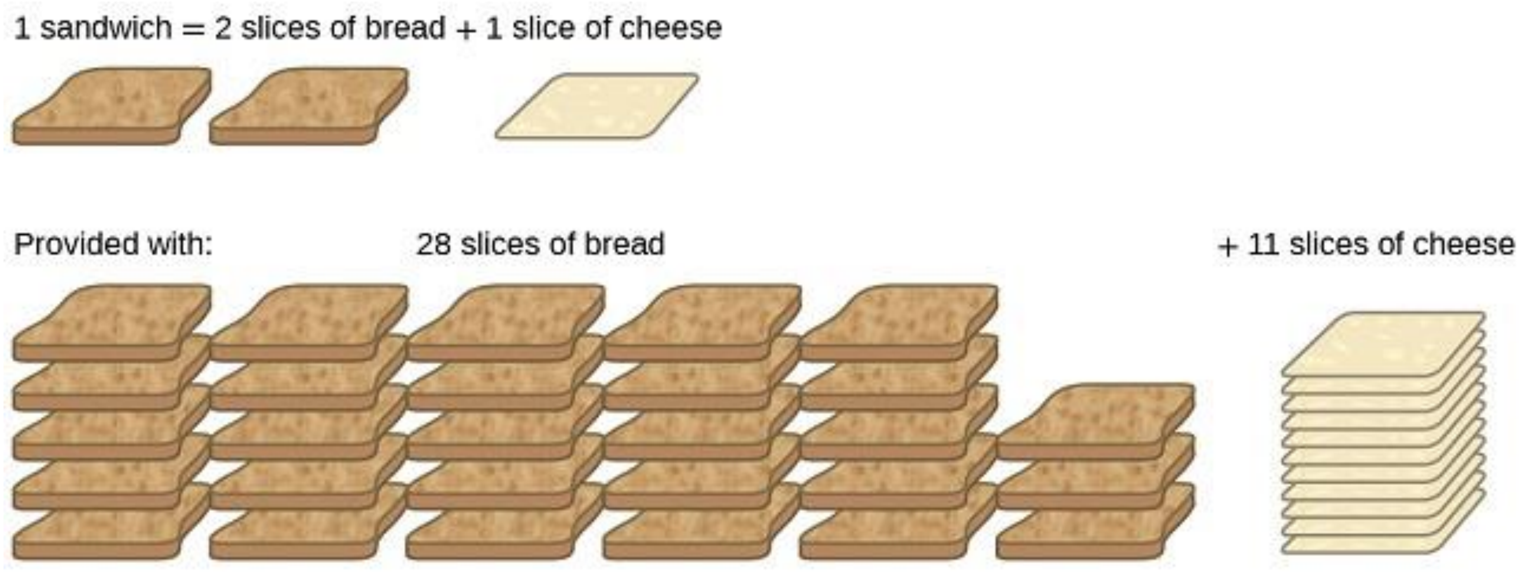
What mass of acetic acid is necessary to completely consume this amount of desmopressin?

$$\text{mass } D \xrightarrow[\times \frac{\text{mol}}{\text{g}} D]{} \underset{\frac{1.12\times10^{-4}}{\text{mol D}}}{\text{mol } D} \xrightarrow[\times \frac{\text{mol A}}{\text{mol D}}]{\times \frac{1\text{ mol A}}{1\text{ mol D}}} \text{mol } A \xrightarrow[\times \frac{\text{g}}{\text{mol}} A]{} \text{mass } A$$

$$= 1.12\times10^{-4}\text{ mol A} \times \frac{60.1\text{ g}}{\text{mol}} = 6.75\text{ mg}$$

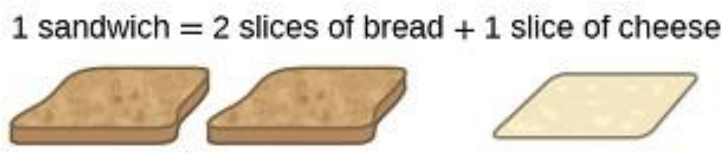
$$1.12\times10^{-4}\text{ mol A}\left(\frac{1\text{ mol D}}{1\text{ mol A}}\right)\left(\frac{60.1\text{ g}}{1\text{ mol}}\right)\left(\frac{1000\text{ mg}}{1\text{ g}}\right) = 6.75\text{ mg}$$

The Sandwich Analogy



How many sandwiches can we make? How much of each ingredient remains?

The Sandwich Analogy



This “recipe” is like a balanced equation.

The Sandwich Analogy

This "recipe" is like a balanced equation.

How many sandwiches can we make given these quantities?

1. Determine *x* (no. of sandwiches) based on bread and cheese *separately*.

The Sandwich Analogy

This "recipe" is like a balanced equation.

How many sandwiches can we make given these quantities?

2. The smaller *x* is associated with the limiting reactant; the other(s) is (are) in excess.

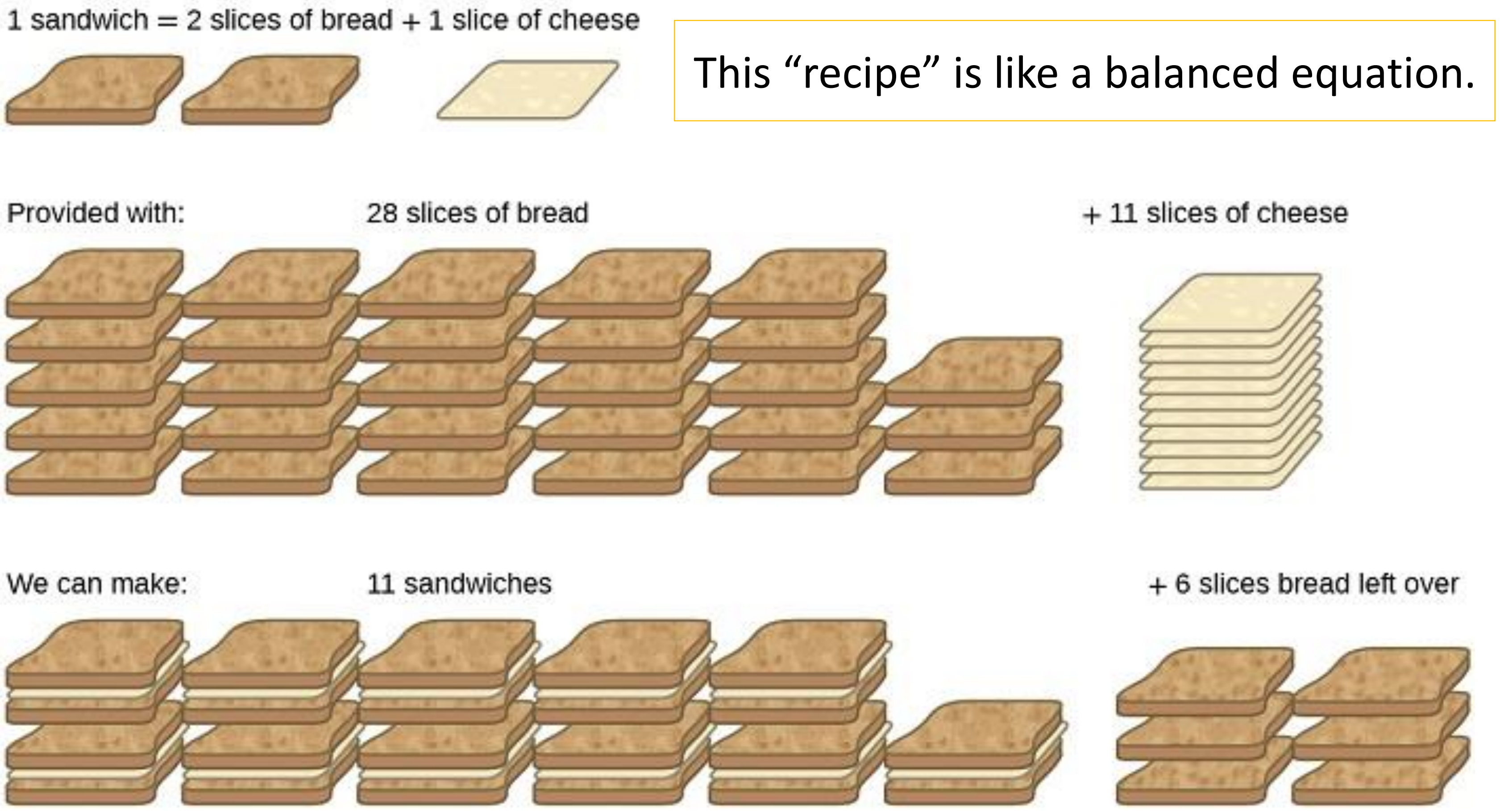
The Sandwich Analogy

This “recipe” is like a balanced equation.

How many sandwiches can we make given these quantities?

3. Using the smaller *x*, calculate the amounts of bread and cheese consumed.

The Sandwich Analogy

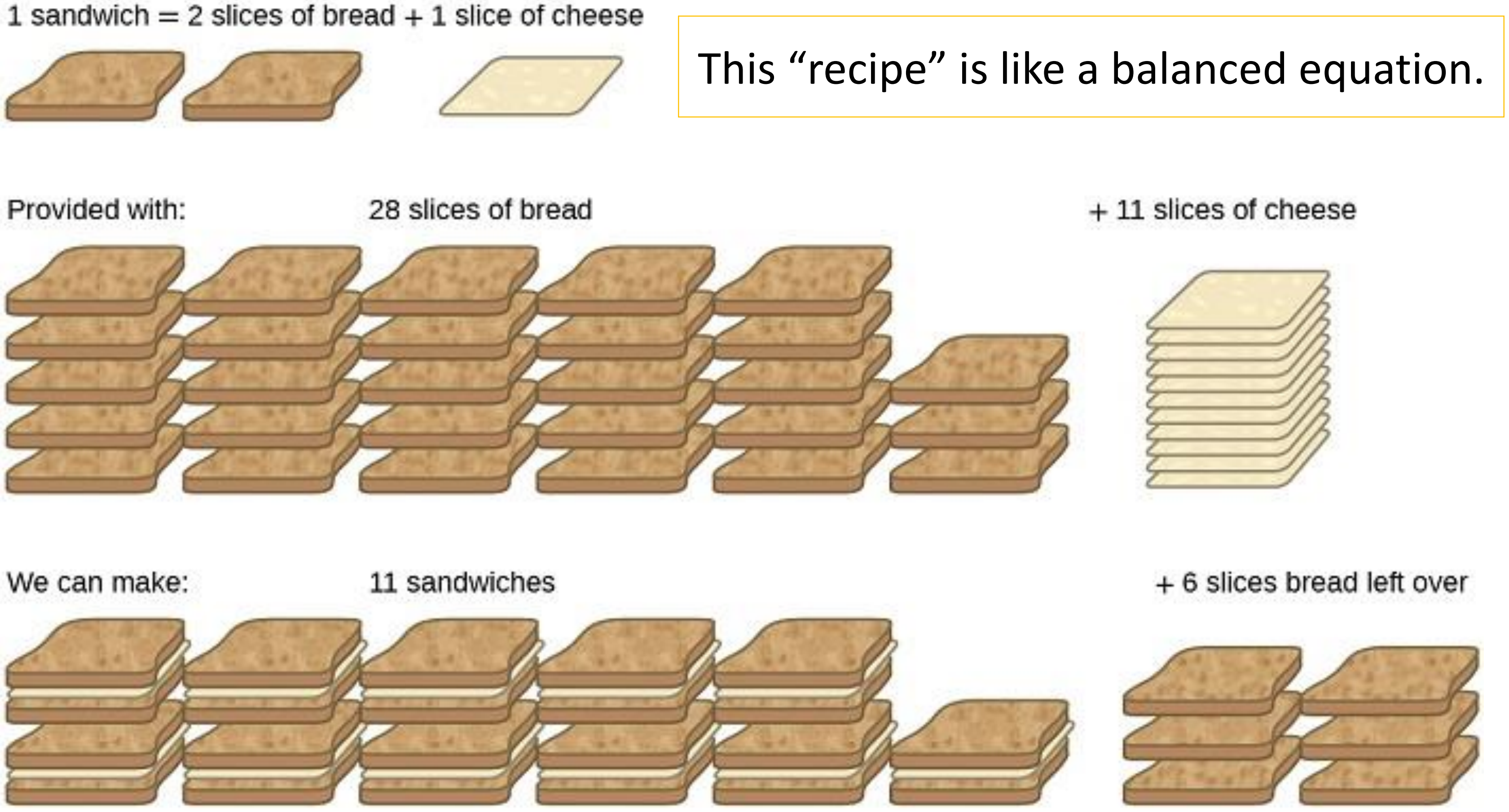


This “recipe” is like a balanced equation.

Initial conditions will be given in problems. *Don’t assume that “matching” amounts are present!*

Here, cheese is the limiting reactant. Only 11 sandwiches can be made despite the 28 slices of bread available.

Limiting Reactant Problems



This "recipe" is like a balanced equation.

To identify the limiting reactant and determine amounts when a reaction is complete, use the balanced chemical equation and given amounts to calculate hypothetical *x*'s for each reactant. The *smallest* (x_{min}) is associated with the limiting reactant. Using x_{min}, determine amounts of reactants consumed and products produced, and find remaining amounts of any excess reactants by subtraction from their original amounts.

The compound α,α’-dibromo-*o*-xylene ($C_8H_8Br_2$, 264.0 g/mol) reacts with lithium metal to give a product containing 16 carbons as well as lithium bromide. A balanced chemical equation for this process is given below.

$$\underset{X}{2\ C_8H_8Br_2} + 4\ Li \rightarrow \underset{Y}{C_{16}H_{16}} + 4\ LiBr$$

In one synthesis of $C_{16}H_{16}$, 101 g of $C_8H_8Br_2$ were combined with 6.63 g of lithium metal.

Determine the number of moles of each reactant.

$101\ g\ C_8H_8Br_2 \longrightarrow 0.382\ mol$

$6.63\ g\ Li \xrightarrow[\times \frac{mol}{g}]{} 0.956\ mol$

The compound α,α'-dibromo-*o*-xylene ($C_8H_8Br_2$, 264.0 g/mol) reacts with lithium metal to give a product containing 16 carbons as well as lithium bromide. A balanced chemical equation for this process is given below.

X

$$2\ C_8H_8Br_2 + 4\ Li \rightarrow C_{16}H_{16} + 4\ LiBr$$

In one synthesis of $C_{16}H_{16}$, 101 g of $C_8H_8Br_2$ were combined with 6.63 g of lithium metal.

Determine the limiting reactant.

$$0.382 \text{ mol X} \xrightarrow{\times \frac{1 \text{ mol rxns}}{2 \text{ mol X}}} 0.191 \text{ mol rxns.} \Rightarrow \text{limiting reactant}$$

smaller x

$$0.956 \text{ mol Li} \xrightarrow{\times \frac{1 \text{ mol rxns}}{4 \text{ mol Li}}} 0.239 \text{ mol rxns.}$$

$$0.191 \text{ mol rxns} \left(\frac{4 \text{ mol LiBr}}{1 \text{ mol rxns}}\right) = \text{mol LiBr produced (theoretical)}$$

Barium nitride (Ba_3N_2) and water react to form barium hydroxide ($Ba(OH)_2$) and ammonia (NH_3). Write a balanced chemical equation for this process.

$$Ba_3N_2 + 6\ H_2O \xrightarrow{1} 3\ Ba(OH)_2 + 2\ NH_3 \quad \checkmark$$

What is the maximum mass of barium hydroxide that can be produced from a mixture of 50.0 g of barium nitride and 20.0 g of water?

g Ba_3N_2 $\longrightarrow$ mol Ba_3N_2 $\longrightarrow$ mol rxns, based on Ba_3N_2 ($x_{Ba_3N_2}$)

g H_2O $\longrightarrow$ mol H_2O $\longrightarrow$ mol rxns, based on H_2O (x_{H_2O})

Limiting reactant corresponds to smaller x.

$\min(x_{Ba_3N_2}, x_{H_2O})$ = the actual no. of rxns.

Barium nitride (Ba_3N_2) and water react to form barium hydroxide ($Ba(OH)_2$) and ammonia (NH_3). Write a balanced chemical equation for this process.

$$Ba_3N_2 + 6\,H_2O \longrightarrow 3\,Ba(OH)_2 + 2\,NH_3$$

Under the conditions of the previous problem, assuming the reaction goes to completion, what mass of the excess reactant is left behind?

$x_{min} \longrightarrow$ mol excess reactant consumed (n_{ex})

subtract n_{ex} from initial moles of excess reactant.

Calcium hydroxide ($Ca(OH)_2$) is formed from the reaction of calcium oxide (CaO) with water (H_2O). Write a balanced chemical equation for this process.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

What mass of calcium hydroxide can be produced from a mixture of 25.0 g of calcium oxide and 12.0 g of water?

$$\text{g CaO} \xrightarrow{\times \text{mol/g}} \underset{0.446\text{ mol}}{\text{mol CaO}} \xrightarrow{\times \frac{1\text{ mol rxns}}{1\text{ mol CaO}}} \underset{0.446\text{ mol rxns}}{X_{CaO}}$$

$$\text{g } H_2O \xrightarrow{\times \frac{\text{mol}}{\text{g}}} \underset{0.667\text{ mol}}{\text{mol } H_2O} \xrightarrow{\times \frac{1\text{ mol rxns}}{1\text{ mol CaO}}} \underset{0.667\text{ mol rxns}}{X_{H_2O}}$$

CaO is limiting.

$$X_{CaO} \xrightarrow{\times \frac{1\text{ mol } Ca(OH)_2}{1\text{ mol rxns}}} \overset{0.446\text{ mol}}{\text{mol } Ca(OH)_2} \xrightarrow{\times \frac{\text{g}}{\text{mol}}} \overset{33.1\text{ g}}{\text{g } Ca(OH)_2}$$

Calcium hydroxide ($Ca(OH)_2$) is formed from the reaction of calcium oxide (CaO) with water (H_2O). Write a balanced chemical equation for this process.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Under the conditions of the previous problem, assuming the reaction goes to completion, what mass of the excess reactant is left behind?

$$X_{CaO} \xrightarrow{\times\, 1\ \text{mol}\ H_2O / 1\ \text{mol rxns}} \text{mol}\ H_2O\ \text{consumed}\ (n_{H_2O})$$

0.446 mol → 0.446 mol

$$n_{f,H_2O} = n_{i,H_2O} - n_{H_2O} = 0.221\ \text{mol}\ H_2O\ \text{remaining}$$

$$(3.98\ g)$$

No labs next week!

- Labor Day → due dates on Tuesday

5.B Stoichiometry

First-year Chemistry Program

Problems Involving Limiting Quantities (5.3)

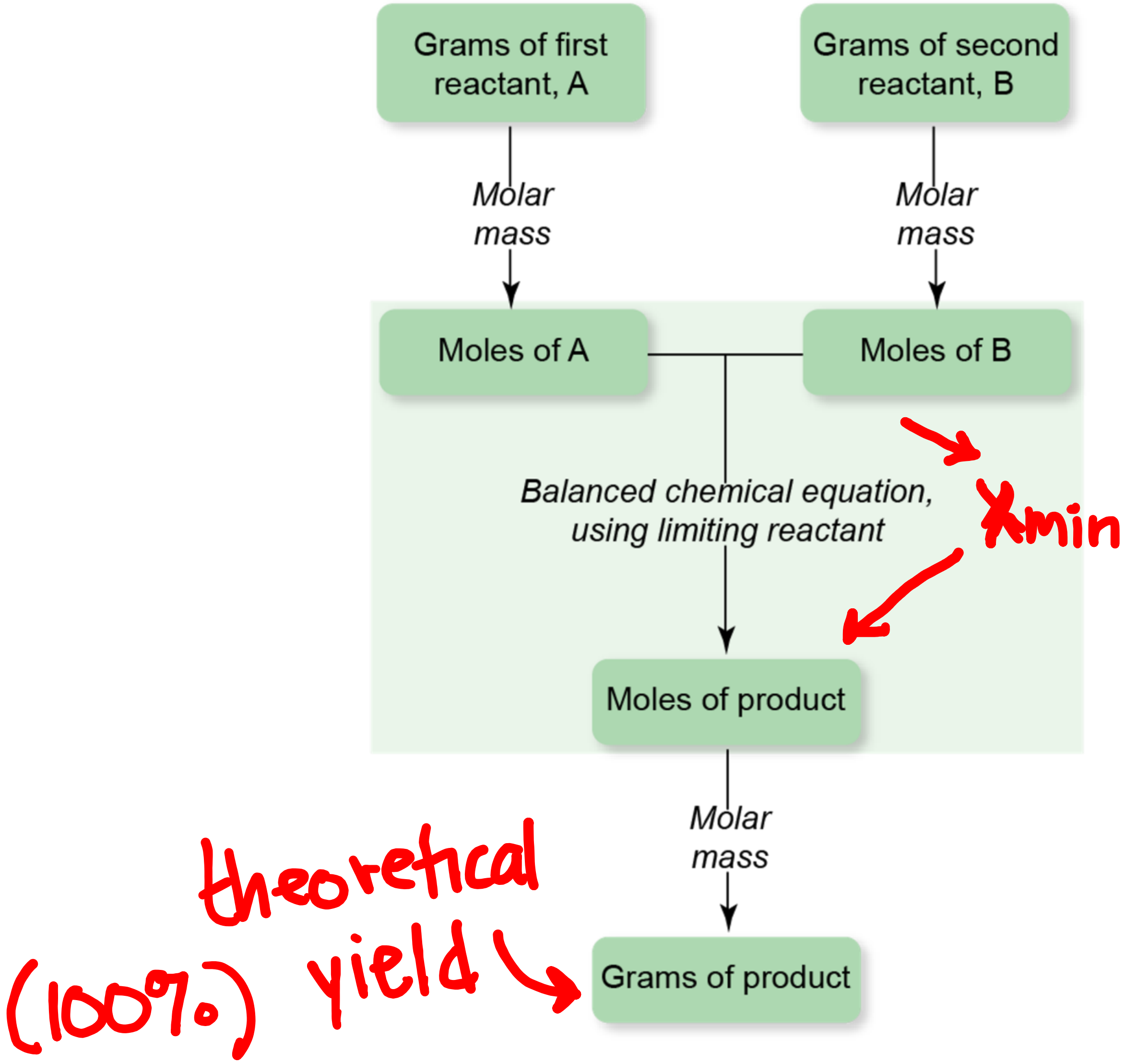


Figure 5.7
Procedure for Limiting-Reactant Problems Involving Masses

Theoretical Yield and Percent Yield (5.4)

- ***Theoretical yield***
  - The ideal amount of product that a reaction can make mathematically.
- ***Actual yield*** < theoretical
  - The amount the reaction produces in the laboratory.
- ***Percent yield***
  - The ratio of actual yield to theoretical yield.

$$\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100\%$$

The diphosphorus pentoxide used to produce phosphoric acid for cola drinks is prepared by burning phosphorus in oxygen.

$\_\ P_4 + \underline{5}\ O_2 \longrightarrow \_\ P_4O_{10}$

What is the limiting reactant when 0.200 mol P_4 are combined with 0.200 mol O_2?

$0.200 \text{ mol } P_4 \left(\frac{1 \text{ mol rxn}}{1 \text{ mol } P_4}\right) = 0.200 \text{ mol rxns } (P_4)$ | $0.040 \text{ mol rxns } (O_2)$

x_{min} limiting rxt

What is the percent yield of diphosphorus pentoxide if 10.0 grams of P_4O_{10} are obtained at the end of the reaction?

theoretical:

$0.040 \text{ mol rxns} \left(\frac{1 \text{ mol } P_4O_{10}}{1 \text{ mol rxns}}\right) = 0.040 \text{ mol } P_4O_{10} \rightarrow 11.4 \text{ g } P_4O_{10}$

$\% Y = \frac{10.0 \text{ g}}{11.4 \text{ g}} \times 100\% = 87.7\% \approx 88\%$

In the last set of problems we considered the reaction below.

X

$2\ C_8H_8Br_2 + 4\ Li \rightarrow C_{16}H_{16} + 4\ LiBr$

In one synthesis of $C_{16}H_{16}$, 101 g of $C_8H_8Br_2$ were combined with 6.63 g of lithium metal. The actual yield of $C_{16}H_{16}$ was 19.6 g. What is the percent yield of $C_{16}H_{16}$?

X is limiting.

$X_{min} = 0.191$ mol rxns

$X_{min} \longrightarrow$ mol $C_{16}H_{16}$

$\times \dfrac{1\ \text{mol}\ C_{16}H_{16}}{1\ \text{mol rxns}}$

0.191 mol $C_{16}H_{16} \rightarrow 39.8$ g

$\%Y = \dfrac{19.6\ g}{39.8\ g} \times 100\% = 49.2\%$

Definition and Uses of Molarity (5.5)

- ***Solution Stoichiometry***
  - Reactants and products may be given as molarities.
  - Molarities and volumes can be used to calculate the number of moles.

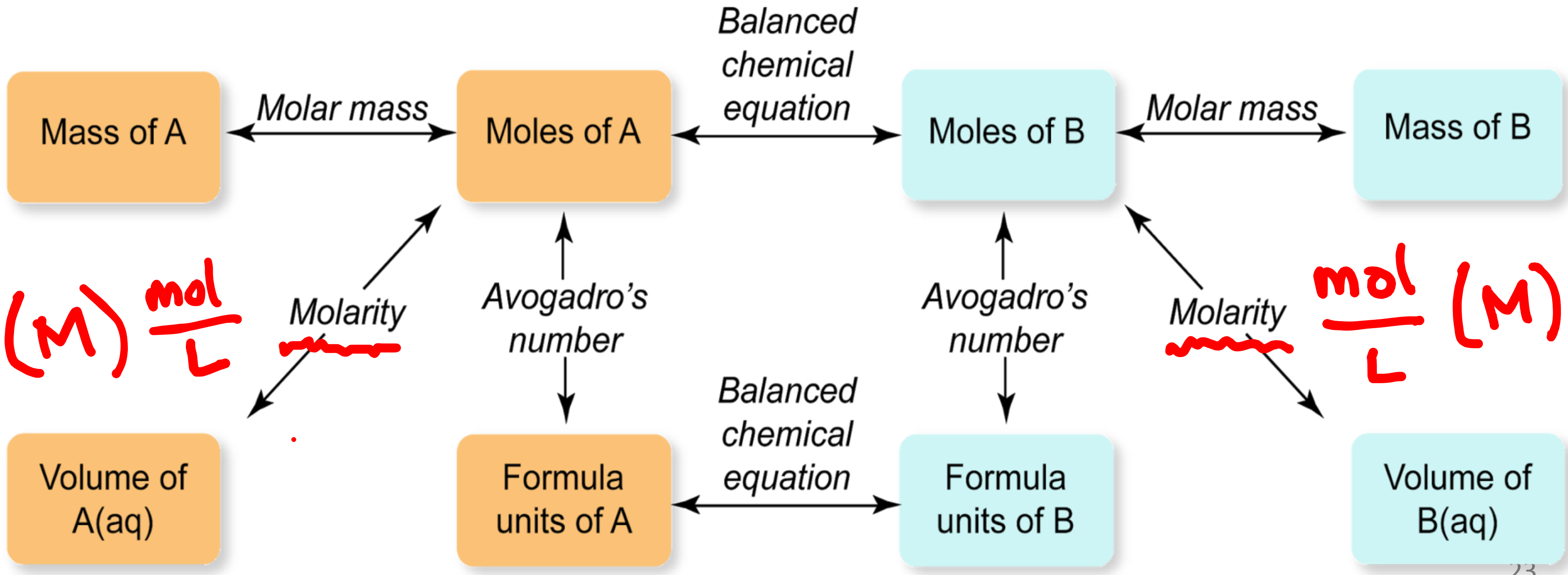
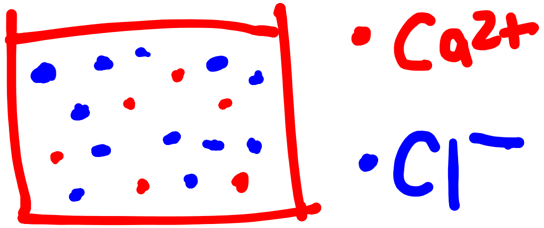


Figure 5.13

Brewing water is commonly "treated" with one or more ionic salts to provide nutrients for yeast, adjust pH, or improve flavor. In one treatment, 0.058 moles of calcium in the form of calcium chloride ($CaCl_2$) are dissolved in 4 gallons of water.

Write a balanced chemical equation for the dissolution of calcium chloride in water.

$$CaCl_2(s) \rightarrow \underline{\ \ }\,Ca^{2+}(aq) + \underline{2}\,Cl^-(aq)$$



How many moles of chloride ions are added to the water in the process? What are the molarities of calcium and chloride ions?

$$0.058 \text{ mol } Ca^{2+} \times \frac{2 \text{ mol } Cl^-}{1 \text{ mol } Ca^{2+}} \rightarrow \text{mol } Cl^- \quad (0.116 \text{ mol } Cl^-)$$

$4.0 \text{ gal} \rightarrow 15.14 \text{ L}$

$$\frac{0.116 \text{ mol } Cl^-}{15.14 \text{ L}} = [Cl^-] = 0.0675 \text{ M}$$

$$[Ca^{2+}] = \frac{[Cl^-]}{2} = 0.0038 \text{ M}$$

Brewing water is commonly "treated" with one or more ionic salts to provide nutrients for yeast, adjust pH, or improve flavor. In one treatment, 0.058 moles of calcium in the form of calcium chloride ($CaCl_2$) are dissolved in 4 gallons of water.

What mass of calcium chloride is needed to create this solution?

$$\text{mol } Ca^{2+} \xrightarrow[\times 1/1]{} \text{mol } CaCl_2 \xrightarrow[\times g/mol]{} g\ CaCl_2$$

$$0.058 \text{ mol } CaCl_2 \longrightarrow 6.44 g\ CaCl_2$$

Let's continue to explore the process of creating a desmopressin solution outlined in this video. We previously encountered the anti-diuretic drug desmopressin in Chapter 3.

If you haven't already, watch the complete video before tackling the problems below.

A mass of 120. mg desmopressin acetate ($C_{48}H_{68}N_{14}O_{14}S_2$, 1129.3 g/mol) is first dissolved in 100. mL of water. Assuming the final solution volume is 100. mL, what is the molarity of desmopressin in this solution?

$$120\ \text{mg DA} \xrightarrow[\times \frac{\text{mol}}{\text{g}}]{} \frac{1.063 \times 10^{-4}\ \text{mol}}{0.100\ \text{L}} = [D]_1 = 1.063 \times 10^{-3}\ \text{M}$$

Let's continue to explore the process of creating a desmopressin solution outlined in [this video](). We previously encountered the anti-diuretic drug desmopressin in Chapter 3.

If you haven't already, watch the complete video before tackling the problems below.

A volume of 1.0 mL of this solution is added to "vehicle," a mixture of simple and cherry syrup, to create a final solution with a volume of 60.0 mL. What is the molarity of desmopressin in the resulting solution?

$[D]_2$

Dilution

$$[D]_1(0.0010\,L) = [D]_2(0.060\,L)$$

mol D = mol D

$$[D]_2 = 17.7 \times 10^{-6}\,M = 17.7\,\mu M$$

Let's continue to explore the process of creating a desmopressin solution outlined in this video. We previously encountered the anti-diuretic drug desmopressin in Chapter 3.

If you haven't already, watch the complete video before tackling the problems below.

$D + A \rightarrow DA$

Verify that the molarity we just calculated corresponds to 0.1 mg of desmopressin acetate per $\underbrace{\text{5 mL of solution}}_{V_{tot}}$ as reported on the video.

mol DA

$$[D] = [DA] = \frac{8.86 \times 10^{-8} \text{ mol DA}}{0.0050 \text{ L}} = 17.7 \, \mu M$$

Calculate each of the following quantities for additional practice with solutions.

Grams of solute in 175.8 mL of 0.0565 M calcium acetate

$0.0565\ M\ Ca(OAc)_2\ (0.1758\ L)(158.2\ g/mol) = 1.57g$

Molarity of a 500. mL solution containing 3.38 g potassium iodide

g KI ⟶ mol KI ⟶ mol KI/L sol'n.

3.38g 20.36 mmol 40.72 mM

Moles of solute in 3.011 L of 0.850 M sodium cyanide

mol NaCN/L sol'n. ⟶ mol NaCN

0.850 M 2.56 mol

Arrange the solutions in order of increasing number of particles in solution assuming that the volumes of the solutions are the same: 0.50 M Na_3PO_4, 1.0 M C_6H_{14}, 1.0 M KCl, 1.0 M $Ca(NO_3)_2$.

total molarity of solutes:

#1	1.0 M	$Ca(NO_3)_2$	4.0 M
	0.50 M	Na_3PO_4	2.0 M
	1.0 M	KCl	2.0 M
	1.0 M	C_6H_{14}	1.0 M

consider dissociation!

5.C Stoichiometry

First-year Chemistry Program

Calculations Involving Other Quantities (5.7)

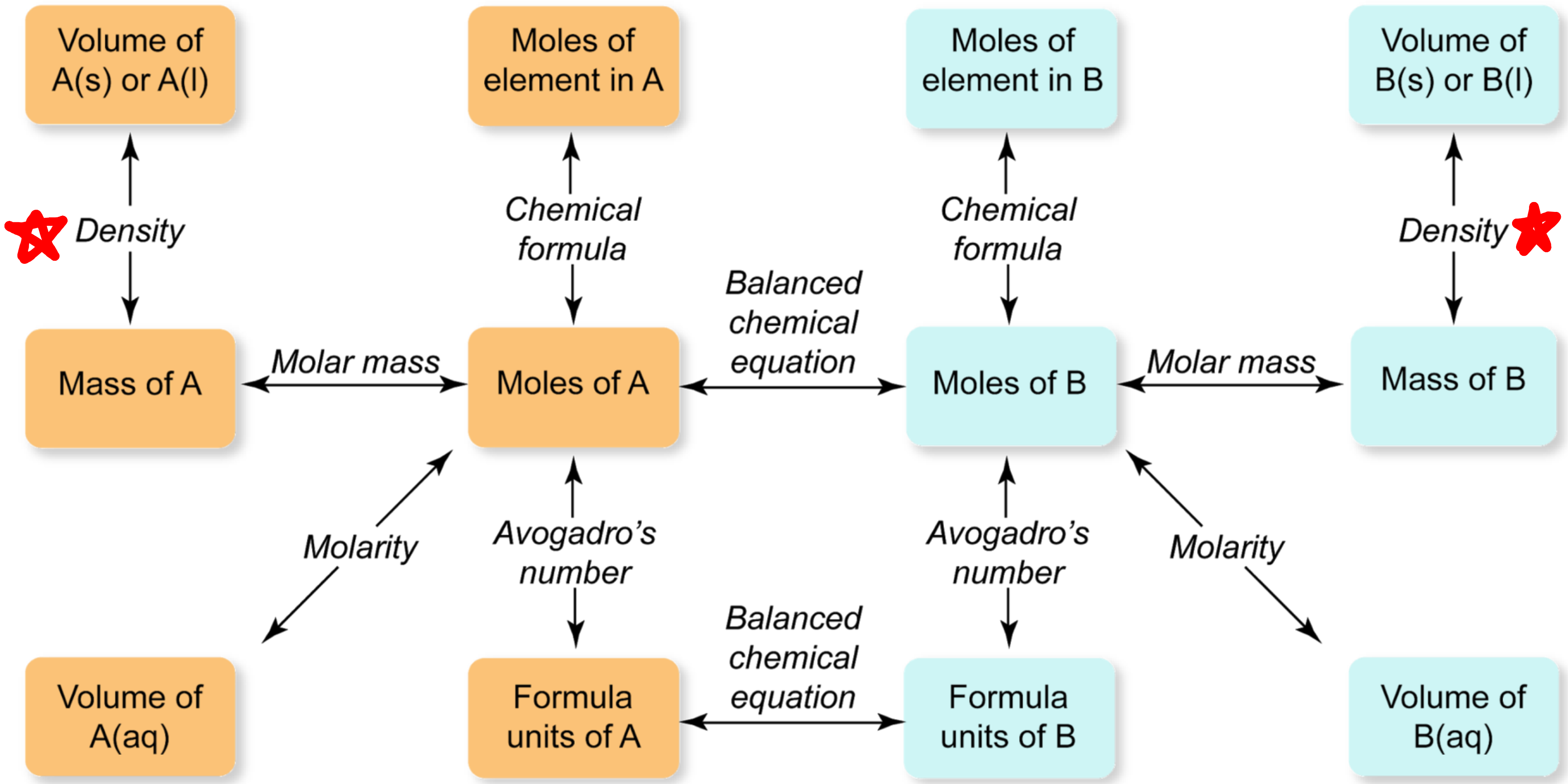


Figure 5.14 Mass, Mole, and Other Conversions

The density of ethanol (C_2H_6O) is 0.789 g/mL. Ethanol reacts with acetic acid ($HC_2H_3O_2$) in a 1:1 molar ratio to yield ethyl acetate ($C_4H_8O_2$) and water (H_2O). What volume of a 2.0 M acetic acid solution is required to completely consume 500. mL of ethanol?

$$\text{Volume EtOH} \xrightarrow{\times \text{g/mL}} \text{mass EtOH} \xrightarrow{\times \text{mol/g}} \text{moles EtOH}$$

$$\downarrow \times \text{1 mol AcOH/mol EtOH}$$

$$\text{vol. AcOH(aq)} \xleftarrow{\times \frac{\text{L soln}}{\text{mol AcOH}}} \text{moles AcOH}$$

$$(4282 \text{ mL} \approx \boxed{4.29 \text{ L}})$$

$$500 \text{ mL}\left(\frac{0.789 \text{ g}}{1 \text{ mL}}\right)\left(\frac{1 \text{ mol EtOH}}{46 \text{ g}}\right)\left(\frac{1 \text{ mol AcOH}}{1 \text{ mol EtOH}}\right)\left(\frac{1 \text{ L}}{2.0 \text{ mol AcOH}}\right)$$

The molar volume of an ideal gas at standard temperature and pressure is 22.4 L/mol.*
Determine the theoretical yield of water and the amount of excess reactant remaining when 18.0 L of H_2 gas and 12.0 L of O_2 gas are combined and react according to the balanced equation below.

$$2\ H_2 + O_2 \longrightarrow 2\ H_2O$$

V_{H_2}, V_{O_2} $\xrightarrow{\times \frac{1\ mol}{22.4\ L}}$ n_{H_2}, n_{O_2} $\longrightarrow$ limiting? $\longrightarrow$ 0.402 mol rxns $\xrightarrow{\times \frac{2\ mol\ H_2O}{mol\ rxns}}$ n_{H_2O} $\longrightarrow$ g H_2O

$\boxed{14.5\text{ g}}$

0.804 mol H_2 → 0.402 mol rxns ★ (X min)

0.536 mol O_2 → 0.536 mol rxns

Titration (5.9) *Balanced eqn.

[] ✓

titrant (known)

analyte (unknown [])

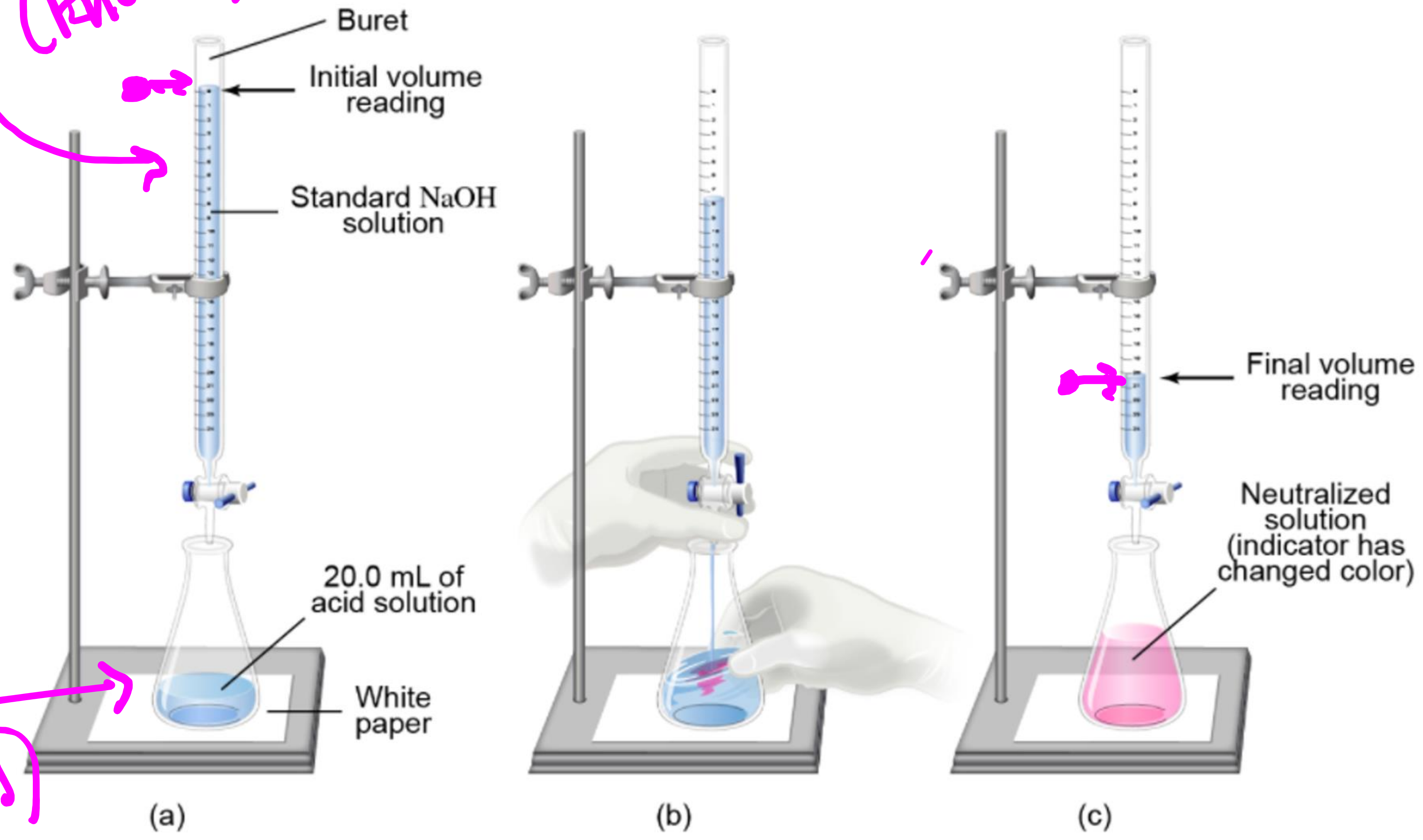


Figure 5.15 Titration Laboratory Setup

Titration (5.9)

1. One reactant, the ***titrant***, is slowly added to the other.
   - Typically, the titrant is in a ***buret*** and the other reactant is in an ***Erlenmeyer flask*** to enable mixing by swirling.
2. An indicator is added to the reaction to indicate the ***end point*** of the titration.
   - At the end point, the reaction is at (or very close to) the ***equivalence point***, where moles of analyte = moles of titrant.
3. The volume of the titrant added is determined by comparing the initial and final buret volumes.

The weak acid hydrazoic acid (HN_3) can be titrated by sodium hydroxide (NaOH) to determine its concentration in solution. The two react according to the balanced chemical equation below.

weak strong

$$1\,HN_3 + 1\,NaOH \rightarrow NaN_3 + H_2O$$

What volume of 0.20 M NaOH is required to completely consume the hydrazoic acid in 25.0 mL of a 0.50 M HN_3 solution?

$$V_{HN_3} \xrightarrow[\times \frac{mol}{L} HN_3]{} mol\ HN_3 \xrightarrow[\times \frac{mol\ NaOH}{mol\ HN_3}]{} mol\ NaOH \xrightarrow[\times L/mol\ NaOH]{} V_{NaOH}$$

0.0125 mol HN_3

$\boxed{62.5\ mL}$

The weak acid hydrazoic acid (HN_3) can be titrated by sodium hydroxide (NaOH) to determine its concentration in solution. The two react according to the balanced chemical equation below.

$HN_3 + NaOH \rightarrow NaN_3 + H_2O$

$\hookrightarrow Na^+ \ N_3^- (aq)$

After the two solutions have been combined and the reaction has run its course, what is the molarity of NaN_3 in the resulting solution? Assume that the reaction goes to completion.

$0.0125 \text{ mol } HN_3 \xrightarrow[\times 1 \text{ mol } NaN_3 / 1 \text{ mol } HN_3]{} \text{mol } NaN_3$

$$\left.\frac{\text{mol } NaN_3}{V_{soln.}}\right\} 0.143 \text{ M}$$

$V_{HN_3} + V_{NaOH} \rightarrow V_{soln.}$

87.5 mL

The weak acid hydrazoic acid (HN_3) can be titrated by sodium hydroxide (NaOH) to determine its concentration in solution. The two react according to the balanced chemical equation below.

$HN_3 + NaOH \rightarrow NaN_3 + H_2O$

What is $[HN_3]$ in a 10.0-mL sample that requires 30.0 mL of 0.15 M NaOH to completely consume the HN_3?

$$V_{NaOH} \xrightarrow[\times \frac{\text{mol NaOH}}{\text{L soln}}]{} \text{mol NaOH} \xrightarrow[\times \frac{\text{mol } HN_3}{\text{mol NaOH}}]{} \frac{\text{mol } HN_3}{V \text{ sol'n.}}$$

10.00 mL

0.45 mol/L

In a common medical laboratory determination of the concentration of free chloride ion in blood serum, a serum sample is titrated with a $Hg(NO_3)_2$ solution.

Hg^{2+}

$$2\,Cl^- + Hg(NO_3)_2 \longrightarrow 2\,NO_3^- + HgCl_2$$

V_{Hg} $[Hg^{2+}]$

What is $[Cl^-]$ in a 0.25-mL sample of serum that requires 1.46 mL of 8.25×10^{-4} M $Hg(NO_3)_2$ to fully consume the Cl^- in the sample?

$$V_{Hg} \xrightarrow{\times \frac{\text{mol } Hg^{2+}}{\text{L soln}} \ (\times [Hg^{2+}])} \text{mol } Hg^{2+} \xrightarrow{\times \frac{2 \text{ mol } Cl^-}{1 \text{ mol } Hg^{2+}}} \frac{\text{mol } Cl^-}{\text{L sol'n}}$$

0.00146 L

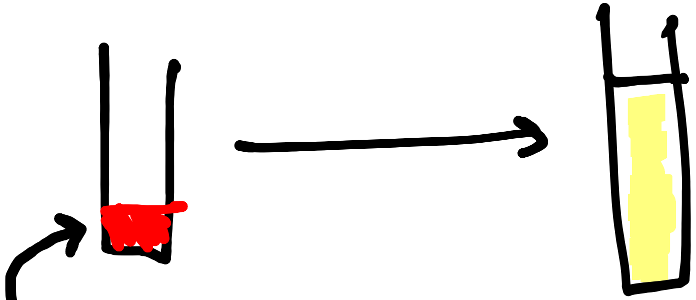
1.20 μmol

2.41 μmol

↑ 0.25 mL

9.64 mM

(0.00964 M)



$[Cl^-]$?

6.A Thermochemistry

First-year Chemistry Program

Objectives

- At the end of this chapter you should be able to:
  - Describe kinetic energy and potential energy.
  - Define work and heat.
  - Summarize the concept of conservation of energy.
  - Discuss state functions.
  - Apply the concept of state function to predict the energy changes involved in reactions.
  - Summarize the roles of enthalpy and heat flow in chemical reactions.
  - Calculate pressure-volume work.
  - Calculate the heat required to change the temperature of a substance.
  - Calculate changes in enthalpy and internal energy in chemical reactions.
  - Apply Hess's law to calculate the enthalpies of different reactions.
  - Determine the enthalpy of formation of a chemical compound from its constituent elements in their standard states.

• system/surroundings

6.A

(First law) $\Delta U = q + w$

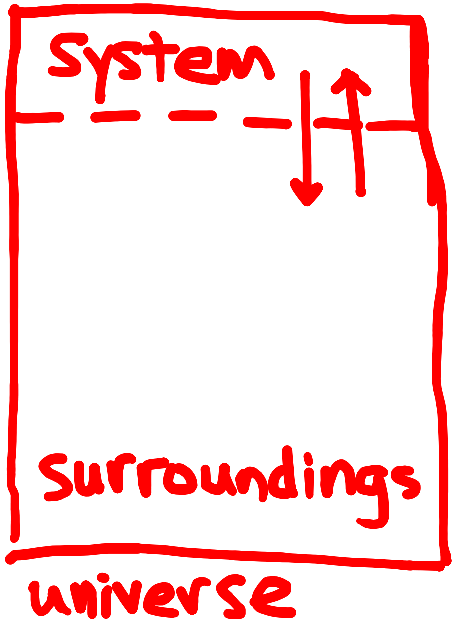
6.B

(c, specific heat)

6.C

Energy, Heat, and Work (6.2)

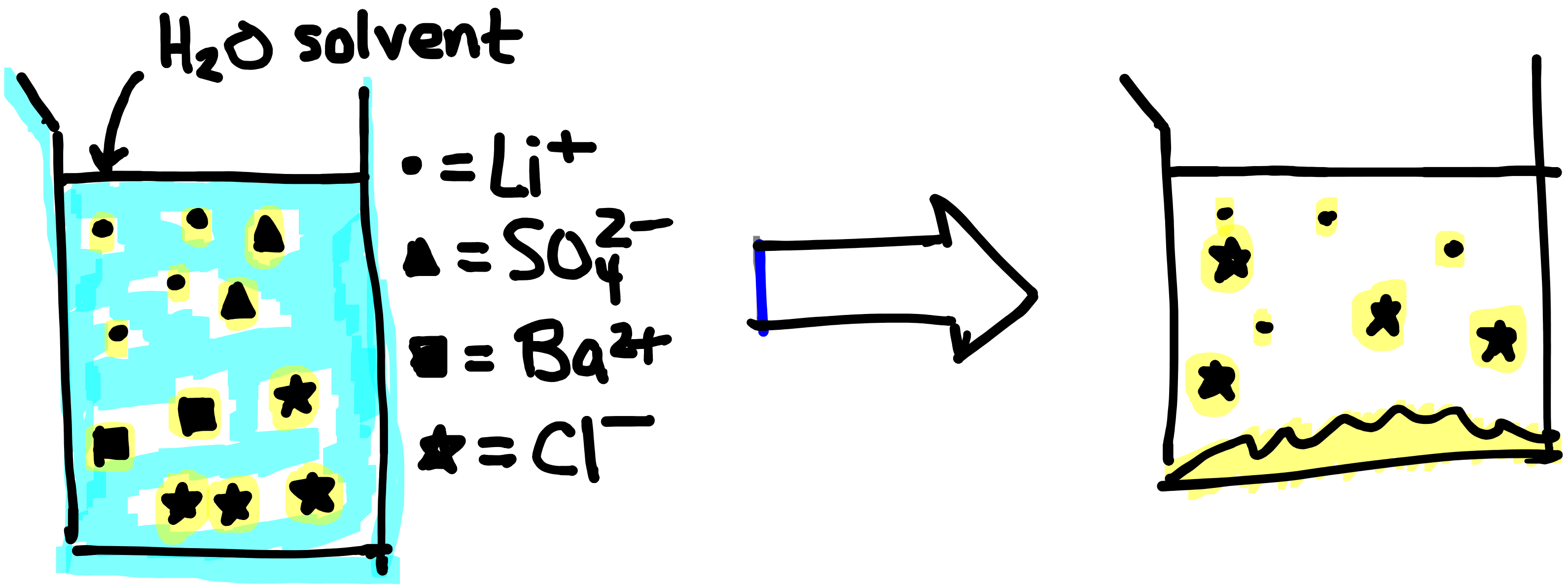
- ***System***
  - The part of the universe under consideration
- ***Surroundings***
  - Everything in the universe except the system
- ***Universe***
  - Universe = system + surroundings



In aqueous solution, lithium sulfate (Li_2SO_4) reacts with barium chloride ($BaCl_2$) to form solid barium sulfate ($BaSO_4$) and aqueous lithium chloride (LiCl). Draw a diagram of this situation and label the system and surroundings, keeping in mind that, as chemists, we are interested in the energy change as the reactants become products.

ΔU

$$Li_2SO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(s) + 2\ LiCl(aq)$$



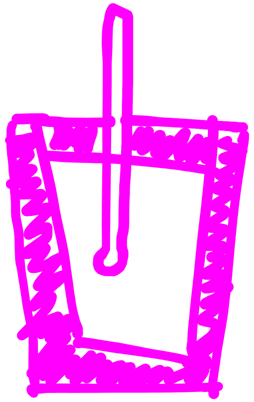
Provide definitions and examples of the following types of systems.

An *isolated* system

- no energy transfer
- no matter in or out

~ = almost isolated

√ = perfectly isolated



earth (~), system surrounded by vacuum (~), Hydro Flask, calorimeter

universe (√)

A *closed* system that can exchange only *heat* with its surroundings

- no matter in or out
- no work ($\Delta V = 0$, rigid)
- sealed, non-insulated container
- heater
- endo/exothermic rxn in closed vessel

Provide definitions and examples of the following types of systems.

A *closed* system that can exchange *heat or work* with its surroundings

- no matter in or out

balloon, piston

electric motor

An *open* system

- matter and energy exchange

cup of coffee, human body

Energy, Heat, and Work (6.2)

- ***Open system***: Both matter and energy can move between the system and the surroundings. E.g.
- ***Closed system***: Energy but not matter can move between the system and the surroundings.
- ***Isolated system***: Neither matter nor energy can leave or enter the system.

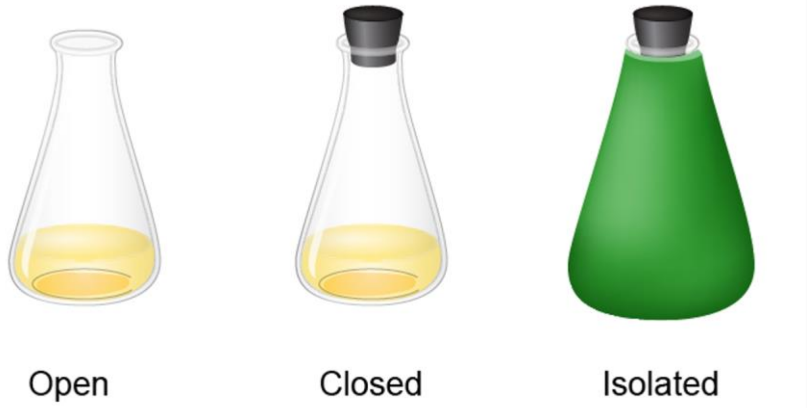


Figure 6.2

Energy, Heat, and Work (6.2)

- ***Work***
  - Previously defined as the result of a force acting through a distance.
  - Denoted as *w*.
- ***Heat***
  - Another way that energy can be transferred.
  - The flow of energy between two objects as the result of differences in temperature.
  - Heat is a process.
  - Denoted as *q*.

Energy, Heat, and Work (6.2)

- ***First law of thermodynamics***:
  - The total energy of the universe is constant.
  - Energy can be neither created nor destroyed, but it CAN be transformed.
  - The sum of the kinetic and potential energies of all the particles that compose the system.

$$\Delta U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0$$

$$\Delta U_{sys} = -\Delta U_{surr}$$

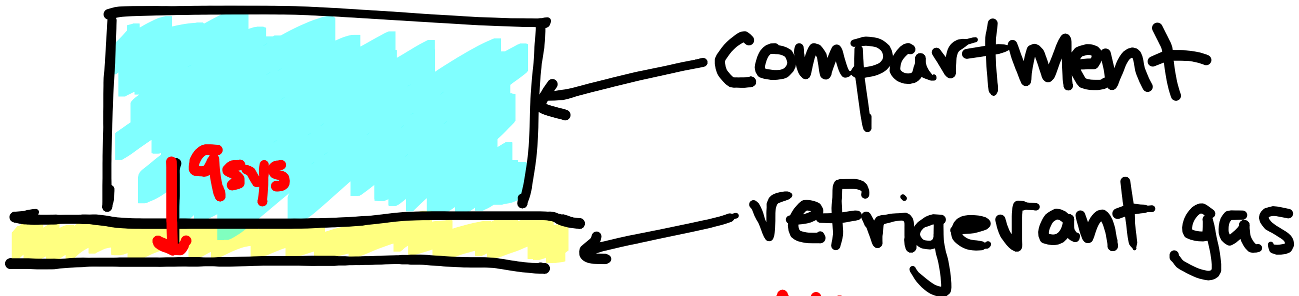
Energy, Heat, and Work (6.2)

- Energy can exchange between the system and surroundings in the forms of work and heat.
- This idea can be expressed in terms of the first law of thermodynamics as:

$$\Delta U = \underbrace{q}_{\text{heat}} + \underbrace{w}_{\text{work}}$$

Inside a refrigerator, a refrigerant gas absorbs 80 cal of heat from the refrigeration compartment and its internal energy increases by 450 J.

Draw a diagram of this situation that includes the refrigerant gas line and the refrigeration compartment. Label the system and surroundings, keeping in mind that, as chemists, we are interested in the internal energy of the gas.



$\Delta U = 450 J$

$q_{sys} > 0$

Inside a refrigerator, a refrigerant gas absorbs 80 cal of heat from the refrigeration compartment and its internal energy increases by 450 J.

Calculate the work done on the gas during this process in Joules, considering the first law of thermodynamics.

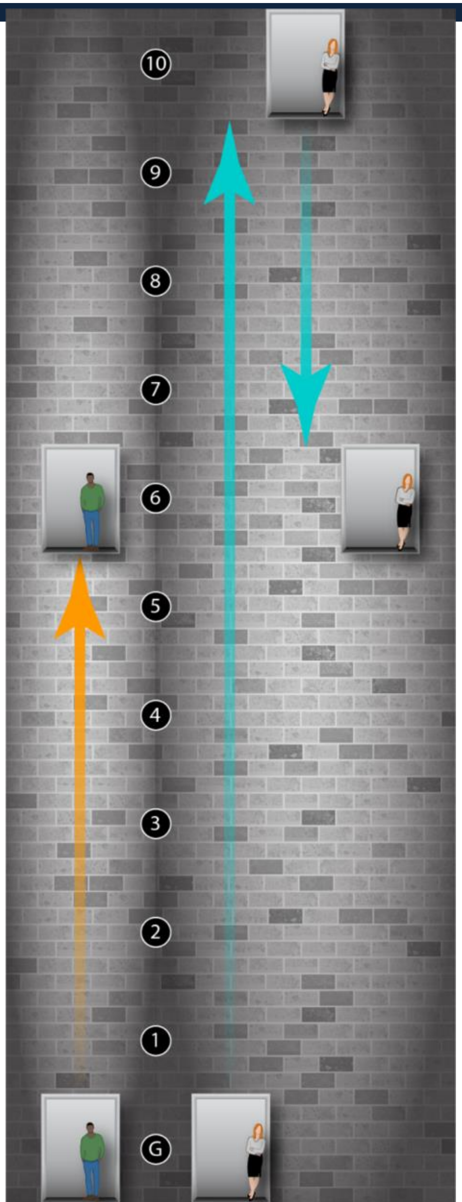
$$\Delta U = q_{sys} + w_{sys}$$

$$+450\,J = +80\,cal + w_{sys}$$

$$w_{sys} = 115.3\,J$$

Energy as a State Function (6.3)

- Internal energy is a ***state function***:
  - Its value depends only on the state of the system, not on how the system arrived at that state.
  - We will encounter other state functions later in this chapter and chapter 18.

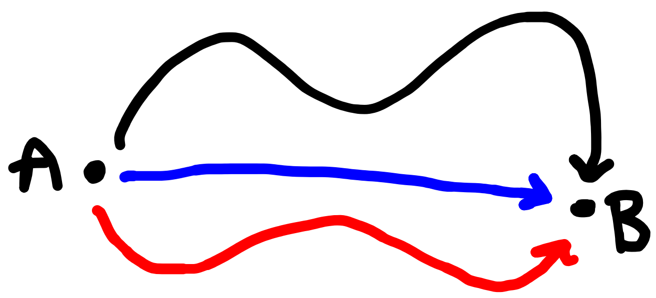


Δh the same!

Figure 6. 6
The height of the elevator is a state function

Energy as a State Function (6.3)

- ***Path functions***
  - Value depends on the path (the sequence of steps taken between initial and final states) taken.
  - ***Work and heat are path functions.***



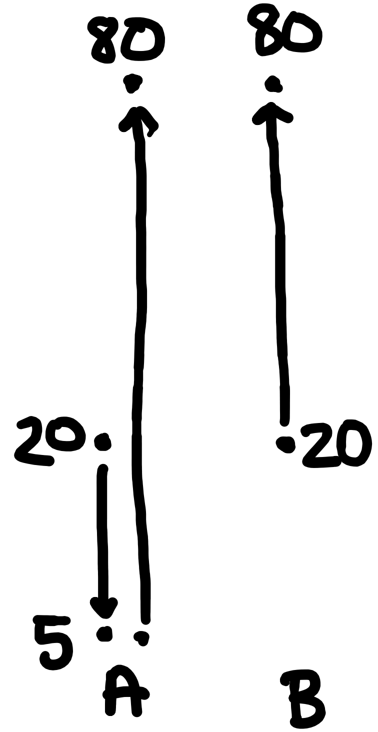
- cf. gas consumption on three trips from A to B.

Consider two identical ~~cans~~ bags of beans **A** and **B** starting at 20 ºC. The ~~cans~~ bags are able to exchange energy with their surroundings but no particles can enter or leave the ~~cans~~ bags. A timer is started and can **A** is cooled to 5 ºC and then heated to 80 ºC. Simultaneously, can **B** is immediately heated to 80 ºC. The timer is stopped when can **A** reaches 80 ºC, at which point can **B** is already at this temperature.

Consider the processes for **A** and **B** that started when the timer was started and ended when the timer was stopped. List two examples of values that are *equal* for both processes and explain why they are equal.

- Change in internal energy (ΔU)
- Change in enthalpy (ΔH)
- Change in temperature (ΔT)

} all changes in state functions!



Consider two identical cans of beans **A** and **B** starting at 20 ºC. The cans are able to exchange energy with their surroundings but no particles can enter or leave the cans. A timer is started and can **A** is cooled to 5 ºC and then heated to 80 ºC. Simultaneously, can **B** is immediately heated to 80 ºC. The timer is stopped when can **A** reaches 80 ºC, at which point can **B** is already at this temperature.

Consider the processes for **A** and **B** that started when the timer was started and ended when the timer was stopped. List two examples of values that are *unequal* for both processes and explain why they are unequal.

$$\left.\begin{array}{l} \bullet \text{ heat } (q) \neq \emptyset \\ \bullet \text{ work done on cans } (w) \end{array}\right\} \begin{array}{l} \text{path functions} \\ \neq \emptyset \end{array}$$

$$\Delta U = q + w$$

10.A Covalent Bonding

First-year Chemistry Program

Objectives

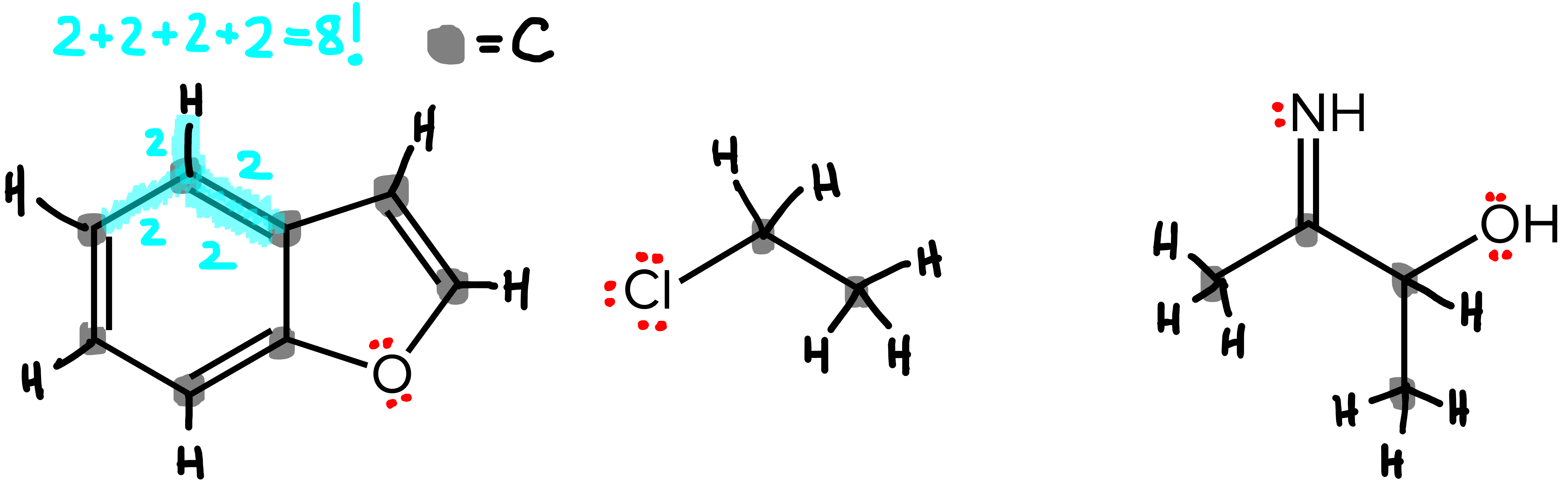
- At the end of this chapter you should be able to:
  - Predict the number of bonds an atom is likely to make in a molecule.
  - Draw Lewis structures for molecules that follow the octet rule.
  - Use electronegativity values to identify the Lewis structure that best represents the molecule.
  - Apply the typical exceptions to the octet rule in drawing Lewis structures, including H, Be, B, radicals, and expanded octets.
  - Determine bond polarity using electronegativity values.
  - Describe the bonding continuum.
  - Discuss how bond length relates to bond strength.

10.A

10.B

ΔH°

Organic molecules are often depicted using a shorthand notation that omits unshared pairs (lone pairs), carbon atoms, and C–H bonds. Carbon atoms are understood to be located at the intersection points of lines and it is assumed that carbon atoms bear enough bonds to hydrogens to satisfy the octet rule. Unshared pairs can be identified by assuming that all atoms in the structure are neutral. Using these ideas, add missing unshared pairs and hydrogen atoms to the structures below.



Lewis Structures (10.2)

- Drawing Lewis Structures
  1. Sum up the *valence* electrons for each atom present in the molecule.
  2. Select a *central atom* and arrange the symbols for the other atoms around it.
     - The central atom is generally the atom that needs to make the most bonds to become stable. Often, this is the least electronegative atom present.
     - It may also be the first atom written in the formula, unless that atom is hydrogen, which can never be a central atom.

Lewis Structures (10.2)

- Drawing Lewis Structures
  3. Connect the central atom to each of the outer atoms with a single bond (represents two electrons)
  4. Distribute the *remaining* valence electrons from step 1 to the outer atoms as lone pairs to complete their octets.
     - Hydrogen is an exception and is complete with a single bond only.
  5. Assign any remaining electrons to the central atom.
  6. If the central atom has less than an octet, move lone pairs from *outer* atoms into shared positions to form double or triple bonds, as needed.

Lewis Structures (10.2)

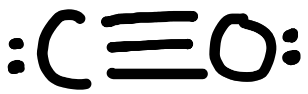
- Drawing Lewis Structures

7. Verify that the final structure:
    - Fulfills the *duet rule* for hydrogen.
    - Fulfills the *octet rule* for C, N, O, and F (incomplete and expanded octets are possible, and exceptions are discussed in Section 10.4)
    - Contains the *exact* number of valence electrons calculated in step 1.

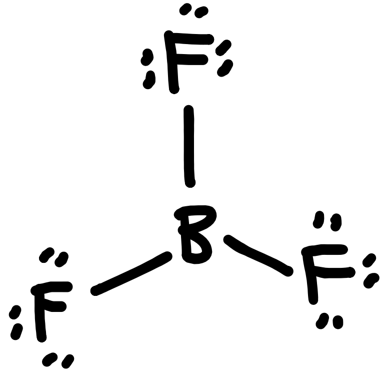
Draw a valid Lewis structure for each of the following molecules.

$4e^-$

CO $6e^-$ 10 valence e^-

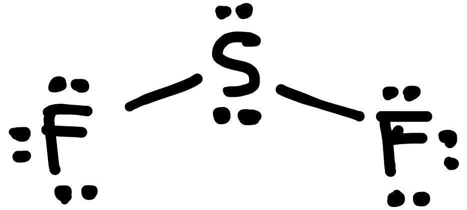


BF_3 24 valence e^-

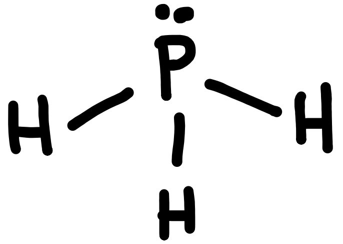


$6e^-$ $7e^- \times 2$

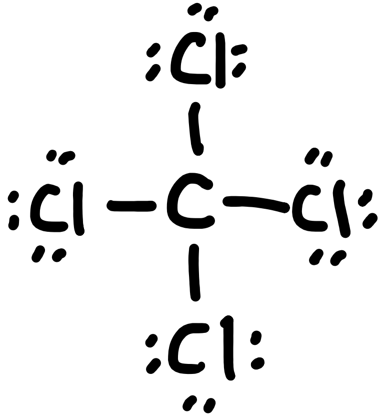
SF_2 20 valence e^-



PH_3 8 valence e^-



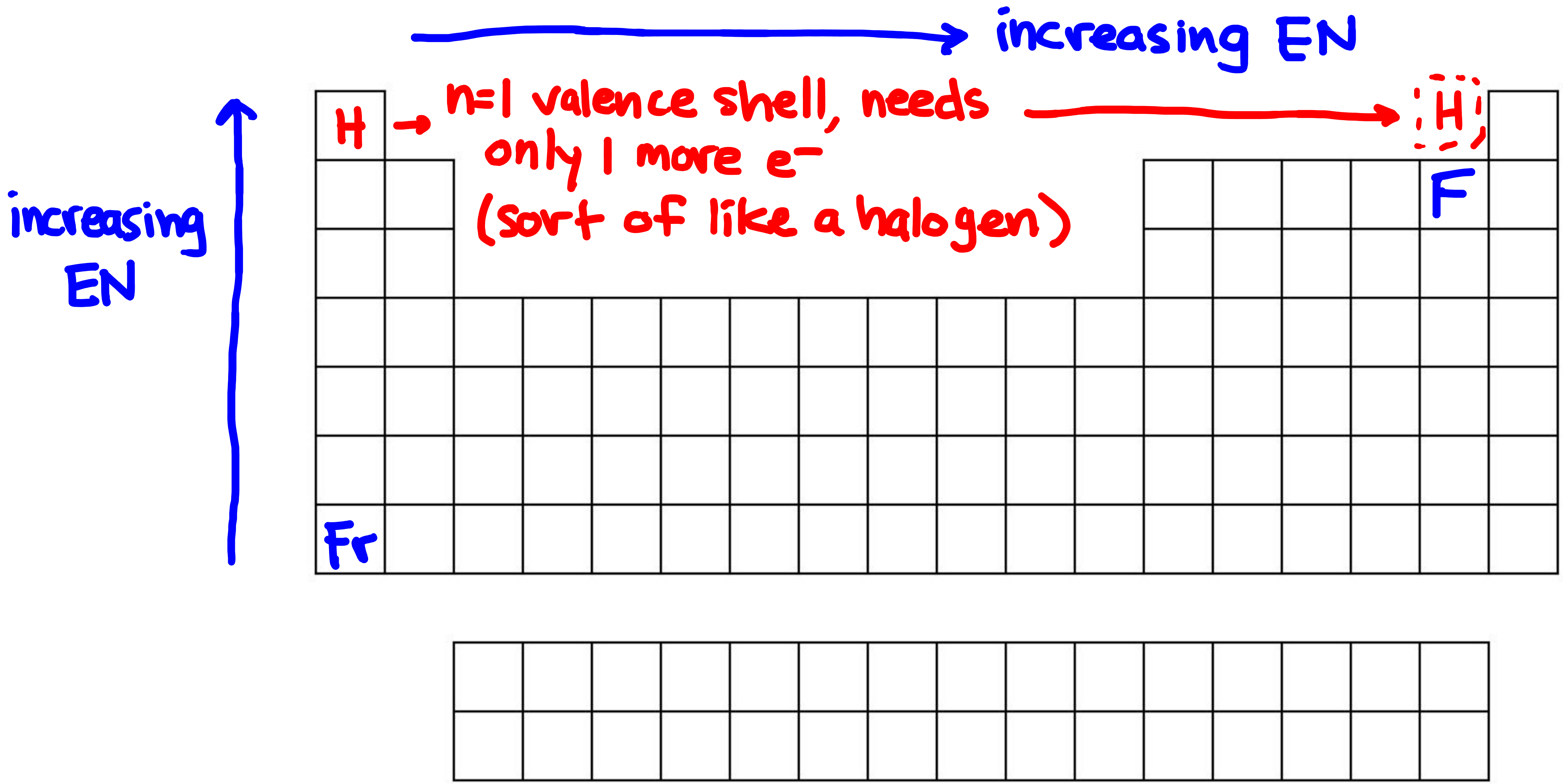
CCl_4 32 valence e^-



Resonance and Formal Charges (10.3)

- ***Electronegativity*** Remember Z_{eff}!
  - The ability of an atom to attract electrons to itself in a bond.
  - Values are established by considering factors such as atomic size, electron configuration, electron affinity, and ionization energy.
  - Often, the Pauling scale is used.
    - But, a new scale just was published in the spring!

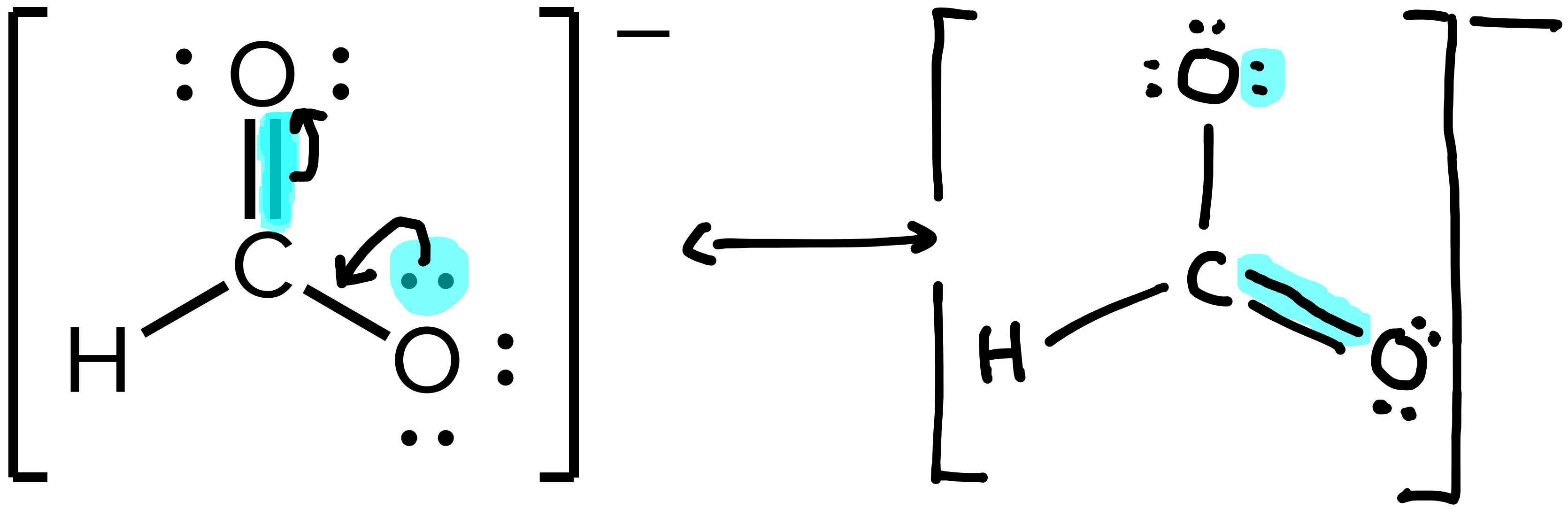
Examine trends in electronegativity (EN) here. On the periodic table below, indicate how electronegativity changes moving left to right across a group and down a period. Identify the one main-group element that doesn't fit with this trend and explain why it doesn't.



Resonance and Formal Charges (10.3)

- In some cases, a molecule cannot be represented accurately by a single Lewis structure but requires multiple structures.
  - These structures differ only in the placement of multiple bonds and lone pairs.
  - Molecules/ions that have such structures are said to exhibit ***resonance*** and the structures are referred to as ***resonance structures***.

The formate ion HCO_2^- has two important resonance structures. One of these structures is drawn below. Draw the other, which also includes one C=O bond and one C–O bond.



Considering electronegativity trends, is the negative charge in formate more likely to reside on carbon or oxygen? Explain.

EN(O) > EN(C), so negative charge (e^-) resides mostly on oxygen.

10.B Covalent Bonding

First-year Chemistry Program

Exceptions to the Octet Rule (10.4)

- ***Incomplete octets***:
  - Hydrogen and helium form duets, not octets because only the 1*s* orbital is occupied in their grounds states.
  - Two period 2 elements *often* have incomplete octets:
    - Beryllium forms molecules with four electrons in its valence shell.
    - Boron atoms, in molecules, generally have six electrons in their valence shells.

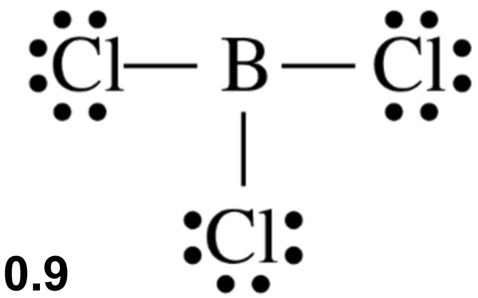


Figure 10.9

Exceptions to the Octet Rule (10.4)

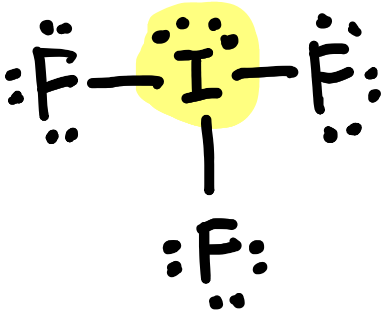
- ***Expanded octets***:
  - If the central element in a molecule or polyatomic ion is in the ***third period or beyond***, it can sometimes expand its valence shell beyond eight electrons (but don't always).
  - Central atoms with expanded octets (also called expanded valence shells) can accommodate more than 8 electrons in bonds or lone pairs.
    - Examples: sulfur in SF_6 and phosphorous in PCl_5

Draw Lewis structures for the following molecules and explain how they violate the octet rule.

= expanded

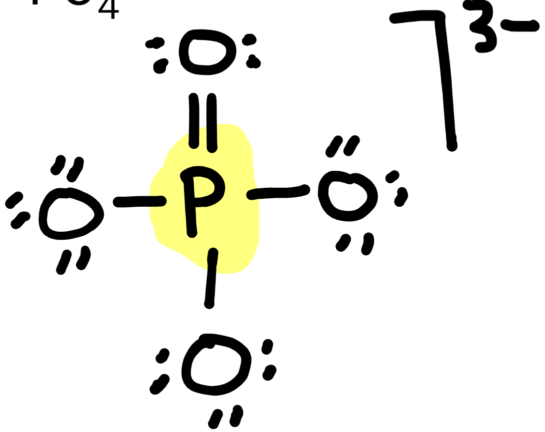
= incomplete

IF_3

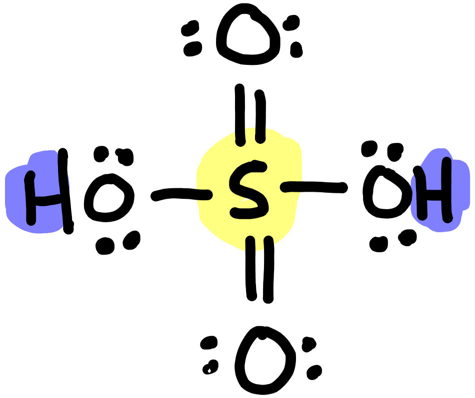


BeH_2

PO_4^{3-}



H_2SO_4



Polar Bonds and the Bonding Continuum (10.5)

- Covalent bonding between atoms of different electronegativities results in a bond in which there is separation of positive and negative charge centers.
  - The two points of positive and negative charge constitute a ***dipole***.
  - Such a bond is referred to as a ***polar bond.***

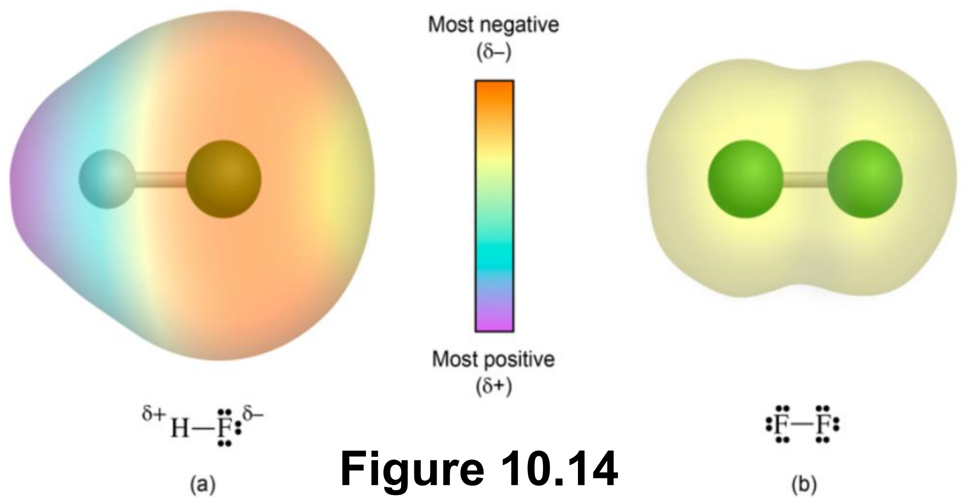


Figure 10.14

These positive and negative *poles* in HF indicate a charge separation and some level of ***ionic character.***

For the first three molecules in the last problem, indicate the more electronegative atom in each bond and use partial charge indicators (δ+ and δ−) to show the orientation of bond dipoles in each molecule.

IF_3

$\overset{\delta+}{\text{I}} - \overset{\delta-}{\text{F}}$

more EN

BeH_2

more EN

$\overset{\delta+}{\text{Be}} - \overset{\delta-}{\text{H}}$

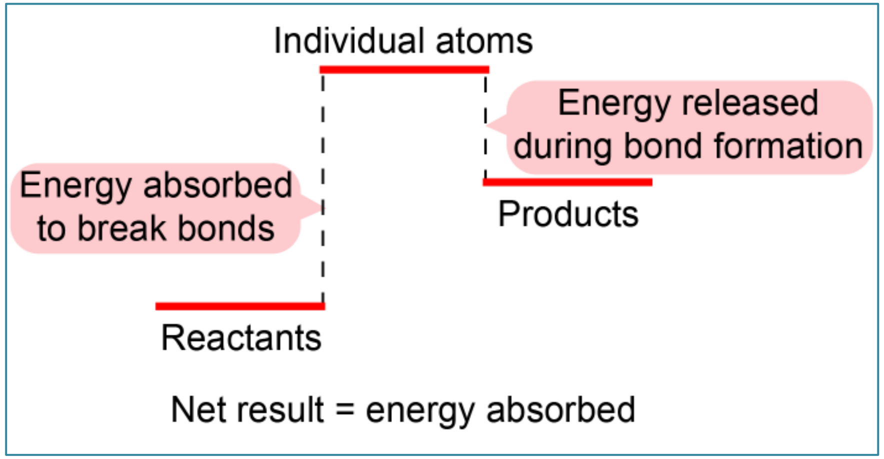
PO_4^{3-}

$\overset{\delta+}{\text{P}} \cdots \overset{\delta-}{\text{O}}$

more EN

Bond Enthalpy (10.6)

Endothermic reaction



Exothermic reaction

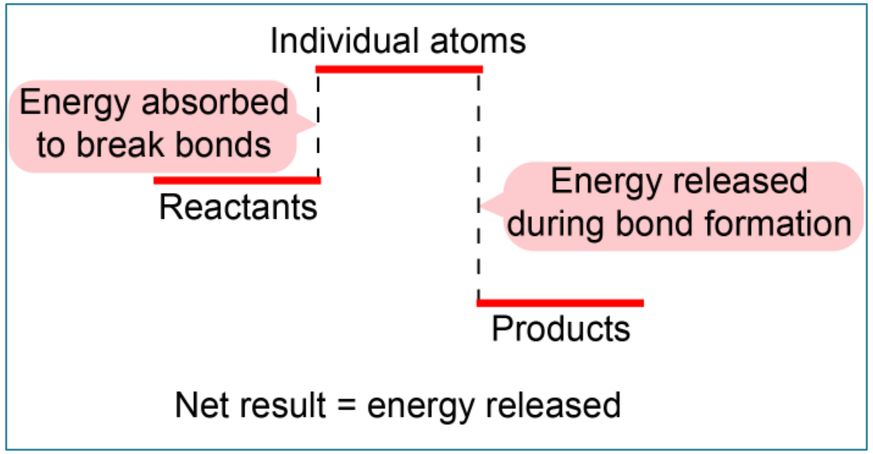


Figure 10.16

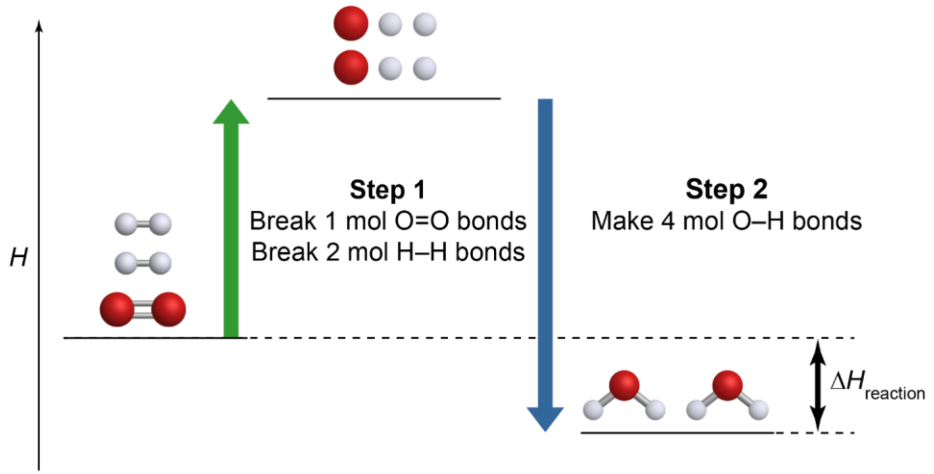
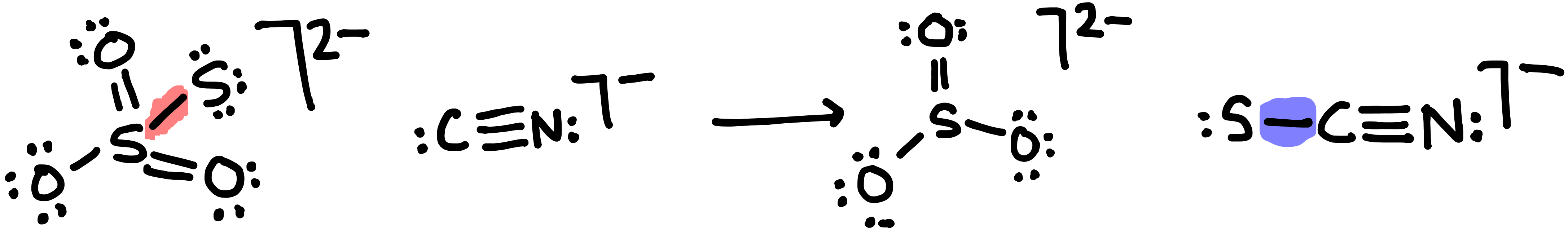


Figure 10.17

Thiosulfate ($S_2O_3^{2-}$) reacts with cyanide (CN^-) to form thiocyanate (SCN^-) and sulfite (SO_3^{2-}). A balanced chemical equation for this process is shown below.

$$S_2O_3^{2-}(aq) + CN^-(aq) \rightarrow SO_3^{2-}(aq) + SCN^-(aq)$$

Draw Lewis structures for the reactant and product molecules and determine the bonds made and broken in this reaction.



bonds broken

bonds made

Thiosulfate ($S_2O_3^{2-}$) reacts with cyanide (CN^-) to form thiocyanate (SCN^-) and sulfite (SO_3^{2-}). A balanced chemical equation for this process is shown below.

$$S_2O_3^{2-}(aq) + CN^-(aq) \rightarrow SO_3^{2-}(aq) + SCN^-(aq)$$

Use the bonds made and broken along with bond enthalpies to calculate the enthalpy change of this reaction.

$225\ \text{kJ} + (-260\ \text{kJ}) = -35\ \text{kJ}$

Absorption of a photon by a molecule can promote the cleavage of covalent bonds in a *homolytic* way (meaning each atom in the bond gets one electron). Bond enthalpy can be used as a rough guide for the energy that a photon needs to break a bond. For each bond listed below, calculate the maximum wavelength of a photon that can break the bond based on its bond enthalpy. Which bonds, if any, can be broken by visible light?

$$\boxed{E = \frac{hc}{\lambda}}$$

O–O
142 kJ/mol
842 nm
infrared

C–O
350 kJ/mol
342 nm ✗
UV

C–S
260 kJ/mol
460 nm
blue light

C–I
240 kJ/mol
498 nm
blue-green light

S–S
225 kJ/mol
531 nm
green light!

Cl–Cl
330 kJ/mol
362 nm ✗
UV

I–I
153 kJ/mol
782 nm
infrared

11.A Molecular Shape and Bonding Theories

First-year Chemistry Program

Objectives

11.A

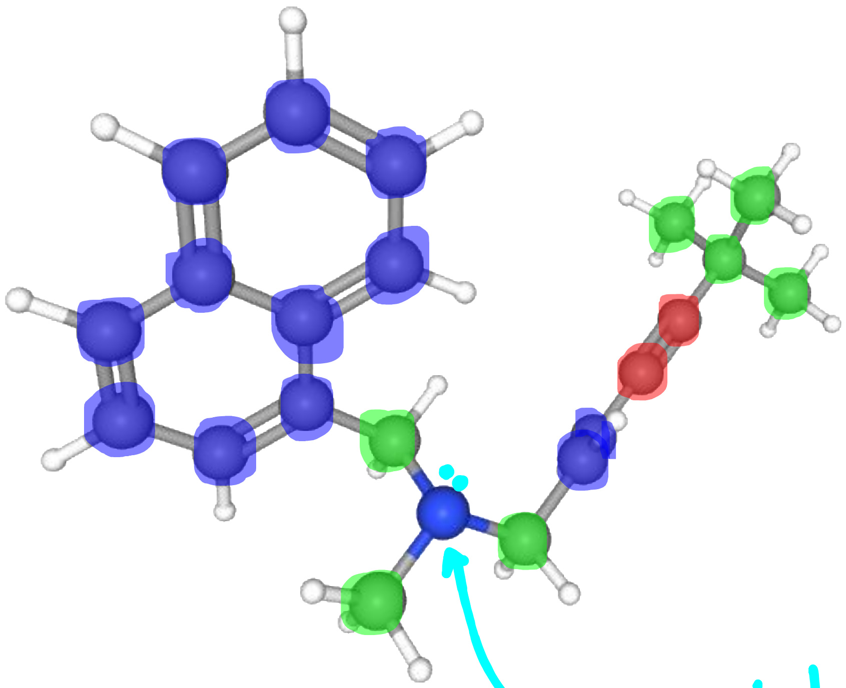
10.A

- At the end of this chapter you should be able to:
  - Use Lewis structures to predict molecular geometry using VSEPR.
  - Identify polar and nonpolar molecules using electronegativity values and molecular shape.
  - Explain valence bond theory.
  - Describe and recognize sp, sp^2, and sp^3 hybrid orbitals from Lewis structures or other images of molecules.
  - Define, describe, and identify sigma and pi bonds in molecules.

10.B

11.B

Examine the three-dimensional structure of the antifungal terbinafine here. Identify atoms in the structure with linear, trigonal planar, and tetrahedral geometry. Identify an atom with tetrahedral electronic geometry but pyramidal molecular geometry.



VSEPR and Molecular Geometry (11.1)

- ***Valence shell electron pair repulsion (VSEPR) theory***
  - The VSEPR model predicts the shape of a molecule based on minimizing repulsion between **electron domains** around the central atom.
    - Electron domains also are called electron groups, regions of electron density, and charge clouds.
    - One electron domain is: a single bond, a double bond, a triple bond, or a lone pair of electrons.
  - Order of repulsion:

    lone pair to lone pair > bonding pair to lone pair > bonding pair to bonding pair

VSEPR and Molecular Geometry (11.1)

step 1

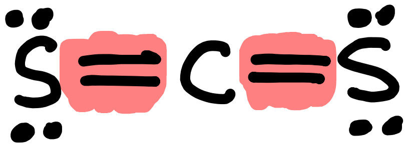
- ***Electron geometry*** looks only at the total number of electron domains.
  – Most stable arrangement of electrons around the central atom results from the least repulsion between electrons.

step 2

- ***Molecular geometry*** is the shape occupied by the atoms in the molecule.
  – Differentiates between bonding and lone pairs of electrons.
  – If there are no lone pairs of electrons on the central atom, then the electron geometry and molecular geometry are the same.

Determine the electronic and molecular geometries of the central atoms in each of the following ions or molecules. Draw Lewis structures for each, determine the number of electron domains around the central atom, write the electronic geometry, and place unshared pairs to determine the molecular geometry.

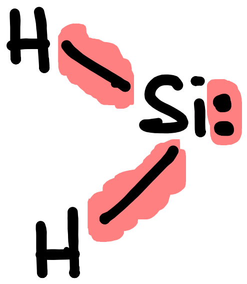
CS_2 2 EDs



linear EG

linear MG

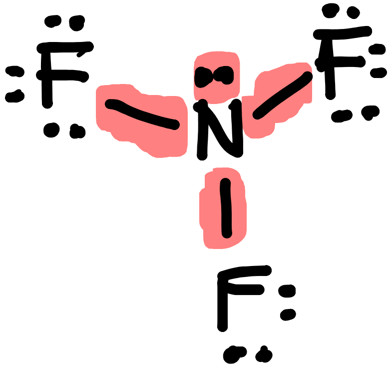
SiH_2 3 EDs



trigonal planar EG

bent MG

NF_3 4 EDs

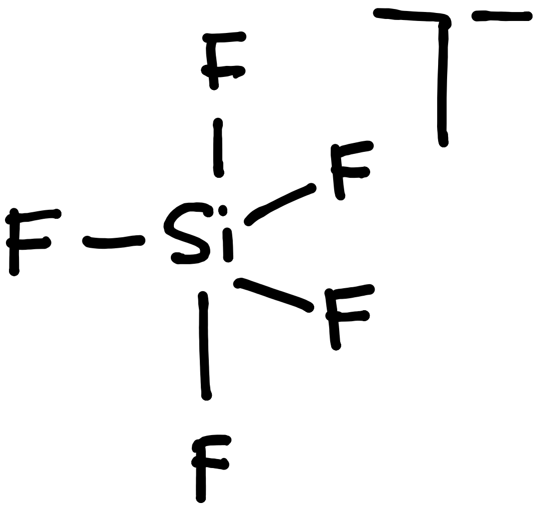


tetrahedral EG

pyramidal MG

Determine the electronic and molecular geometries of the central atoms in each of the following ions or molecules. Draw Lewis structures for each, determine the number of electron domains around the central atom, write the electronic geometry, and place unshared pairs to determine the molecular geometry.

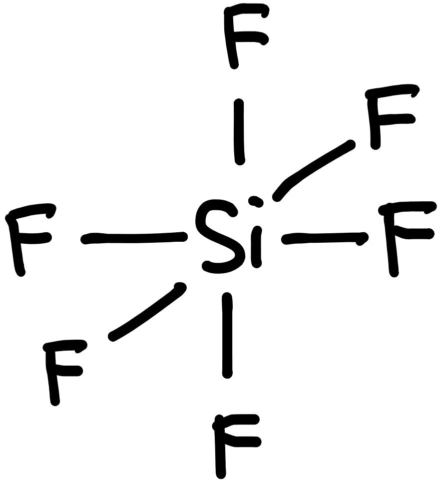
SiF_5^- 5 EDs



trig. bipyramidal EG

trig. bipyramidal MG

SiF_6 6 EDs

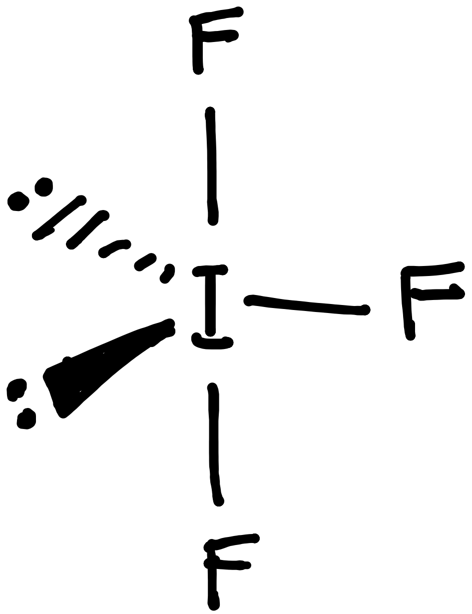


octahedral EG

octahedral MG

So-called "hypervalent iodine" compounds contain iodine linked to three or more atoms or groups. IF_3 is one of the simplest examples of this kind of compound. What are the electronic and molecular geometries of IF_3?

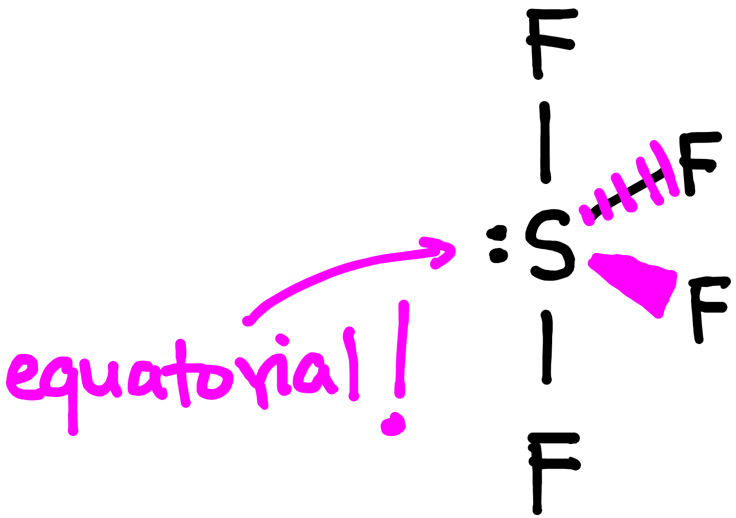
4 EDs trigonal bipyramidal EG



*Place lone pairs equatorial in TBP.

T-shaped MG

Sulfur tetrafluoride (SF_4) is an important fluorinating reagent. Draw a Lewis structure for this compound and determine its electronic and molecular geometries at sulfur.



5 EDs

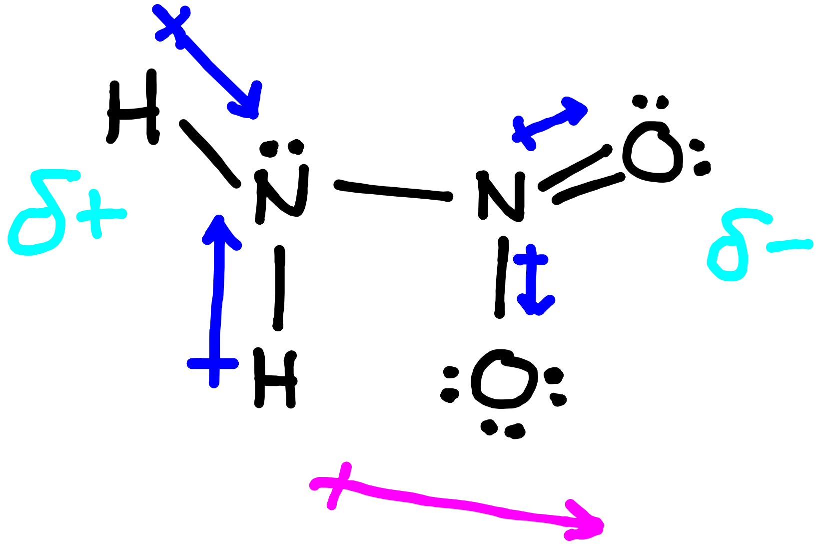
TBP EG

see-saw MG

Polar and Nonpolar Molecules (11.2)

- Polarity of a molecule can be predicted by combining the knowledge of:
  - Bond dipoles
  - Molecular geometry

The compound nitramide has the formula H_2NNO_2. Draw a Lewis structure for this compound and determine whether it is polar or nonpolar. If the molecule has a permanent dipole moment, draw its direction.



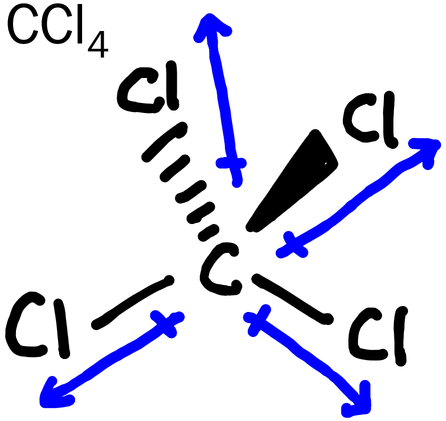
bond dipoles

molecular dipole

polar molecule

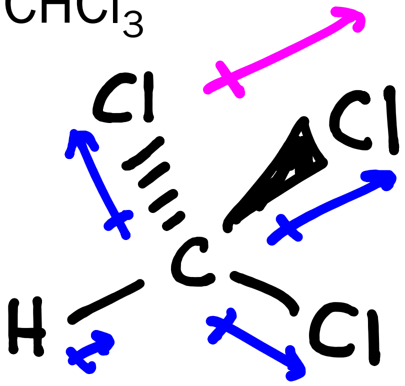
The following molecules all contain polar covalent bonds. Which are polar molecules and which have no permanent dipole?

CCl_4



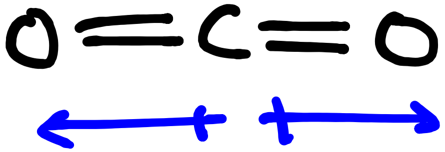
nonpolar

$CHCl_3$



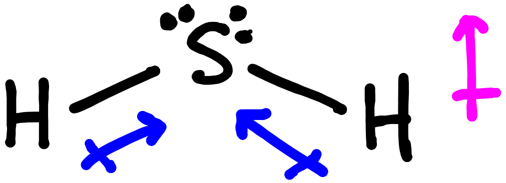
polar

CO_2



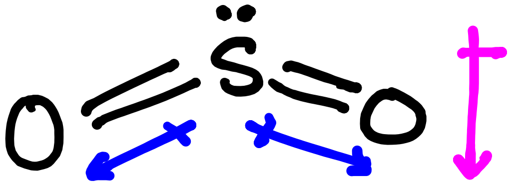
nonpolar

H_2S



polar

SO_2



polar

11.B Molecular Shape and Bonding Theories

First-year Chemistry Program

Valence Bond Theory: Hybrid Orbitals and Bonding (11.3)

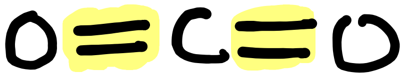
- ***Hybrid Orbitals***
  - Created by a linear combination of atomic orbitals, producing an equal number of hybrid orbitals (remember that orbitals are mathematical in nature).
    - Orientation of hybrid orbitals explain observed molecular geometries
    - Central atoms are most likely to hybridize

Determine the hybridization at the central atom in each of the molecules below.

# of e⁻ groups?

CO_2

linear

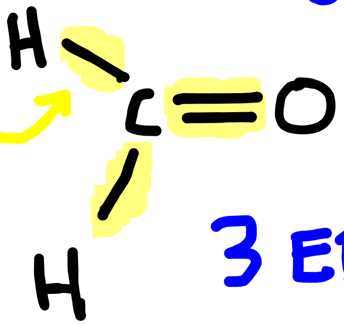


2 EDs → sp^1

H_2CO

trigonal planar

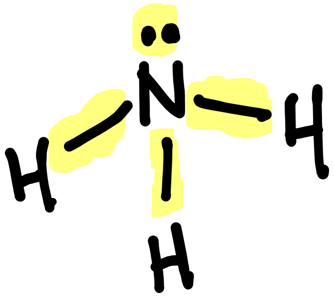
electron domain (ED)



3 EDs → sp^2

NH_3

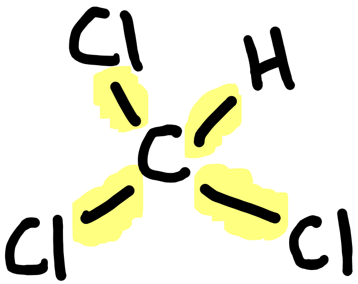
tetrahedral



4 EDs → sp^3

$CHCl_3$

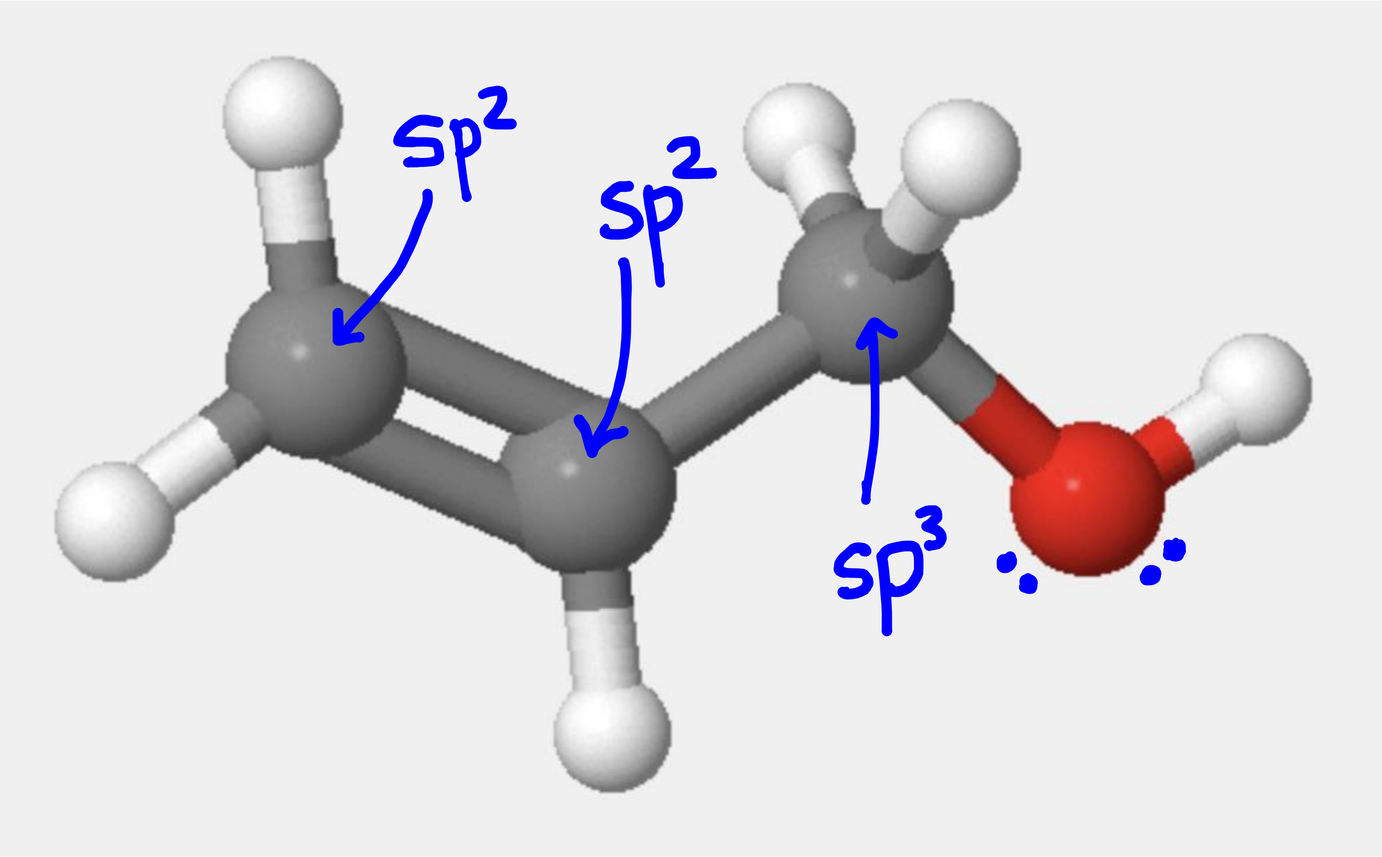
tetrahedral



4 EDs → sp^3

Hybrid atomic orbitals are mathematical constructions created by scaling and adding the hydrogenic atomic orbitals (2*s*, 2*p*, etc.) on a single atom. Overlap of hybrid orbitals generates localized bonding orbitals, where we can imagine the electrons in bonds live.

A three-dimensional model of allyl alcohol is here. Determine the hybridizations of the carbon atoms in this molecule.



Valence Bond Theory: Hybrid Orbitals and Bonding (11.3)

- ***Sigma (σ) bond***
  - Formed via constructive interference (overlap of orbitals that are ***in-phase***)
    - Direct or head-on overlap of orbitals in the internuclear axis
    - All bonds (single, double, or triple) have one sigma bond

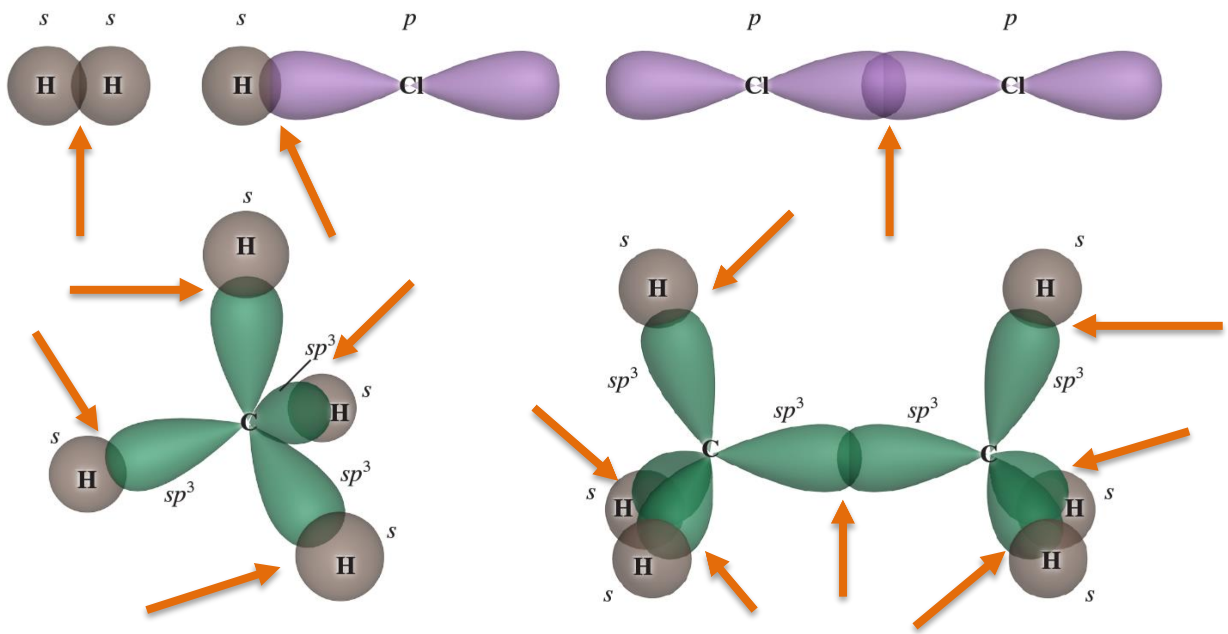


Figure 11.23

Valence Bond Theory: Hybrid Orbitals and Bonding (11.3)

- ***Pi (π) bond***
  - Formed via constructive interference (overlap of orbitals that are in-phase)
    - Side-to-side overlap of orbitals *above and below* the internuclear axis
    - A double bond is one sigma bond and one pi bond

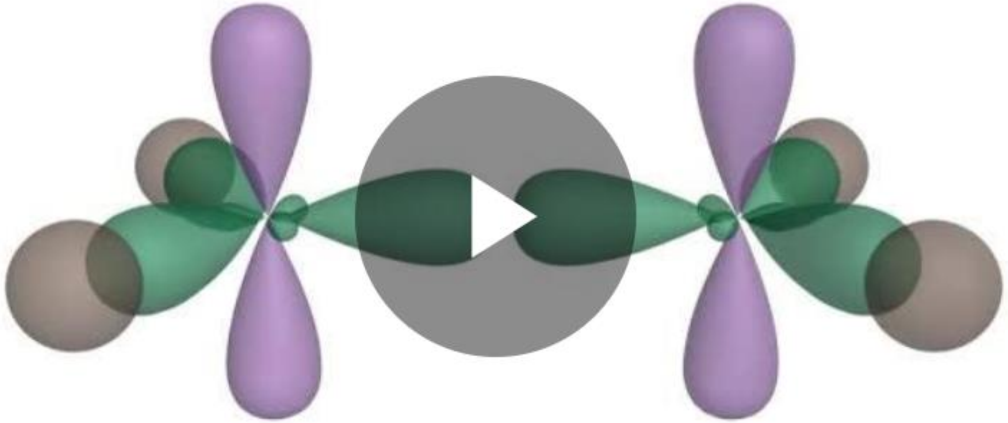
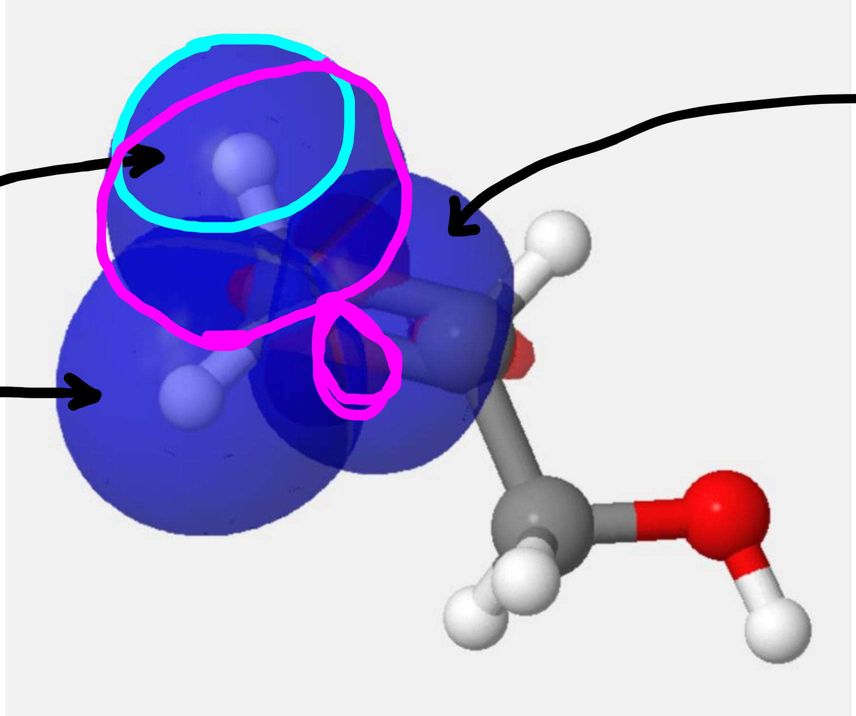


Figure 11.25 π Bond Animation: *sp*^{2}

Hybrid atomic orbitals are mathematical constructions created by scaling and adding the hydrogenic atomic orbitals (2*s*, 2*p*, etc.) on a single atom. Overlap of hybrid orbitals generates localized bonding orbitals, where we can imagine the electrons in bonds live.

A three-dimensional model of allyl alcohol is here. Clicking on bonds in the structure will display various molecular orbitals associated with each bond. After identifying an atom with *sp*^{2} hybridization, click *once* on each bond to the atom to display bonding orbitals. Using the language of hybridization and valence bond theory, describe the composition of each bonding orbital.

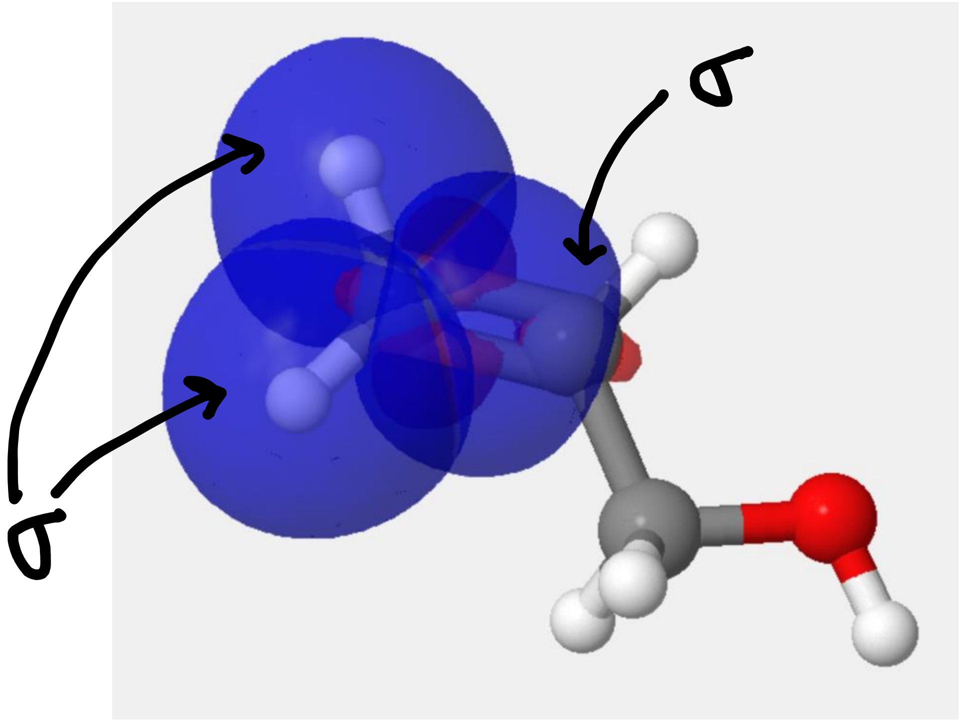
sp^2 + sp^2
on C1 on C2



sp^2 on C + 1s on H

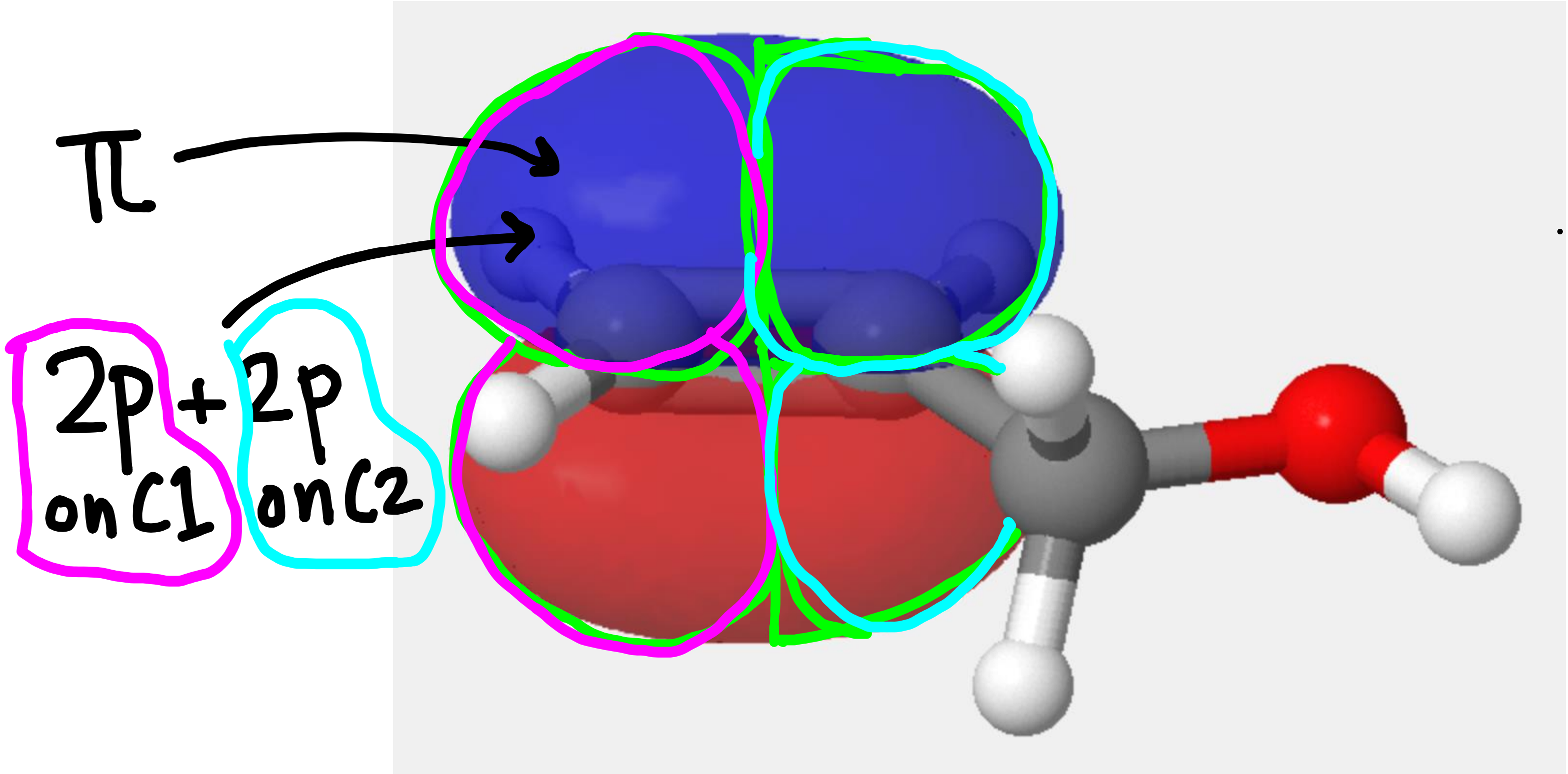
Hybrid atomic orbitals are mathematical constructions created by scaling and adding the hydrogenic atomic orbitals (2*s*, 2*p*, etc.) on a single atom. Overlap of hybrid orbitals generates localized bonding orbitals, where we can imagine the electrons in bonds live.

A three-dimensional model of allyl alcohol is [here](). Clicking on bonds in the structure will display various molecular orbitals associated with each bond. After identifying an atom with sp^2 hybridization, click *once* on each bond to the atom to display bonding orbitals. Are the bonding orbitals displayed sigma (σ) or pi (π) orbitals? Explain how you know.



Hybrid atomic orbitals are mathematical constructions created by scaling and adding the hydrogenic atomic orbitals (2*s*, 2*p*, etc.) on a single atom. Overlap of hybrid orbitals generates localized bonding orbitals, where we can imagine the electrons in bonds live.

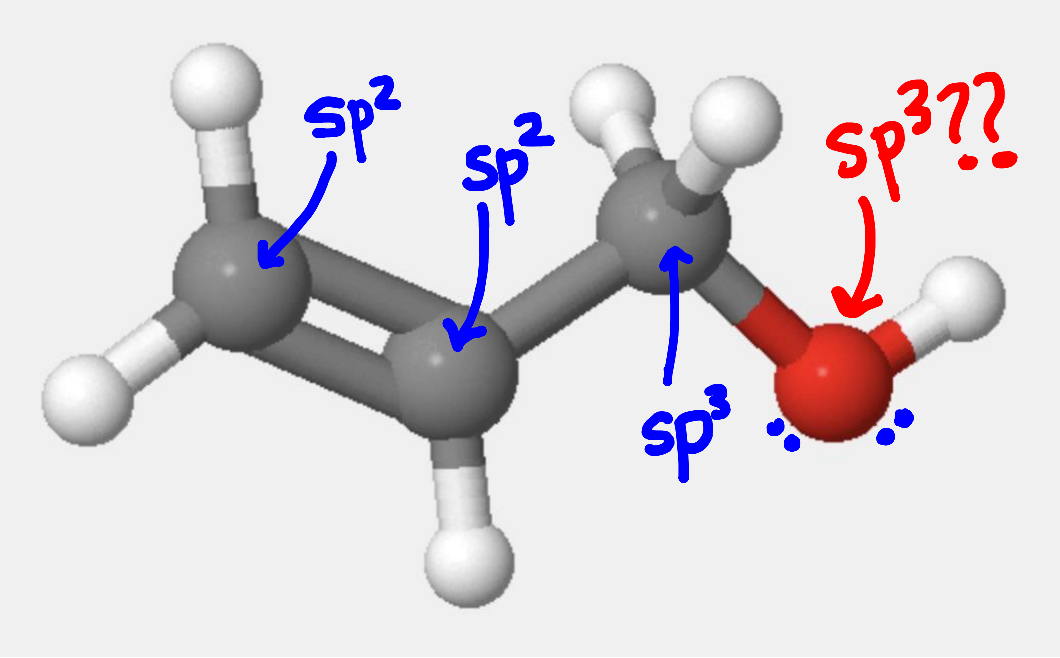
A three-dimensional model of allyl alcohol is [here](). Click *twice* on the double bond in the structure. What type of orbital is displayed? Describe its composition: what atomic orbitals are combined to construct it?

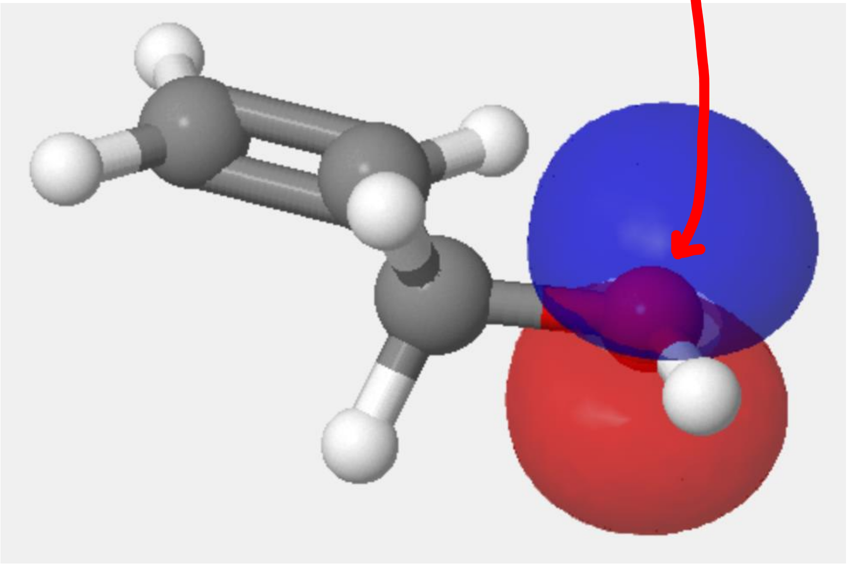


Hybrid atomic orbitals are mathematical constructions created by scaling and adding the hydrogenic atomic orbitals (2*s*, 2*p*, etc.) on a single atom. Overlap of hybrid orbitals generates localized bonding orbitals, where we can imagine the electrons in bonds live.

A three-dimensional model of allyl alcohol is here. click on the O–C and O–H bonds. Then, click on the oxygen atom to display a hybrid orbital holding a lone pair. What hybridization is suggested by this arrangement of orbitals? Does it match your prediction? (*NOTE:* Aside from this example, we will not consider further the hybridization of atoms bearing more than one lone pair.)

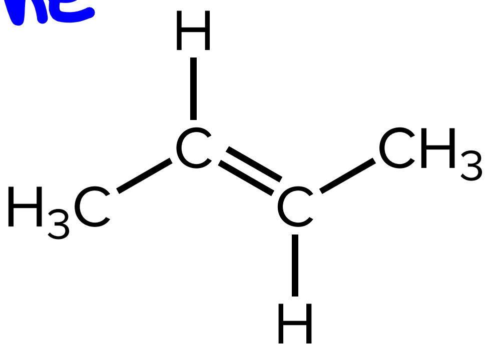
sp^2 with an unhybridized 2p!



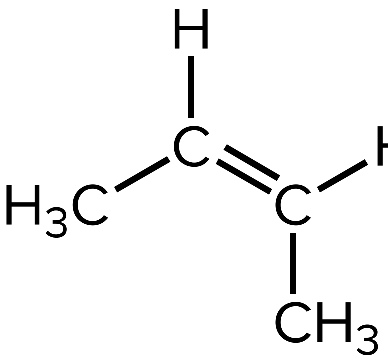


There are two forms of the compound 2-butene that cannot be interconverted except under harsh conditions: *cis*- and *trans*-2-butene. Analogous forms of the related compound butane interconvert extremely rapidly. Use valence bond theory to explain the difference in behavior of butene and butane.

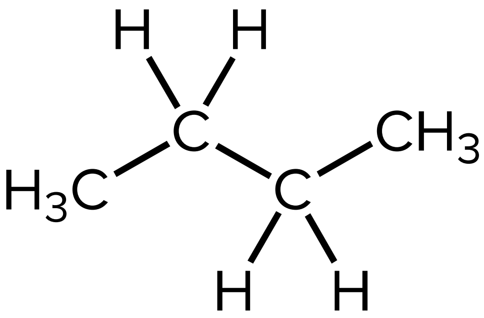
check out the allyl alcohol model for interactive images.



trans-2-butene

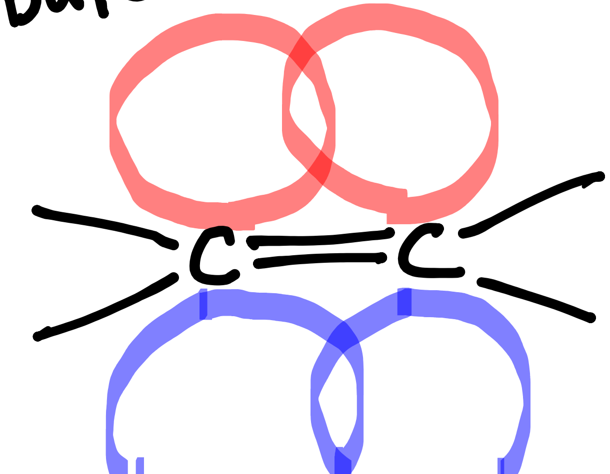


cis-2-butene



butane

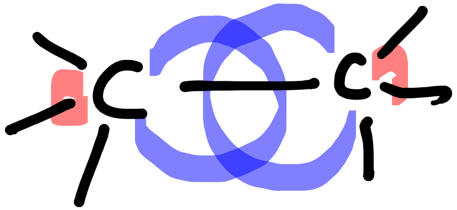
butene



rotation would ruin overlap

butane

rotation doesn't affect overlap



12.A Liquids and Solids

First-year Chemistry Program

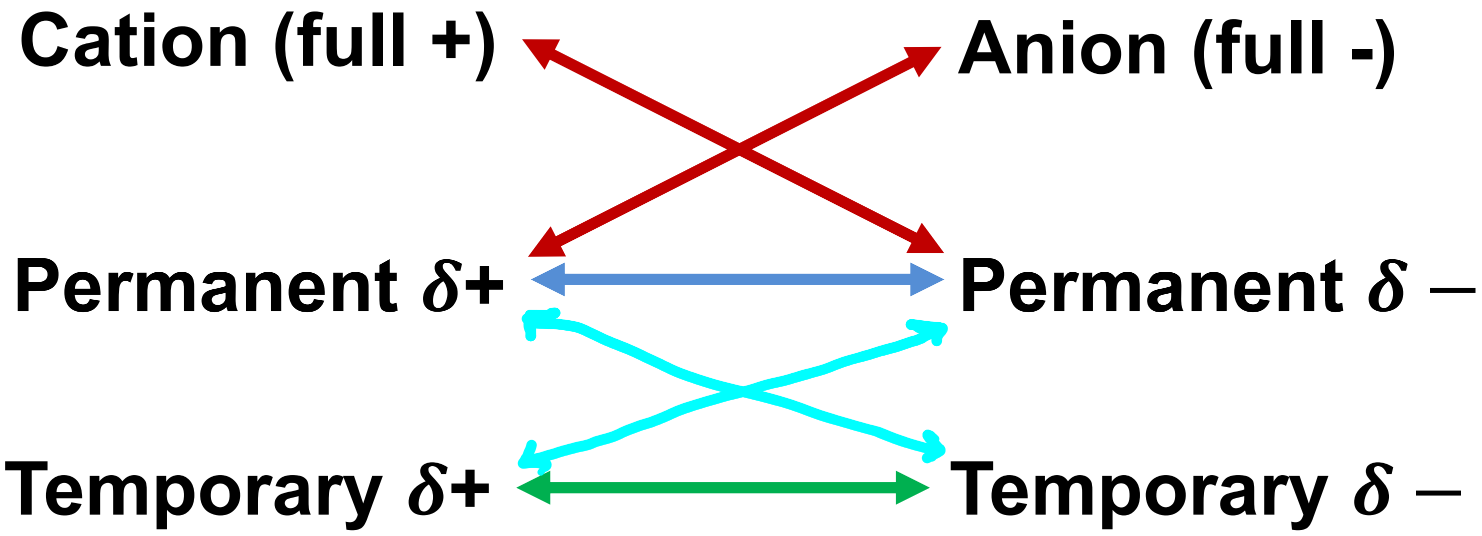
Objectives

- At the end of this chapter you should be able to:
  - List and describe the four types of intermolecular forces and identify the predominant intermolecular force for specific substances.
  - List and define terms related to phase changes.
  - Calculate energy changes related to phase changes.
  - Interpret heating curves.
  - Predict relative vapor pressures based on intermolecular forces.
  - Define, describe, and interpret phase diagrams.
  - Describe the structure of various cubic unit cells.

Intermolecular Forces (12.1)

- ***Intra***molecular forces are chemical bonds that hold together individual molecules. They are **MUCH** stronger than any of the ***inter***molecular forces
- ***Inter*molecular forces:**
  - Forces of attraction between molecules in a sample
  - Originate from the interactions among full (ionic) charges, permanent partial charges, and temporary partial charges on molecules, atoms, or ions.

Intermolecular Forces (12.1)



dipole-induced dipole } mixtures only

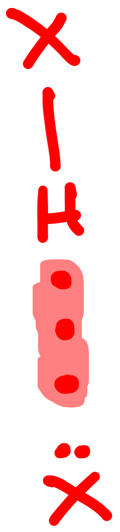
Ion-dipole attractions

Dipole-dipole attractions
or hydrogen bonding interactions

London forces

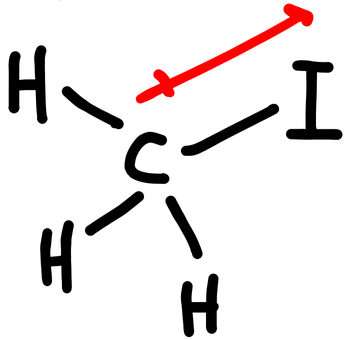
Intermolecular Forces (12.1)

- ***Hydrogen bonding interactions*** are a particularly strong, special case of dipole-dipole interaction, and typically are stronger than other dipole–dipole attractions.
  - The partial positive charge on an H atom that is covalently bonded to an O, N, or F atom is attracted to the partial negative charge on an O, N, or F atom *in another molecule*.
  - Requirements:
    - A ***hydrogen bonding donor molecule*** containing a partially positive H atom bonded to N, O or F
    - A ***hydrogen bonding acceptor molecule*** containing a partially negative N, O or F with lone pair electrons



Identify all of the intermolecular forces in pure samples of each compound below. If more than one force is operating, identify the predominant IMF.

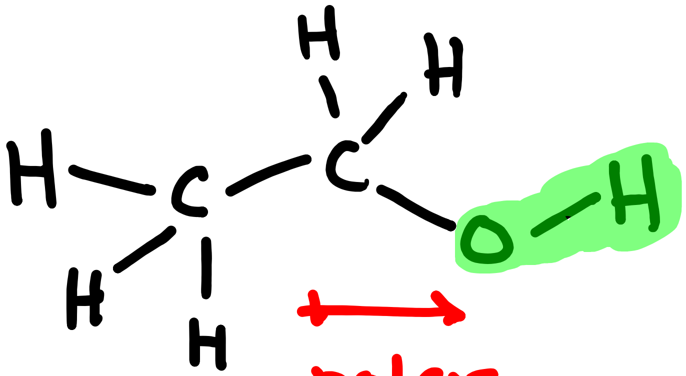
CH_3I



Polar

- Dipole-dipole
- London

CH_3CH_2OH



polar

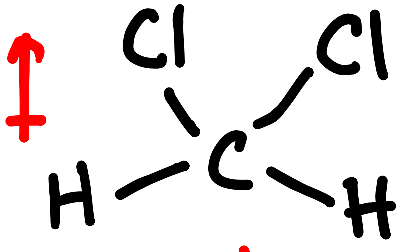
- Hydrogen bonding
- Dipole-dipole
- London

Br_2

non-polar

- London

CH_2Cl_2

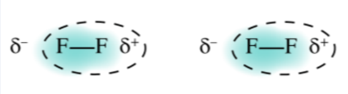
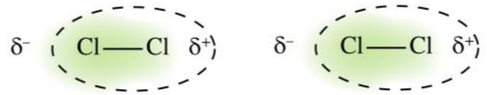
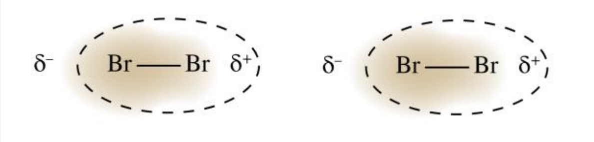
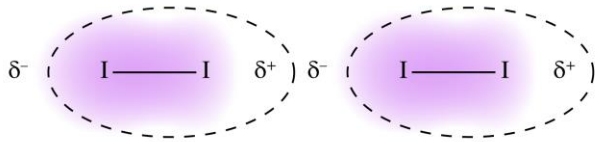


polar

- Dipole-dipole
- London

Explain why, under ordinary conditions, elemental fluorine and chlorine both exist as gases, bromine exists as a liquid, and iodine exists as a solid.

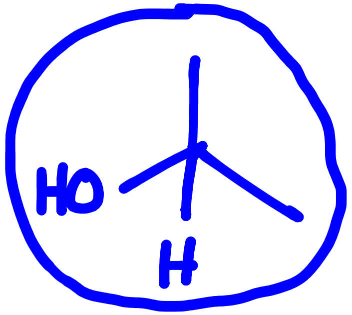
London forces

Halogen	Atomic Radius (pm)	Boiling Point (K)	Diagram
Fluorine	60	85	
Chlorine	100	239	
Bromine	117	332	
Iodine	136	457	

largest molecule, greatest polarizability

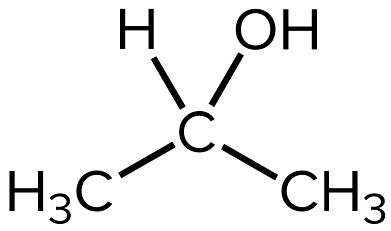
polarizability

Suggest a reason why the boiling point of 2-propanol (77 ºC) is much lower than the boiling point of 1-propanol (97 ºC).



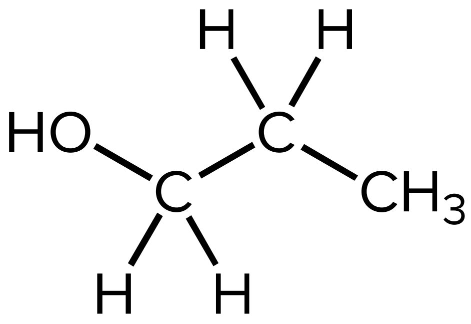
Weaker London forces,

smaller SA (surface area)



2-propanol

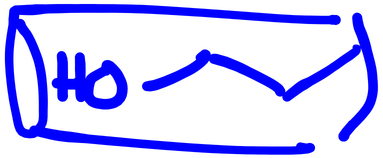
hydrogen bonding



1-propanol

hydrogen bonding

97ºC



stronger London forces

Polarizability

Phase Changes and Heating Curves (12.3)

- ***Heating curves*** are graphs showing the variation in the temperature of a sample as it is heated at constant rate and constant pressure.

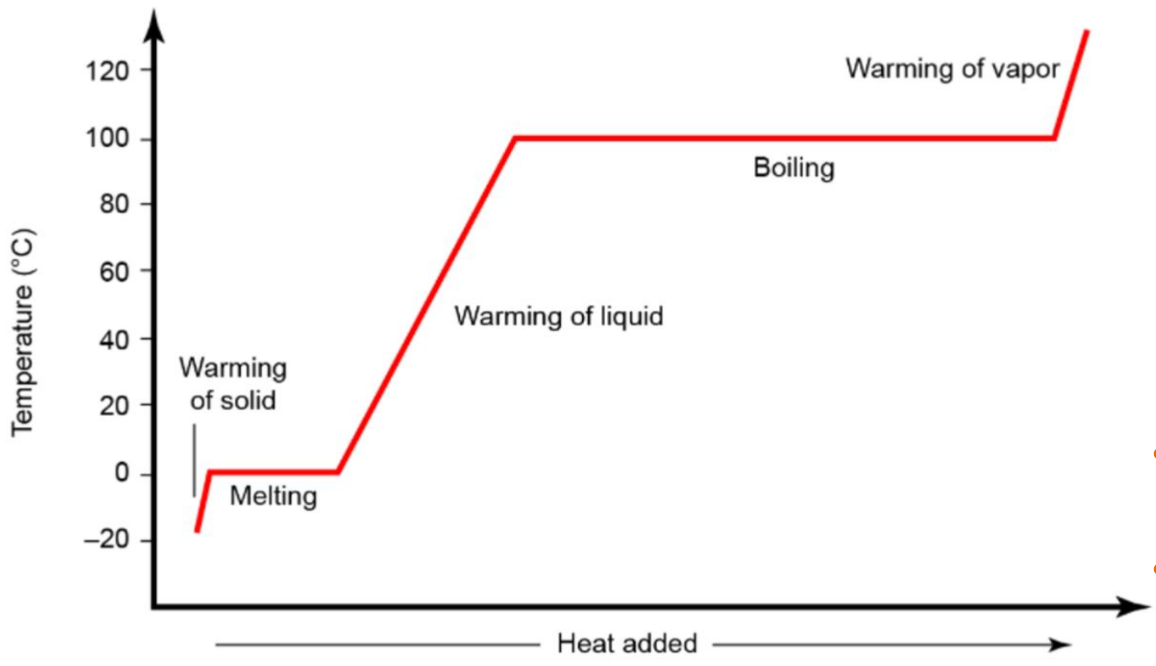


Figure 12.16

Warming solid: q = $mc(\Delta T)$

Melting: q = $n(\Delta H_{fus})$

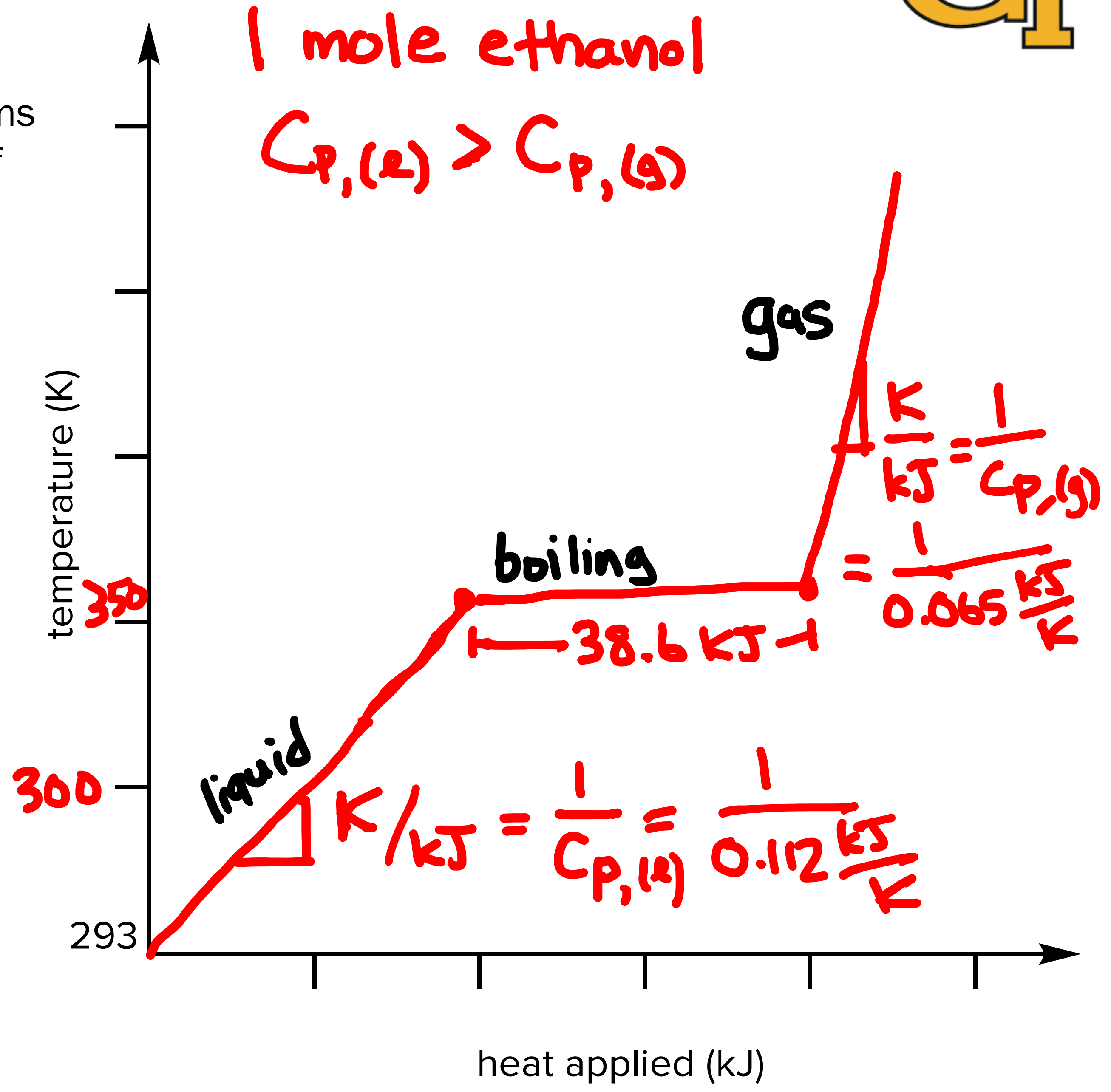
Warming liquid: q = $mc(\Delta T)$

Boiling: q = $n(\Delta H_{vap})$

Warming gas: q = $mc(\Delta T)$

- Specific heats of substances are phase dependent.
- Change the sign on ΔH if cooling.

Use thermochemical data on the NIST Chemistry WebBook to generate a heating curve for one of the following solvents: (a) ethanol; (b) diethyl ether; (c) tetrahydrofuran; (d) dichloromethane. Make an effort to draw the heating curve to scale. Assume all heating happens at a constant pressure of 1 atmosphere and that 1 mole of substance is being heated; extend the curve at least 40 K above the boiling point. For dichloromethane gas, assume $c_P = 55$ J/mol·K (a good approximation below 350 K).



Phase Diagrams (12.5)

- A ***phase diagram*** shows the phase of a specific substance under all possible pressure–temperature combinations.

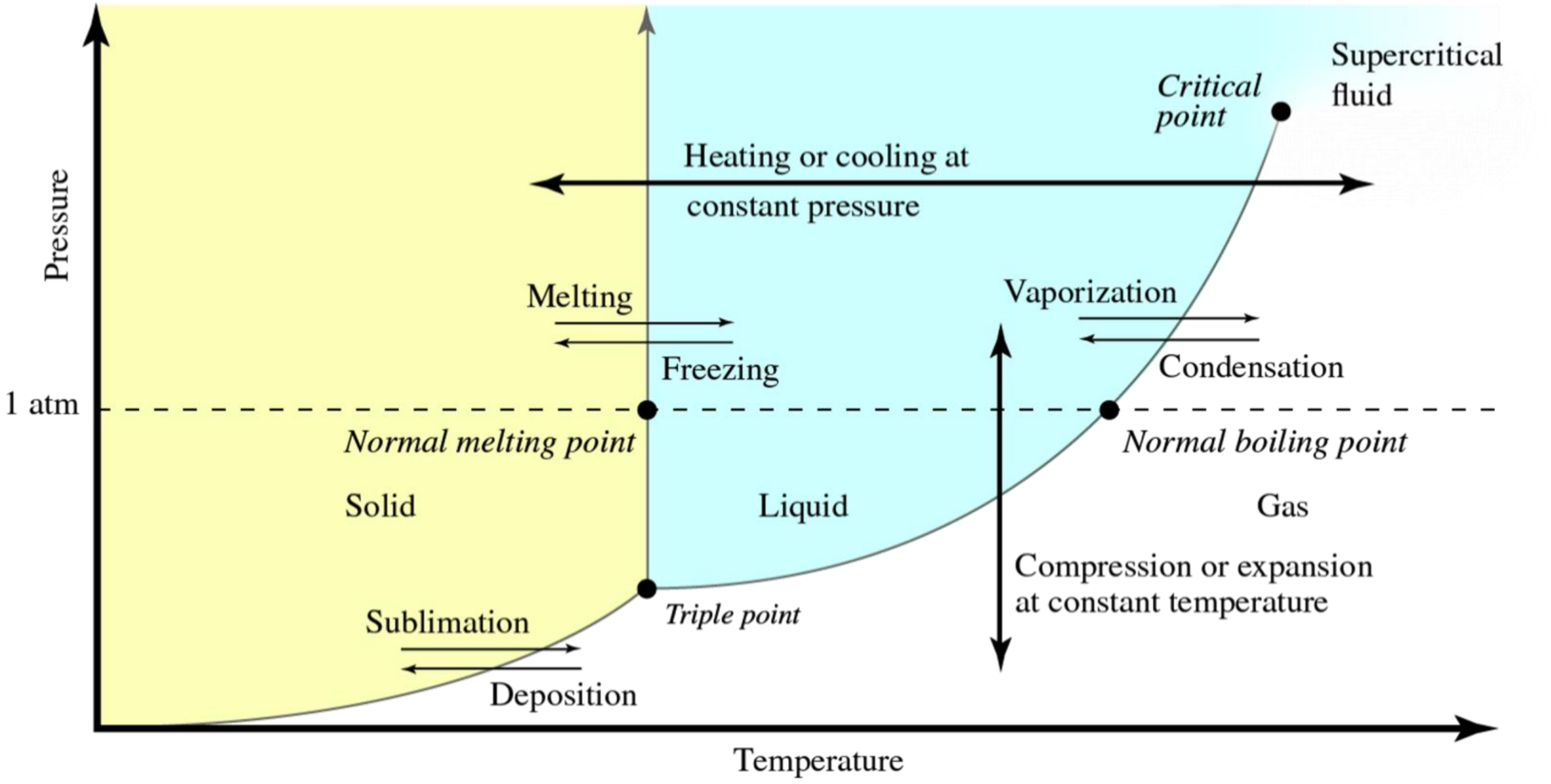
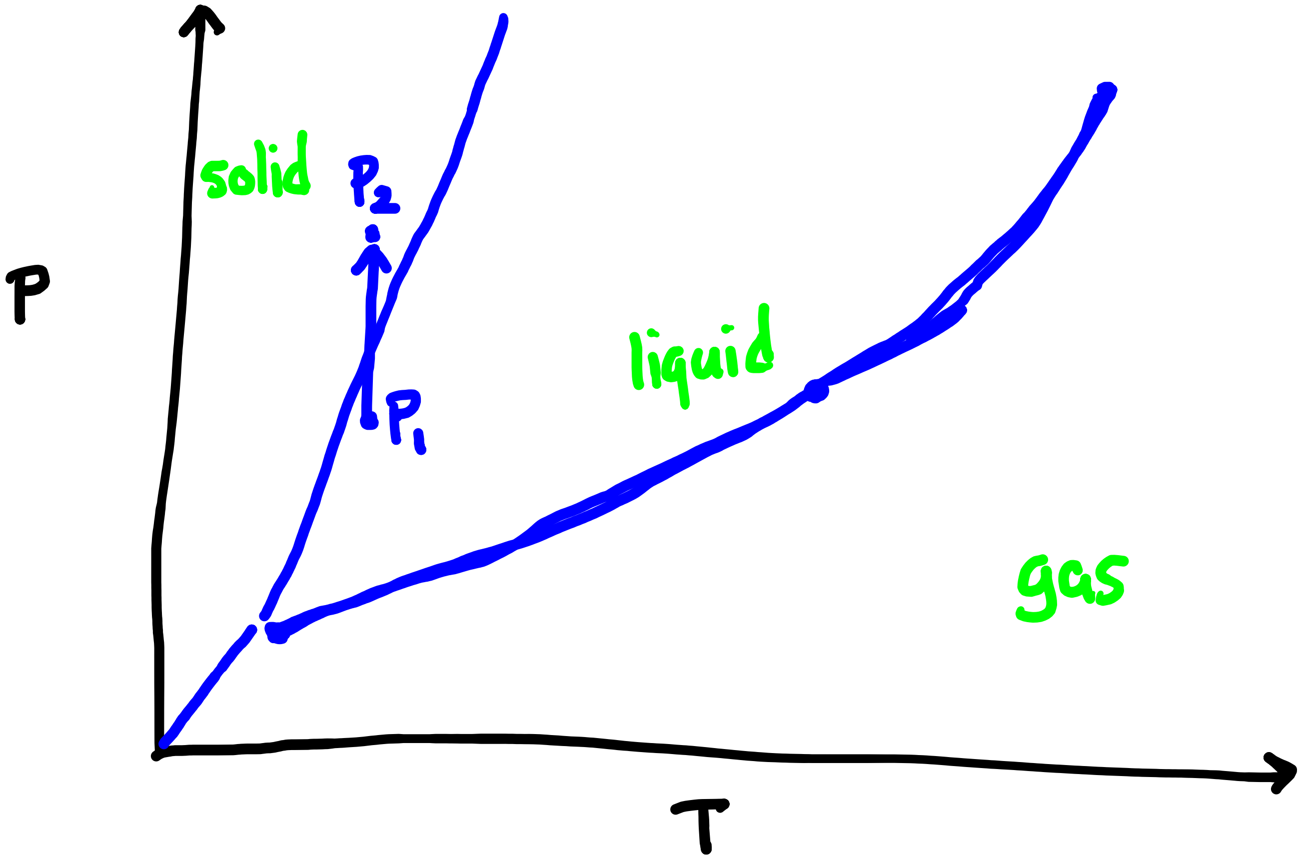


Figure 12.25

Create a phase diagram for bromine (Br_2) using the following information. [(reference video)]

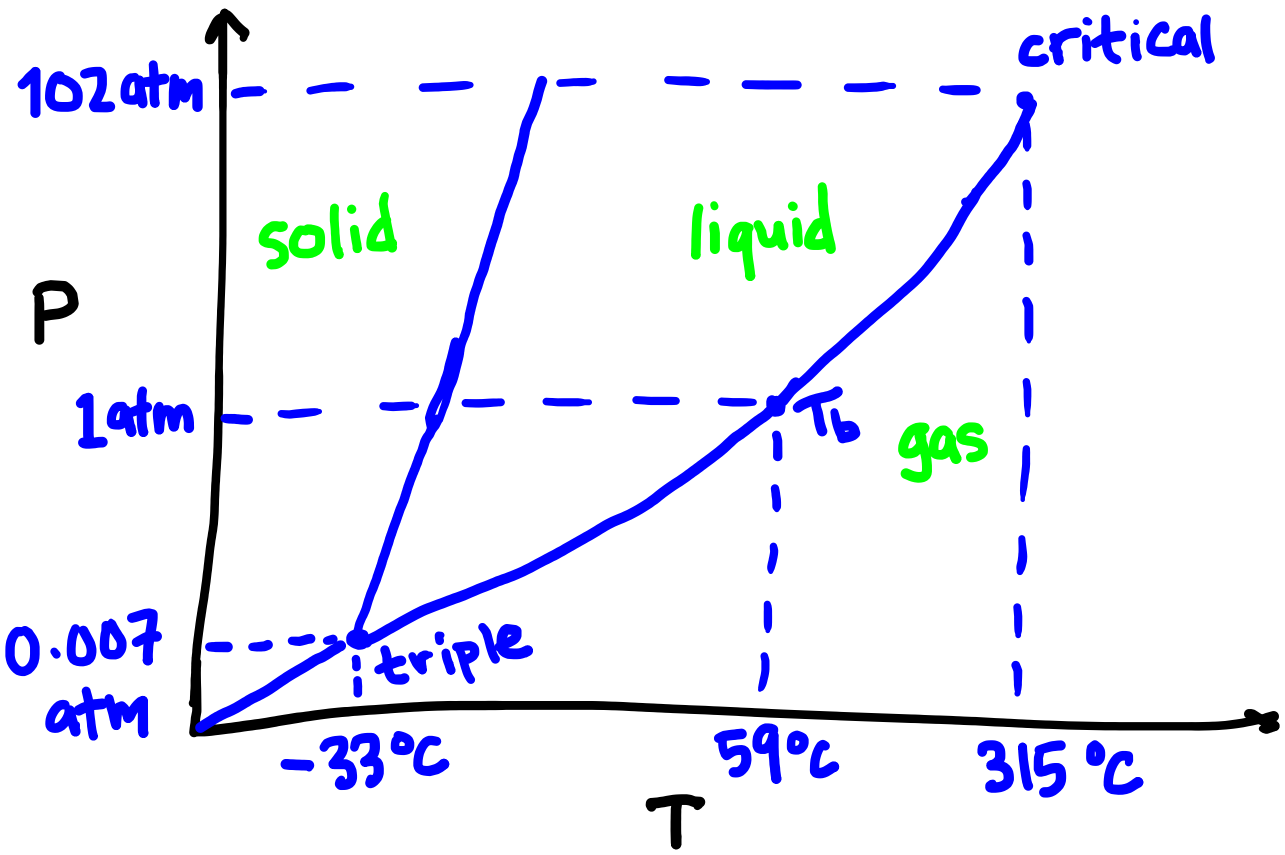
A. The critical point occurs at (102 atm, 315 °C). crit
B. The triple point occurs at (0.007 atm, −33 °C). triple
C. The normal boiling point is 59 °C. T_b
D. The density of the solid is greater than the density of the liquid at all pressures.



$\uparrow P,\ (l) \rightarrow (s)$

Create a phase diagram for bromine (Br_2) using the following information. [(reference video)]

A. The critical point occurs at (102 atm, 315 °C). critical
B. The triple point occurs at (0.007 atm, –33 °C). triple
C. The normal boiling point is 59 °C. T_b
D. The density of the solid is greater than the density of the liquid at all pressures.



↳ increasing P causes (l) → (s) phase transition

The Unit Cell and the Structure of Crystalline Solids (12.7)

- The ***unit cell*** is the simplest repeating unit of a crystal structure and arises from how the layers of particles are arranged.

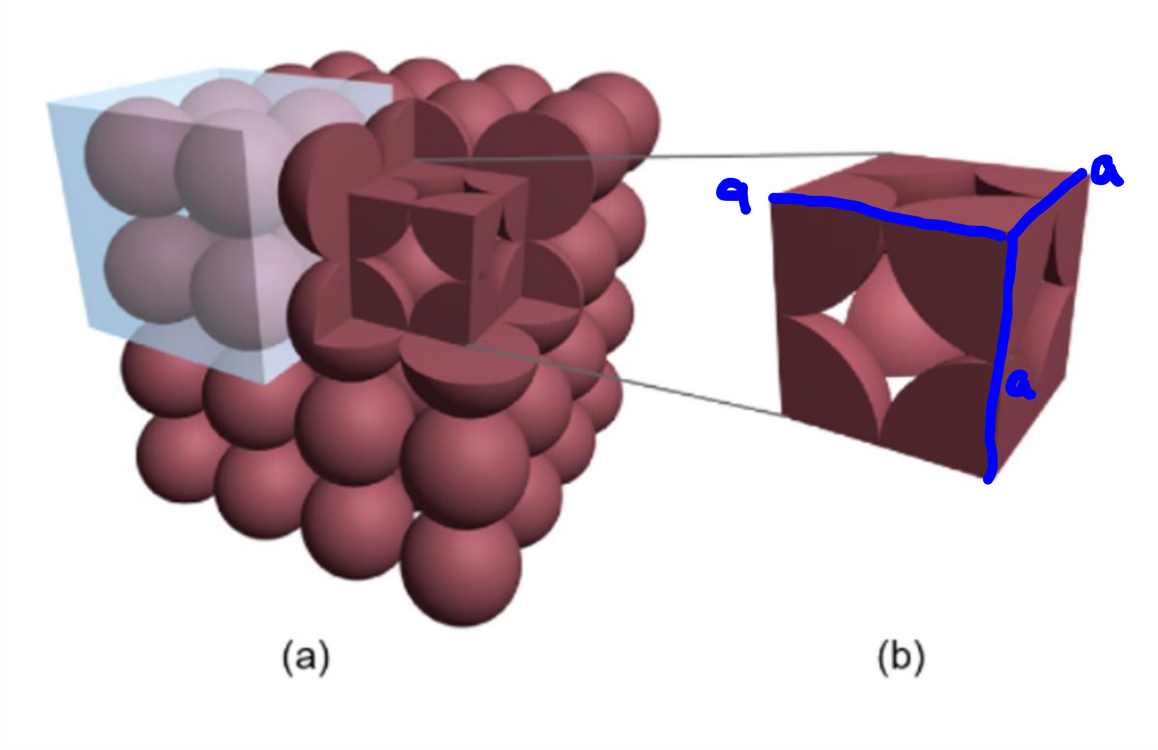
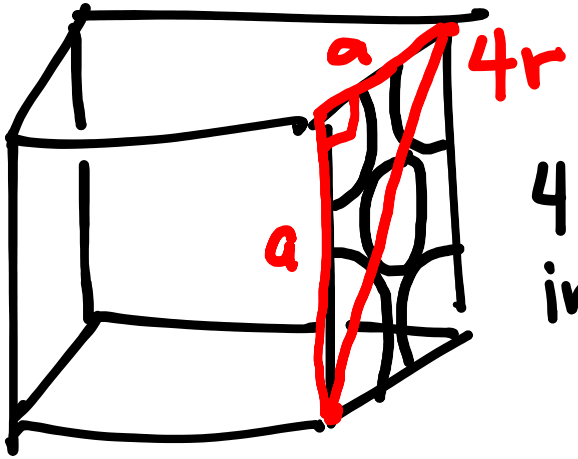


Figure 12.32

Examine the unit cells linked below. For each, determine the number of atoms inside each unit cell (*only* inside the bounding box!) and calculate the packing factor as the percentage of space inside the unit cell filled by atoms. Examples of metals that crystallize in each lattice type are listed; using the identity of the metal and its crystal structure, calculate the density of the metal.

[Cubic close packing (ccp) or face-centered cubic (fcc)] | silver metal (Ag)

107.9 amu, 144 pm
m r



4 atoms in unit cell

$\Downarrow$

$M = 4m$

$$(4r)^2 = 2a^2$$

$$a = \frac{4r}{\sqrt{2}}$$

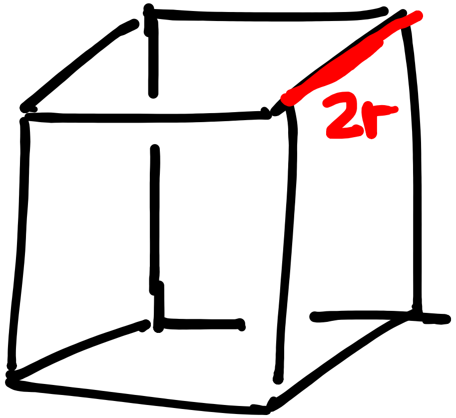
$$V = a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3$$

$$\rho = \frac{M}{V} = \frac{4m}{(4r/\sqrt{2})^3} = 10.6 \text{ g/mL}$$

Examine the unit cells linked below. For each, determine the number of atoms inside each unit cell (*only* inside the bounding box!) and calculate the packing factor as the percentage of space inside the unit cell filled by atoms. Examples of metals that crystallize in each lattice type are listed; using the identity of the metal and its crystal structure, calculate the density of the metal.

Simple cubic | polonium metal (Po)

$m = 209$ amu, $r = 168$ pm



$V = (2r)^3$

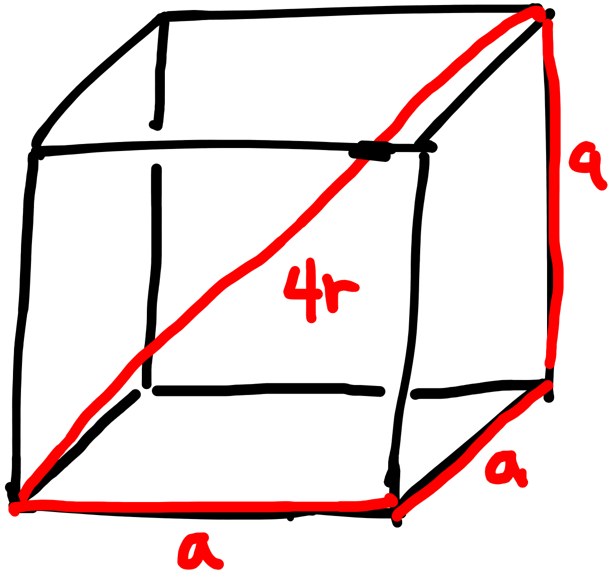
1 atom inside unit cell

$M = 1m$

$$\rho = \frac{m}{(2r)^3} = 9.15 \text{ g/mL}$$

Examine the unit cells linked below. For each, determine the number of atoms inside each unit cell (*only* inside the bounding box!) and calculate the packing factor as the percentage of space inside the unit cell filled by atoms. Examples of metals that crystallize in each lattice type are listed; using the identity of the metal and its crystal structure, calculate the density of the metal.

Body-centered cubic (bcc) | sodium metal (Na)



$$3a^2 = (4r)^2$$

$$a = \frac{4r}{\sqrt{3}}$$

$$V = \left(\frac{4r}{\sqrt{3}}\right)^3$$

2 atoms inside the unit cell

Zinc metal crystallizes in the hexagonal close packing (hcp) structure, which has a packing factor equal to that of fcc. Compare and contrast this structure with the fcc structure. How are the structures different despite their equal packing factors?

13.A Solutions

First-year Chemistry Program

Objectives

- At the end of this chapter you should be able to:
  – Explain, using the energetics of the solution process, how to predict which types of solvents are most likely to dissolve a given solute.

intermolecular forces!

The Solution Process (13.1)

- A ***solution*** is any homogeneous mixture that can be made up of almost any two phases of matter.
  - The dissolved substance is the ***solute*** and the substance it is dissolved in is the ***solvent***.

The Solution Process (13.1)

- Substances dissolve in one another if the solute and solvent are able to form intermolecular attractions.
  - We often refer to the “like dissolves like” rule. In other words, substances with the same types of intermolecular forces tend to dissolve in each other.
  - Consider three factors:
    - Solute-solute attractions
    - Solvent-solvent attractions
    - Solute-solvent attractions
  - For a solution to form: solute-solvent attractions $\geq$ solute-solute and ~~solute~~-solvent attractions

    solvent

Describe the process of solution formation in terms of interactions between solute and solvent particles. For each step of the process, indicate whether the step is likely to be endothermic or exothermic and whether the change in entropy (ΔS) is likely to be positive or negative.

"more disordered" products

1. Break solute-solute, $\Delta H_1 > 0$, $\Delta S_1 > 0$
2. Break solvent-solvent, $\Delta H_2 > 0$, $\Delta S_2 > 0$
3. Form solute-solvent, $\Delta H_3 < 0$, $\Delta S_3 < 0$

Draw molecular-level depictions of the solute particles and their immediate environment when $CaCl_2$ is dissolved in water. Pay careful attention to the orientation of the water molecules! See the Water tab of this simulation.

One approach to thinking about solution thermodynamics for ionic solutes in water involves conceiving of the solution process as ionization followed by hydration:

$MX(s) \rightarrow M^+(g) + X^-(g)$	ionization
$M^+(g) \rightarrow M^+(aq)$	hydration of M^+
$X^-(g) \rightarrow X^-(aq)$	hydration of X^-
$MX(s) \rightarrow M^+(aq) + X^-(aq)$	solution formation ΔH_s

Determine the enthalpy of solution for MgF_2 using the following data. Is the formation of an aqueous solution of magnesium fluoride endothermic or exothermic?

Lattice energy of MgF_2: 2908 kJ/mol ΔH_1
Enthalpy of hydration of Mg^{2+}: –1926 kJ/mol ΔH_2
Enthalpy of hydration of F^-: –524 kJ/mol ΔH_3

$$MgF_2(s) \rightarrow Mg^{2+}(aq) + \underline{2}F^-(aq), \Delta H_s$$

$$\Delta H_s = \Delta H_1 + \Delta H_2 + \underline{2}\Delta H_3$$

respect stoichiometry!

Indicate which molecule in each pair is more likely to dissolve in water, drawing Lewis structures where necessary. Explain differences in solubility using intermolecular forces.

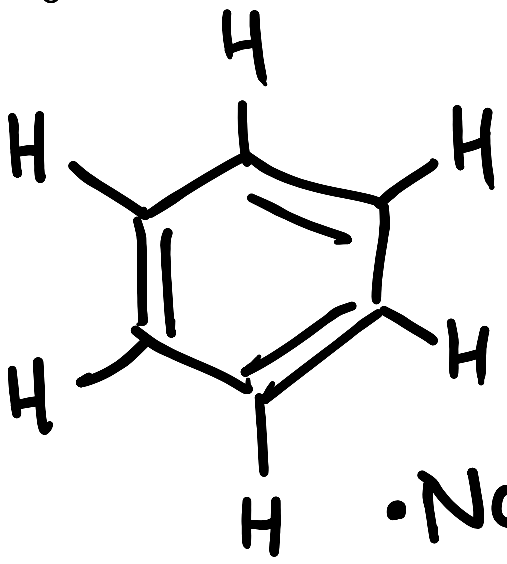
$NaNO_3$

Na^+ NO_3^-

- ion-dipole forces w/ water
- more likely to dissolve

ionic

C_6H_6



- London forces, dipole-induced dipole forces w/ water
- Not likely to dissolve (immiscible)

nonpolar

Indicate which molecule in each pair is more likely to dissolve in water, drawing Lewis structures where necessary. Explain differences in solubility using intermolecular forces.

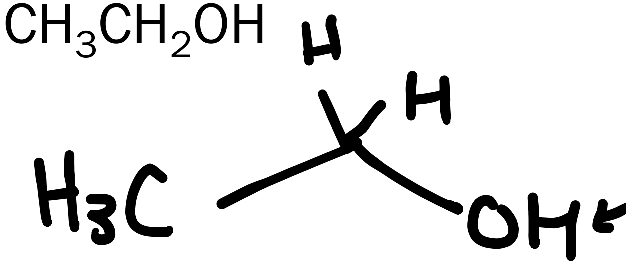
C_2H_6

$H_3C - CH_3$

- Only dipole-induced dipole forces w/ H_2O
- Not likely to dissolve

nonpolar

CH_3CH_2OH



H bonding!

- H bonding w/ water
- Likely to dissolve

polar

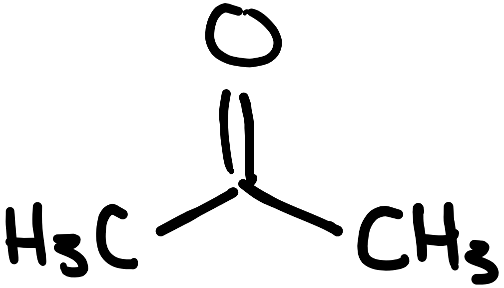
Indicate which molecule in each pair is more likely to dissolve in water, drawing Lewis structures where necessary. Explain differences in solubility using intermolecular forces.

C_5H_{12}

- Nonpolar → won't dissolve in H_2O

nonpolar

$CH_3C(=O)CH_3$



- Dipole-dipole forces w/ water
- AND H bonding!!
- Likely to dissolve

polar