Chapter 3

Stoichiometry

Chemical Stoichiometry

- The study of quantities of materials consumed and produced in chemical reactions.
- Basically:

  Chemical accounting and inventory

Counting by weighing

If a collection of objects has too many members to count directly, we can still get an accurate measurement of their count in a sample if we know the mass of each object.

- Weigh the sample
- Weigh each object

$$\text{No of objects} = \frac{\text{Weight of sample}}{\text{Weight of each object}}$$

700. g

Each jelly bean = 1.12g

$$\text{No. of jelly beans in the jar} = \frac{700.\ g}{1.12\ g} = 625$$

Or get the same by dimensional analysis:

We start with the quantity proportional to what we want.
Number of beans is proportional to the mass of the sample.

$$700.\ \cancel{g} \times \frac{1\ \text{bean}}{1.12\ \cancel{g}} = 625\ \text{beans}$$

What if each jelly bean is not exactly 1.12g?

- It doesn't matter, as long as

➢ we know the average mass of jelly beans (1.12g)

➢ our sample has a large number of jelly beans

Practice

A pile of marbles weigh 394.80 g. 10 marbles weigh 37.60 g. How many marbles are in the pile?

$$\text{Avg. Mass of 1 Marble} = \frac{37.60\ g}{10\ \text{marbles}} = 3.76\ g\ /\ \text{marble}$$

$$\frac{394.80\ g}{3.76\ g} = 105\ \text{marbles}$$

$$394.80\ \cancel{g} \times \frac{10\ \text{marbles}}{37.60\ \cancel{g}} = 105\ \text{marbles}$$

Atoms, coming in huge numbers, are perfect for "counting by weighing".

- If we know the average mass of the atoms of an element,
- and we know the mass of a sample of that element,

then we know the number of atoms in that sample

Atomic masses ("atomic weight")

"Atomic mass" of an element is an average quantity

- It is a weighted average of isotopic masses
- because elements almost always have more than one isotope with significant abundance

But before we deal with averaging isotopic masses,
let's understand the "atomic mass unit"
(used to be denoted by ***a.m.u***, nowadays just ***u***)

Atomic Mass Unit

Atomic mass unit is meant to approximate the atomic mass number.
But in general it can't be exactly equal to it.

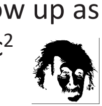
Things would be simple if:

- protons and neutrons had the same exact mass
- and their masses did not depend on the kind of nucleus they are in
- Then, knowing the proton and neutron mass, we could calculate the mass of any isotope
  - ^{13}C would have a mass of exactly 13*u*
  - ^{35}Cl would have a mass of exactly 35*u*

Alas,

- protons and neutrons have slightly different masses,
- and their exact masses depend on the kind of nucleus they are in

  nuclear energies involved in binding these particles are large enough to show up as measurable mass, because $E=mc^2$



So, the mass of an atom, measured in atomic mass units *(u)*,

- instead of simply corresponding to the number of protons and neutrons in a nucleus (i.e. "mass number"),
- needs to be "calibrated" on a particular nucleus
  - ➢ ^{12}C was chosen
- It is <u>almost</u> equal to the mass number, but not quite, for all elements and isotopes, except the calibration isotope ^{12}C, whose mass is <u>defined</u> to be 12*u*

- So,
- ^{12}C is the standard for atomic mass, with a mass of exactly 12 atomic mass units (u).
- The masses of all other atoms are measured relative to this standard.

- So, if $^{\mathbf{48}}$**Ti** is measured to be 3.9957 times heavier than ^{12}C,

➢ then its atomic mass is 3.9957x12 = **47.948*u***

Atomic Mass

Elements occur in nature as mixtures of isotopes

Atomic mass of an <u>element</u>

(as opposed to an isotope)

is a weighted average of isotopic masses

Atomic Mass

For example, for Carbon:

% Abundance	Isotope
98.89%	^{12}C
1.11%	^{13}C

Simply "atomic mass" for an element

<u>Average Atomic Mass for Carbon:</u>

98.89% of 12 u + 1.11% of 13.0034 u

Exactly equal to mass number (12)

not exactly 13

$(0.9889)(12\text{ u}) + (0.0111)(13.0034\text{ u}) =$ **12.01 u**

Even though natural carbon does not contain even a single atom with mass 12.01, for stoichiometric purposes, we can consider carbon to be composed of only one type of atom with a mass of 12.01 (like our average jellybean)

This enables us to count atoms of natural carbon by weighing a sample of carbon.

Practice

An element consists of 62.60% of an isotope with mass 186.956 u and 37.40% of an isotope with mass 184.953 u. Calculate the average atomic mass and identify the element.

Average Atomic Mass =

$(0.6260)(186.956\text{ u}) + (0.3740)(184.953\text{ u}) = 186.2\text{ u}$

⇩

Rhenium (Re)

We can identify an element by its average atomic mass (the "atomic mass" reported in the periodic table)

It's not the same as identifying the element from the isotopic mass (which we can't)

Practice

Indium has atomic number 49 and atomic mass 114.8 u. Naturally occurring indium contains a mixture of indium-112 and indium-115, respectively. What is the approximate ratio of the indium-112 abundance to that of the indium-115?

Remember: <u>**Isotopic mass numbers**</u> can be used to *approximate* <u>**isotopic masses**</u>.

a) 7:93
b) 25:75
c) 50:50
d) 75:25
e) 93:7

Concept question

If a sample of zinc (Zn) and a sample of aluminum (Al) contain the same number of atoms, which of the following claims is true?

Zn: 65.38 a.m.u.
Al: 26.98 a.m.u.

a) The mass of Zn sample is more than twice that of the Al sample.
b) The mass of Zn sample is more than that of the Al sample, but it is less than twice as much.
c) The mass of Al sample is more than twice as the mass of the Zn sample.
d) The mass of Al sample is more than that of the Zn sample, but it is less than twice as much.
e) The two samples have equal masses.

The concept of “mole”

In chemistry it’s the count of atoms that matter.

2 hydrogen atoms combined with 1 oxygen atom form a water molecule.

It’s not about their masses per se.

We need a concept that keeps track of the number of atoms (or other entities):

1 mole = $6.02214076 \times 10^{23}$ entities

Avogadro’s Number
(defined to be exact in 2019)

Avogadro’s number is now defined exactly as $6.02214076 \times 10^{23}$, but is usually used with 3 or 4 significant figures:

6.022×10^{23} entities/mole

- “elementary entities”, or “characteristic units”
- Not just atoms or molecules
- Can be atoms, ions, molecules, formula units, electrons, protons, neutrons, photons, etc.

The unit “mole” represents a count.
Just like “dozen” represents a count.

So, in principle, we can use “mole” to count things other than atoms or molecules:

1 mole of marbles, that is 6.022×10^{23} of them, can cover the surface of the Earth to a depth of 50 miles

If you had 1 mole of dollars, you could spend 1 billion dollars every second and you wouldn’t run out of money for 19 million years

But why 6.022 x 10^{23} particles per mole?

Why not a simpler, smaller number?

We need it to be of the order of 10^{23} because atoms are extremely light, and it takes that many of them to have the kind of masses we normally deal with (i.e. human-scale quantities)

Why 6.022…, and not 1?

It allows us to calculate the mass of 1 mole (molar mass) directly from atomic masses. We use the same numbers but use grams instead of a.m.u!

1 carbon-12 atom has a mass of **12 a.m.u.**

6.022 x 10^{23} carbon-12 atoms (i.e. 1 mole of ^{12}C) have a mass of **12 grams**

The atomic mass of iron (Fe) is **55.845 a.m.u**

(the average mass of iron atoms is 55.845 a.m.u.)

6.022 x 10^{23} iron atoms (i.e. 1 mole of iron) have a mass of **55.845 grams**

The symbol for “mole” is “mol”

- Not much shorter than “mole”
- But it allows us to use the singular form just as with the symbols for meter or gram.

1.5 mole or 1.5 moles?
0.75 mole or moles?

We just say:
1.5 mol
0.75 mol

Practice

Calculate the number of iron atoms in a 4.48 mol sample of iron.

Practice

Which of the following is closest to the average mass of one atom of copper?

a) 63.55 g
b) 52.00 g
c) 58.93 g
d) 65.38 g
e) 1.055×10^{-22} g

Practice

Which of the following 100.0-g samples contains the greatest number of atoms?

a) Magnesium b) Zinc c) Silver d) Calcium
e) Same for all

What is the "characteristic entity" of Carbon?
A Carbon **atom**

What is the "characteristic entity" of Oxygen gas?
An O_2 **molecule**

What is the "characteristic entity" of Calcium Chloride?
A $CaCl_2$ **formula unit**

Remember, ionic compounds don't have molecules. Formula unit is the "pretend molecule" that contains the smallest number of ions in the right proportions.

How many C atoms in 1 mole of Carbon?

How many O_2 molecules in 1 mole of Oxygen gas?

How many O <u>atoms</u> in 1 mole of Oxygen gas?

How many formula units in 1 mole of $CaCl_2$?

How many Cl atoms in 1 mole of $CaCl_2$?

What is the mass of 1 mole of Carbon?

What is the mass of 1 mole of Oxygen gas?

What is the mass of 1 mole of $CaCl_2$?

Practice

Calculate the number of copper atoms in a 63.55 g sample of copper.

Practice

Rank the following according to number of atoms (greatest to least):

a) 107.9 g of silver
b) 70.0 g of zinc
c) 21.0 g of magnesium

The mass of one molecule (**molecular mass**) is the sum of the masses of all the atoms in the molecule.

The mass of one formula unit (**formula mass**) is the sum of the masses of all the atoms in the molecule.

Multiply the atomic mass of each atom by its count in the formula

Molecular Mass of H_2O $= (2 \times \overset{H}{1.008}\ u) + (1 \times \overset{O}{16.00}\ u) = 18.02\ u$

Formula Mass of $Ba(NO_3)_2$ $= (1 \times \overset{Ba}{137.33}\ u) + (2 \times \overset{N}{14.01}\ u) + (6 \times \overset{O}{16.00}\ u)$
$= 261.35\ u$

Molar mass of a compound has the same numerical value, but with units of grams instead of atomic mass units.

We can simply sum up the molar masses of each atom in the formula.

Molar Mass of H_2O $= (2 \times \overset{H}{1.008}\ g) + (1 \times \overset{O}{16.00}\ g) = 18.02\ \frac{g}{mol}$

Molar Mass of $Ba(NO_3)_2$
$= (1 \times \overset{Ba}{137.33}\ g) + (2 \times \overset{N}{14.01}\ g) + (6 \times \overset{O}{16.00}\ g)$
$= 261.35$ g/mol

Make sure you distinguish between molar mass of **atoms of an element** and molar mass of the **molecules it might naturally exist as**.

Molar mass of nitrogen (N atoms) = 14.01 g/mol
Molar mass of Nitrogen gas (**N_2**) = 28.02 g/mol

Molar mass of oxygen (O atoms) = 16.00 g/mol
Molar mass of Oxygen gas (**O_2**) = 32.00 g/mol

It's important to remember the distinction between moles of the atoms of an element and the moles of molecules of the element as it exists in nature.

For example, when we consider how many moles of oxygen exists in a certain amount of a compound, we will be thinking of atoms of oxygen, not molecules of oxygen.

Practice

For which of the following compounds does 1.00 g represent 2.27×10^{-2} mol?

a) H_2O
b) CO_2
c) NH_3
d) C_2H_6

Practice

How many moles of oxygen is contained in 2.0 mol CO_2?

This is simple enough to think in terms of proportions:

1 mol CO_2 contains 2 mol O

2.0 mol CO_2 contains $\frac{2.0}{1}$ (2) = 4.0 mol O

But we really should start thinking in terms of dimensional analysis, for when things get complicated.

Using dimensional analysis:

$$2.0\ \cancel{\text{mol CO}_2} \times \frac{2\text{ mol O}}{1\ \cancel{\text{mol CO}_2}} = 4.0\text{ mol O}$$

Practice

How many moles of hydrogen is contained in 1.5 mol NH_3?

Again, in terms of proportions:

1 mol NH_3 contains 3 mol H

1.5 mol NH_3 contains $\frac{1.5}{1}$ (3) = 4.5 mol H

Using dimensional analysis:

$$1.5\ \cancel{\text{mol NH}_3} \times \frac{3\text{ mol H}}{1\ \cancel{\text{mol NH}_3}} = 4.5\text{ mol H}$$

Practice

The mass of 0.820 mol of a substance composed of diatomic molecules is 131 g. Identify the molecule.

a) F_2
b) Cl_2
c) Br_2
d) I_2

Practice

Consider separate 100.0 gram samples of each of the following:

H_2O, N_2O, $C_3H_6O_2$, CO_2

Rank them from greatest to least number of oxygen atoms in the sample.

Percent Composition of Compounds

Mass percent of an element:

$$\text{mass \%} = \frac{\text{mass of element in compound}}{\text{mass of compound}} \times 100\%$$

Mass % is an intensive property

It doesn't care about sample mass

We can choose a convenient sample mass:

Molar mass if we know the formula

For iron in iron(III) oxide, (Fe_2O_3):

$$\text{mass \%} = \frac{\overbrace{2(55.85\text{ g})}^{\text{Mass of Fe in one mol of Fe}_2\text{O}_3}}{\underbrace{2(55.85\text{ g}) + 3(16.00\text{ g})}_{\text{Mass of one mol of Fe}_2\text{O}_3}} \times 100 = 69.94\%$$

Practice

Consider separate 100.0 gram samples of each:

H_2O, N_2O, $C_3H_6O_2$, CO_2

Rank them from highest to lowest percent oxygen by mass.

The ranking is the same as for number of oxygen atoms per 100 grams

more oxygen atoms ➔ more oxygen mass

Molecular and Empirical Formulas

Molecular formula

Actual formula of the compound

for example, C_6H_6

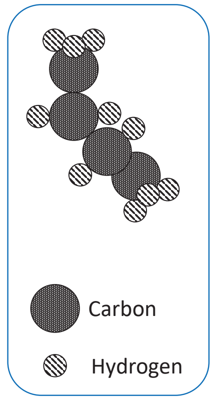
Empirical formula

The number of atoms (their subscripts) are the smallest set of integers possible, in the same ratios as in the molecular formula

For $C_6H_{12}O_6$, the empirical formula is CH_2O

For C_6H_6 , the empirical formula is CH

What is the empirical formula of the compound whose molecule looks as follows?



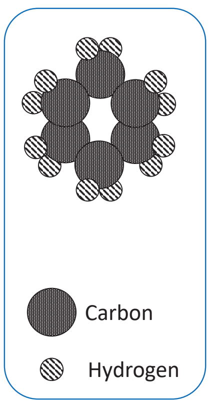
Molecular formula: C_4H_{10}

$\downarrow \div 2$

Empirical formula: C_2H_5

Subscripts 2 and 5 can't be simplified further

What is the empirical formula of the compound whose molecule looks as follows?



Molecular formula: C_6H_{12}

$\downarrow \div 6$

Empirical formula: CH_2

Subscripts (implied) 1 and 2 can't be simplified further

Finding molecular formula, given the molar mass of the compound and its empirical formula

$$\mathbf{n} = \frac{\text{Molar mass of molecular formula}}{\text{“Molar mass” of empirical formula}}$$

Number of atoms in the empirical formula is smaller by the factor **n**

Number of atoms in the molecular formula is greater by the factor **n**

$\text{Empirical formula} \xrightarrow{\text{x } \mathbf{n}} \text{Molecular formula}$

$\text{Molecular formula} \xrightarrow{\div \mathbf{n}} \text{Empirical formula}$

Suppose we know the following:

- The empirical formula is CH
- The molar mass of the compound is 78 g/mol

We can find the molecular formula using the ratio of molar mass to that of the empirical formula (which is 13 g/mol)

Molar mass of molecular formula C_6H_6 = 78 g/mol

“Molar mass” of empirical formula CH = 13 g/mol

n = 78 / 13 = **6**

$CH \xRightarrow{\text{x } 6} C_6H_6$

$C_6H_6 \xRightarrow{\div 6} CH$

Of course we are not always given the empirical formula

- We can find the empirical formula from elemental percent mass compositions
  - ➢ Mass % of each element making up the compound
- Even if we don't know the molar mass

Finding the **empirical formula** from mass % of elements
-- If we don't know the molar mass

1. Take (exactly) 100g sample (just a convenient number; see next step)
2. Then the mass of each element is equal to its percentage
3. Convert each element's mass to moles of the element
   -- will be "ugly" non-integer values
4. Divide each mole amount by the smallest mole amount
5. If a result is close to an integer (e.g. 1.97=2, 1.02=1, etc.), round off to nearest integer
6. If a result ends with a fraction that resembles ½, ⅓, ¼ or their multiples (e.g 1.75, 2.49, 1.33, 1.67), multiply all results by the corresponding denominator
   - ➢ e.g. multiply each by 3 if one of the results is 1.67 since 0.67 is a multiple (double) of ⅓
7. Repeat for all fractions (if you multiply each by 4 because of a .25 or .75, do not multiply by 2 because of a .5)
8. The integers obtained are the subscripts in the empirical formula

Practice

The composition of adipic acid is 49.3% C, 6.9% H, and 43.8% O (by mass). Find its empirical formula.

We consider a 100-g sample of the compound.

Mass percentages equal masses in that case.

$$\text{C:}\quad 49.3\text{ g} \times \frac{1\text{ mol}}{12.01\text{ g}} = 4.10\text{ mol} \xrightarrow{\div 2.74} 1.5 \xrightarrow{\times 2} 3$$

$$\text{H:}\quad 6.9\text{ g} \times \frac{1\text{ mol}}{1.01\text{ g}} = 6.83\text{ mol} \xrightarrow{\div 2.74} 2.5 \xrightarrow{\times 2} 5$$

$$\text{O:}\quad 43.8\text{ g} \times \frac{1\text{ mol}}{16.0\text{ g}} = 2.74\text{ mol} \xrightarrow{\div 2.74} 1 \xrightarrow{\times 2} 2$$

Smallest mol

Need doubling to become integers

$C_3H_5O_2$

Practice

Using the empirical formula ($C_3H_5O_2$) and the molar mass of adipic acid (146 g/mol), find the molecular formula.

"molar mass" of empirical formula $C_3H_5O_2$ = 73 g/mol

n = 146 / 73 = **2**

$$C_3H_5O_2 \xrightarrow{\times 2} C_6H_{10}O_4$$

Alternative (better?) method to find molecular formula

We still need molar mass, but don't need the empirical formula

We can use the elemental % mass composition directly on the molar mass of the compound to find the mass (and then moles) of each element in one mole of the compound

Number of moles of an element in one mole of the compound is equal to the number of atoms of the element in one molecule (i.e. the subscript in the molecular formula)

We bypass the potentially cumbersome process of finding the empirical formula first

Molar mass of the compound, Mass % of element → Mass of element in 1 mol of the compound → Moles of element in 1 mol of the compound = Subscripts in molecular formula

Practice

The composition of adipic acid is 49.3% C, 6.9% H, and 43.8% O (by mass), and has a molar mass of 146 g/mol. Find the *molecular formula without finding the empirical formula first.*

We consider the mass of 1 mol of the compound: 146 g

We then calculate the mass and moles of each element

Moles of element in 1 mol of compound = Subscript in formula

$$\text{C:}\quad (0.493)(146\text{ g}) = 72.0\text{ g} \times \frac{1\text{ mol}}{12.01\text{ g}} = 6\text{ mol}$$

$$\text{H:}\quad (0.069)(146\text{ g}) = 10.1\text{ g} \times \frac{1\text{ mol}}{1.01\text{ g}} = 10\text{ mol}$$

$$\text{O:}\quad (0.438)(146\text{ g}) = 64.0\text{ g} \times \frac{1\text{ mol}}{16.0\text{ g}} = 4\text{ mol}$$

$C_6H_{10}O_4$

Given molar mass and % mass compositions, we can find the empirical formula by continuing the alternative method:

Find molecular formula first

Simplify it to the smallest integer subscripts

- ➢ By dividing the subscripts in the molecular formula by their "greatest common factor"

- In practice it amounts to dividing them by small integers like 2 or 3 and stop when doing so would yield fractional numbers

For example:

Given the molecular formula of $C_6H_{10}O_4$

Divide by 2

Empirical formula: $C_3H_5O_2$

By the way:

Remember, ionic compounds don’t have molecules.

The formula for an ionic compound already has the simplest ratios of the ions.

$NaCl$ **not** Na_2Cl_2

not Na_3Cl_3

The chemical formula of an ionic compound is typically the empirical formula.

Typically? 🤔

Sometimes the formula of an ionic compound is not its empirical formula.

If one or both of the ions are polyatomic, the simplest ratio of ions might not correspond to the empirical formula.

$Na_2C_2O_4$ is the formula for sodium oxalate and it is different from its empirical formula $NaCO_2$

The formula for compounds of mercury (I) ion, Hg_2^{2+}, must contain Hg in pairs:

Hg_2Cl_2 and not $HgCl$

$(Hg_2)_3(PO_4)_2$ and not Hg_3PO_4

So, the formula of an ionic compound may still be a multiple of its empirical formula, with the right polyatomic ion, with the right charge, combined with the right ion of the opposite charge.

But we generally avoid dealing with ionic compounds when it comes to “molecular formula” versus empirical formula, since they don’t have actual molecules.

The empirical formula of styrene is CH; its molar mass is 104.1 g/mol. What is the molecular formula of styrene?

a) C_2H_4
b) C_8H_8
c) $C_{10}H_{10}$
d) C_6H_6

Chemical Equations

<u>Description of a reaction:</u>

1 mole of ethanol reacts with 3 moles of oxygen to produce 2 moles of carbon dioxide and 3 moles of water.

or …

1 molecule of ethanol reacts with 3 **<u>molecules</u>** of oxygen to produce 2 **<u>molecules</u>** of carbon dioxide and 3 **<u>molecules</u>** of water

<u>Representation of a chemical reaction:</u>

A chemical <u>equation</u>

$$\underbrace{C_2H_5OH + 3O_2}_{\text{reactants}} \longrightarrow \underbrace{2CO_2 + 3H_2O}_{\text{products}}$$

	Reactants	Products
	$C_2H_5OH + 3O_2 \longrightarrow$	$2CO_2 + 3H_2O$
C:	(1)(2)=**2**	(2)(1)=**2**
H:	(1)(5)+1=**6**	(3)(2)=**6**
O:	(1)(1)+(3)(2)=**7**	(2)(2)+(3)(1)=**7**

The equation is balanced.

All atoms present in the reactants are accounted for in the products.

Reaction equation can also contain information about the physical state of the reactants and products

State	Symbol
Solid	*(s)*
Liquid	*(l)*
Gas	*(g)*
Dissolved in water	*(aq)*

$$CaCO_3\,(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

- The balanced equation represents an overall **ratio** of reactants and products, **not** what actually happens during a **given** reaction, which can involve **arbitrary** amounts of reactants.
- Use the coefficients in the balanced equation to calculate the amount of each reactant that is used, and the amount of each product that is formed.

Balancing Chemical Equations

1. Determine what reaction is occurring. What are the reactants, the products, and the physical states involved?
2. Write the *unbalanced* equation that summarizes the reaction described in step 1.
3. Balance the equation by inspection. The same number of each type of atom needs to appear on both reactant and product sides. Do NOT change the formulas of any of the reactants or products.
4. If a polyatomic ion (SO_4^{2-}, NO_3^-, etc.), as part of a compound or alone, seems to survive the reaction intact, treating it like an "atom" may simplify balancing significantly.

Practice

Which of the following correctly balances the chemical equation given below? There may be more than one correct balanced equation. If a balanced equation is incorrect, explain why.

$$CaO + C \rightarrow CaC_2 + CO_2$$

I. $CaO_2 + 3C \rightarrow CaC_2 + CO_2$

II. $2CaO + 5C \rightarrow 2CaC_2 + CO_2$

III. $CaO + 2.5C \rightarrow CaC_2 + 0.5CO_2$

IV. $4CaO + 10C \rightarrow 4CaC_2 + 2CO_2$

Balancing chemical equations:

- doesn't need to be an "art form"
- doesn't need to involve "trial and error"
- can be done by applying general rules

A truly general method for more challenging reactions is more complicated than what we will see and use here, but it still would not be a trial-and-error process.

That is a widely repeated misconception

A general method for balancing reactions (involving neutral substances only)

1. Identify those elements that occur in **only one compound** (*not* an element like O_2(g) or Cu(s)) on **each side** of the equation.
   — If more than one element qualifies, select the one that occurs in the compound with the most kinds of elements.
2. Balance the equation in the selected element.
   — In balancing an element, you fix the coefficient of one reactant and one product. Write the coefficient even if it is just 1, so you can easily see which compounds are "done" at any point.
3. Find an element that occurs in **only one compound whose coefficient we haven't found yet**. Repeat until all compounds have coefficients.
4. Balance any substances that are elements.

If you obtain fractional coefficients at any stage, multiply all known coefficients by the denominator of the fraction

Balancing reactions, Step 1

$KMnO_4 + HCl \rightarrow MnCl_2 + KCl + Cl_2 + H_2O$

Find element(s) that occur in one compound on each side:

- K in compound with with Mn, O, Cl ($KMnO_4$, KCl)
- Mn in compound with K, O, Cl ($KMnO_4$, $MnCl_2$)
- O in compound with K, Mn, H ($KMnO_4$, H_2O)
- H in compound with Cl, O (HCl, H_2O)

K, Mn , and O are the best choices to start balancing since they are associated with 3 elements while H is associated with 2.

As we balance each element, formulas will be assigned coefficients. The coefficient marks the formula of a substance as "done".

Balancing reactions, Step 2

$1\,KMnO_4 + HCl \rightarrow MnCl_2 + KCl + Cl_2 + 4\,H_2O$

Let's choose to balance **O** first to demonstrate how we produce the first pair of coefficients:

- To balance the first element, use its subscript in the product as coefficient for the reactant in which it occurs, and
- Use its subscript in the reactant as coefficient for the product in which it occurs
- Note: We explicitly write the coefficient even if it is 1 in order to mark the substance as "done" and distinguish it from those that did not receive a coefficient yet ("coefficientless").

Balancing reactions, Step 3

$1\,KMnO_4 + HCl \rightarrow MnCl_2 + KCl + Cl_2 + 4\,H_2O$

After the first step, we find and balance elements that <u>occur in only one *coefficientless* **compound**</u> (i.e. can't be an elemental substance like Cl_2) in the entire equation.

- K and Mn that occurred in the same compound as O and qualified as the first element to balance are natural candidates for the second step because now $KMnO_4$ has a coefficient, leaving these elements occurring in only one coefficientless compound.
- H also qualifies.
- Cl doesn't qualify because it occurs in multiple compounds, not to mention as an elemental substance (which should be handled last)

Balancing reactions, Step 3 (cont.)

$1\,KMnO_4 + HCl \rightarrow MnCl_2 + 1\,KCl + Cl_2 + 4\,H_2O$

We can choose to balance K, which is pretty trivial here.

Next:

Mn is the obvious choice to balance next, since it qualified to be the first element to balance and was in $KMnO_4$, which gained a coefficient. So now it occurs in only one coefficientless compound, $MnCl_2$.

Balancing reactions, Step 3 (cont.)

$1\,KMnO_4 + HCl \rightarrow 1\,MnCl_2 + 1\,KCl + Cl_2 + 4\,H_2O$

Balancing Mn is again pretty trivial.

Next:

Now H is the only element that occurs in only one coefficientless compound.

Balancing reactions, Step 3 (cont.)

$1\,KMnO_4 + 8\,HCl \rightarrow 1\,MnCl_2 + 1\,KCl + Cl_2 + 4\,H_2O$

We now balance H: $x\,(1) = (4)(2) \Rightarrow x = 8$

Next:

The only element that hasn't been balanced is Cl

Balancing reactions, Step 5

$$1\,KMnO_4 + 8\,HCl \rightarrow 1\,MnCl_2 + 1\,KCl + \frac{5}{2}Cl_2 + 4\,H_2O$$

We now balance Cl: $(8)(1) = (1)(2) + (1)(1) + x(2) \Rightarrow x = 5/2$

The equation is now balanced, but we normally want integer coefficients

Balancing reactions, Step 6

$$1\,KMnO_4 + 8\,HCl \rightarrow 1\,MnCl_2 + 1\,KCl + \frac{5}{2}Cl_2 + 4\,H_2O$$

We now multiply all coefficients by 2 (i.e. the denominator of 5/2)

$$2\,KMnO_4 + 16HCl \rightarrow 2MnCl_2 + 2\,KCl + 5\,Cl_2 + 8\,H_2O$$

The equation is now balanced with the smallest integer coefficients

Balancing an equation might need a bit of math in addition to the rules

We start balancing the following example in the usual way

$$Cu + H_2SO_4 + \rightarrow CuSO_4 + SO_2 + H_2O$$

Find element(s) that occur in one **compound** on each side:

H is the only element that qualifies

Balance **H**

$$Cu + 1\,H_2SO_4 \rightarrow CuSO_4 + SO_2 + 1\,H_2O$$

Again, note: We explicitly write the coefficient even if it is 1 in order to mark the substance as "done" and distinguish it from those that did not receive a coefficient yet ("coefficientless").

$$Cu + 1\,H_2SO_4 \rightarrow x\,CuSO_4 + y\,SO_2 + 1\,H_2O$$

After the first step, we find and balance elements that occur in only one *coefficientless* **compound**

- No elements occur in only one coefficientless compound
- We assign x, y, etc. as coefficients to the remaining compounds
- Then solve for the unknowns x, y, etc. by setting up the balancing equations for the remaining elements occurring only in compounds

Balance S: $(1)(1) = x\,(1) + y\,(1) \Rightarrow x = 1 - y$

Balance O: $(1)(4) = x\,(4) + y\,(2) + (1)(1) \Rightarrow 4 = 4x + 2y + 1$

$\Rightarrow 4 = \boxed{4-4y} + 2y + 1 \Rightarrow 4 = 5 - 2y \Rightarrow y = ½ \Rightarrow x = 1 - ½ = ½$

Substituted for x

$$Cu + 1\,H_2SO_4 \rightarrow ½\,CuSO_4 + ½\,SO_2 + 1\,H_2O$$

Get rid of fractional coefficients by multiplying all **known** coefficients by 2 (the denominator of 2)

$$Cu + 2\,H_2SO_4 \rightarrow 1\,CuSO_4 + 1\,SO_2 + 2\,H_2O$$

$$Cu + 2\,H_2SO_4 \rightarrow 1\,CuSO_4 + 1\,SO_2 + 2\,H_2O$$

Now that we are done with balancing elements that occur in compounds only, we balance the elemental substance

$$x\,Cu + 2\,H_2SO_4 \rightarrow 1\,CuSO_4 + 1\,SO_2 + 2\,H_2O$$

$$1\,Cu + 2\,H_2SO_4 \rightarrow 1\,CuSO_4 + 1\,SO_2 + 2\,H_2O$$

Now the entire equation is balanced.
We normally omit coefficients equal to 1

$$\boxed{Cu + 2\,H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2\,H_2O}$$

Balancing combustion reactions

$$C_cH_hO_o + \ x\, O_2 \rightarrow \ c\, CO_2 + \ \mathbf{h/2}\, H_2O$$

Combustion:

A "fuel" containing C, H, O reacting with O_2 to produce CO_2 and H_2O

- We don't need to use the general rules
- We "follow" and balance the carbon and hydrogen:
  - All the C in CO_2 comes from the C in the fuel
  - All the H in H_2O comes from the H in the fuel
- Oxygen is not so simple, but becomes simple to balance after we balance C and H

  x = [c + (h/2 – o)/2] **but there is no need memorize that**

$$1\, C_2H_6O + \quad O_2 \rightarrow 2CO_2 + 3H_2O$$

We start with one molecule of "fuel" (C_2H_6O here)

Balance carbon and hydrogen first:

- **Number of CO_2 molecules** equals the number of C atoms in the fuel molecule (each CO_2 molecule has one C atom)

  $(1)(2) = x\,(1) \Rightarrow x = 2$

- **Number of H_2O molecules** is half the number of H atoms in the fuel molecule (each H_2O molecule has 2 H atoms)

  $(1)(6) = x\,(2) \Rightarrow x = 3$

- Then balance oxygen

We now balance O:

$$C_2H_6O + \ 3\, O_2 \rightarrow 2\, CO_2 + 3\, H_2O$$

$(1)(1) + x\,(2) = (2)(2) + (3)(1) \Rightarrow x = 3$

Concept question

Which of the following is/are true concerning balanced chemical equations? There may be more than one true statement.

I. The number of molecules is conserved.

II. The coefficients tell you how much of each substance you have.

III. Atoms are neither created nor destroyed.

IV. The coefficients indicate the mass ratios of the substances used.

V. The sum of the coefficients on the reactant side equals the sum of the coefficients on the product side.

Stoichiometric Calculations:
About amounts of reactants and products

Note:

- The number of atoms of each type of element must be the same on both sides of a balanced equation.
- Subscripts must not be changed to balance an equation.
- A balanced equation tells us the ratio of the number of molecules which react and are produced in a chemical reaction.
- Coefficients can be fractions, although they are usually given as smallest possible integers.

Practice

When the equation

$NH_3 + O_2 \rightarrow NO + H_2O$

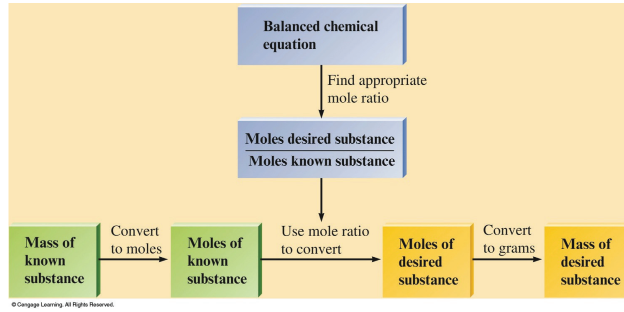
is balanced with the smallest set of integers, the sum of the coefficients is

a) 4
b) 12
c) 14
d) 19
e) 24

Calculating Masses of Reactants and Products in Reactions

1. Balance the equation for the reaction.
2. Convert the known mass of the reactant or product to moles of that substance.
3. Use the balanced equation to set up the appropriate mole ratios.
4. Use the appropriate mole ratios to calculate the number of moles of the desired reactant or product.
   - ➢They are the "conversion factors" between moles of different substances
5. Convert from moles back to grams if required by the problem.

Calculating Masses of Reactants and Products in Reactions



Example

Consider the following reaction:

$$P_4(s) + 5\,O_2(g) \rightarrow 2\,P_2O_5(s)$$

If 6.25 g of phosphorus is burned, what mass of oxygen does it combine with?

$$6.25\ \cancel{g\ P_4} \times \frac{1\ \cancel{mol\ P_4}}{123.88\ \cancel{g\ P_4}} \times \frac{5\ \cancel{mol\ O_2}}{1\ \cancel{mol\ P_4}} \times \frac{32.00\ g\ O_2}{1\ \cancel{mol\ O_2}} = \mathbf{8.07\ g\ O_2}$$

Practice (Part I)

Methane (CH_4) reacts with the oxygen in the air to produce carbon dioxide and water.

Ammonia (NH_3) reacts with the oxygen in the air to produce nitrogen monoxide and water.

Write balanced equations for each of these reactions.

Practice (Part II)

$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$

$4NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$

What mass of ammonia would produce the **<u>same amount of water</u>** as 1.00 g of methane reacting with excess oxygen?

1. Find amount of water produced from 1.00 g of methane

   mass of CH_4 $\xrightarrow{\text{molar mass}}$ moles of CH_4 $\xrightarrow{\text{rxn. coeff.}}$ moles of water

2. Find amount of ammonia needed to produce the amount of water calculated above.

   moles of water $\xrightarrow{\text{rxn. coeff.}}$ moles of NH_3 $\xrightarrow{\text{molar mass}}$ mass of NH_3

Practice (Part II)

$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$

$4NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$

What mass of ammonia would produce the **<u>same amount</u>** of water as 1.00 g of methane reacting with excess oxygen?

$$1.00\ \cancel{g\ CH_4} \times \frac{1\ \cancel{mol\ CH_4}}{16.04\ \cancel{g\ CH_4}} \times \underbrace{\frac{2\ mol\ H_2O}{1\ \cancel{mol\ CH_4}}}_{\boxed{\text{2 mol } H_2O \text{ from 1 mol } CH_4}} = 0.1247\ mol\ H_2O$$

We now calculate the amount of NH_3 needed to produce the same amount of water.
Starting the calculation from the amount of water.

$$0.1247\ \cancel{mol\ H_2O} \times \underbrace{\frac{4\ \cancel{mol\ NH_3}}{6\ \cancel{mol\ H_2O}}}_{\boxed{\text{4 mol } NH_3 \text{ gives 6 mol } H_2O}} \times \frac{17.03\ g\ NH_3}{1\ \cancel{mol\ NH_3}} = \mathbf{1.42\ g\ NH_3}$$

To solve problems:

- You need to connect what's given to what's asked
- Often there is a chain of connections
- You just need to construct that chain
  - ➢You must figure out what piece of information you need for each link in the chain

You need to practice solving many problems

There is no way around it!

Limiting Reactant

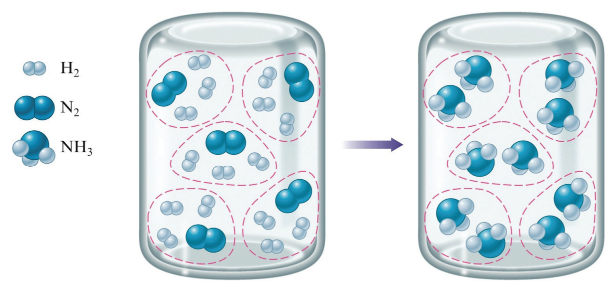
If the reactants are not present in ratios exactly in line with the chemical equation, one of them will be limiting, and the others will automatically be in excess.

Limiting Reactant

- The reactant that runs out first and thus limits the amounts of products that can be formed.
- Other reactants would lead to more product, but they can't because the limiting reactant runs out
- If we calculate the amount of product each reactant would produce if it was completely consumed, limiting reactant would correspond to the least product.
  - **Maximum amount of product the reaction can produce is the amount that can be produced by the limiting reactant**

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

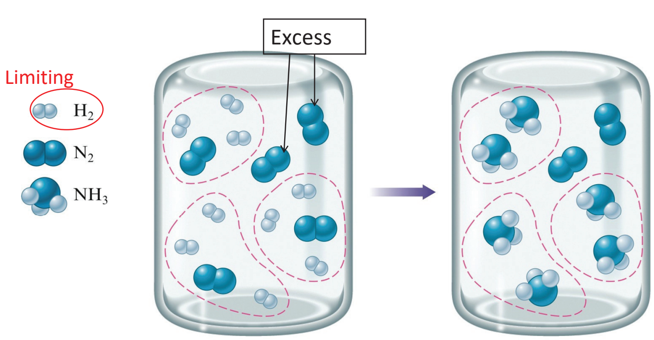
Stoichiometric mixture: No excess or limiting reactants



Before the reaction After the reaction

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

Limiting reactant mixture



Before the reaction After the reaction

Concept question

Which of the following reaction mixtures could produce the greatest amount of product? Each involves the reaction symbolized by the equation:

$$2H_2 + O_2 \rightarrow 2H_2O$$

a) 4 moles of H_2 and 4 moles of O_2

b) 4 moles of H_2 and 6 moles of O_2

c) 4 moles of H_2 and 2 mole of O_2

d) 6 moles of H_2 and 2 moles of O_2

e) They all produce the same amount of product.

Note:

We cannot simply add the total moles of all the reactants to decide which reactant mixture makes the most product.

Amount of product depends on the amount of limiting reactant only

Finding the limiting reactant doesn't actually require calculating the amount of product!

$$aA + bB \rightarrow cC$$

moles of **C** from **A** = (moles of **A**) $\frac{c}{a}$ ← "*a* moles of A gives *c moles of C*"

Remember your basic algebra $x\frac{y}{z} = \frac{x}{z}y$

moles of **C** from **A** = $\frac{\text{(moles of A)}}{a}\, c$

moles of **C** from **B** = $\frac{\text{(moles of B)}}{b}\, c$

The coefficient of the product affects the product amount equally for all reactants

It's the ratio (moles of reactant)/(coefficient of reactant) that determines which reactant would produce the least product

The reactant with the smallest value for the ratio

$$\frac{\text{no. of moles of reactant}}{\text{coefficient of reactant in reaction equation}}$$

is the limiting reactant

When
"Reactants are present in *stoichiometric* amounts"

- The mole amounts of all reactants are in the ratios dictated by the coefficients in the balanced reaction equation
- All reactants have the same ratio $\frac{\text{moles available}}{\text{coefficient in equation}}$
- No limiting reactant
- Another way to look at it: all reactants are limiting

If the reaction equation is

2 A + 3B → 2C

and if we have

	A		B	
2 moles of A, 3 moles of B	$\frac{2}{2}=1$	=	$\frac{3}{3}=1$	A and B in stoichiometric amounts
3 moles of A, 4.5 moles of B	$\frac{3}{2}=1.5$	=	$\frac{4.5}{3}=1.5$	
20 moles of A, 30 moles of B	$\frac{20}{2}=10$	=	$\frac{30}{3}=10$	

moles / coefficient

But if we have

	A		B	
2 moles of A, 2 moles of B	$\frac{2}{2}=1$	>	$\frac{2}{3}=0.67$	B is limiting
2 moles of A, 3.5 moles of B	$\frac{2}{2}=1$	<	$\frac{3.5}{3}=1.17$	A is limiting

Concept question

The limiting reactant in a reaction

a) has the smallest coefficient in a balanced equation.
b) is the reactant for which you have the fewest number of moles.
c) has the lowest ratio of $\frac{\text{moles available}}{\text{coefficient in balanced equation}}$
d) none of these
e) all of these

Practice

You react 10.0 g of **A** with 10.0 g of **B** according to the reaction equation

$$A + 3B \longrightarrow 2C + D$$

What mass of product **C** will be produced given that the molar masses of A, B, and C are 10.0 g/mol, 20.0 g/mol, and 30.0 g/mol, respectively?

Steps:

1. Convert reactant masses to moles
2. Find limiting reactant
3. If we know the molar mass of C, we can:
   Find moles of product formed by the limiting reactant
   Convert moles of product to mass of product

Practice (cont.)

$$\underset{10.0\text{ g}}{\mathbf{A}} + \underset{10.0\text{ g}}{\mathbf{3B}} \longrightarrow \underset{?\text{ g}}{\mathbf{2C}} + \mathbf{D}$$

m.m.(A) = 10.0 g
m.m.(B) = 20.0 g

First, convert reactant masses to moles
Then find the limiting reactant

Divide moles by coefficient

A: $10.0\ \cancel{\text{g A}} \times \dfrac{1\ \text{mol A}}{10.0\ \cancel{\text{g A}}} = 1.00\ \text{mol A} \rightarrow \dfrac{1.00}{1} = 1.00$

B: $10.0\ \cancel{\text{g B}} \times \dfrac{1\ \text{mol B}}{20.0\ \cancel{\text{g B}}} = 0.500\ \text{mol B} \rightarrow \dfrac{0.500}{3} = 0.167$ Smaller

→ B is limiting

Practice (cont.)

$$\underset{10.0\text{ g}}{\mathbf{A}} + \underset{10.0\text{ g}}{\mathbf{3B}} \longrightarrow \underset{?\text{ g}}{\mathbf{2C}} + \mathbf{D}$$

m.m.(A) = 10.0 g
m.m.(B) = 20.0 g
m.m.(C) = 30.0 g

- We can calculate the moles of C produced, using the coefficients in the reaction equation
- We can continue to calculate the mass of C if we know its molar mass

Moles of the limiting reactant

$$0.500\ \text{mol B} \times \frac{2\ \text{mol C}}{3\ \text{mol B}} \times \frac{30.0\ \text{g C}}{1\ \text{mol C}} = 10.0\ \text{g C produced}$$

according to the reaction equation

Practice (cont.)

What if we wanted to know how much is left of each reactant after the reaction is complete?

	A	**+ 3B**	**→ 2C**	**+ D**
Before reaction:	10.0 g	10.0 g	0 g	
After reaction:	? g	0 g	10.0 g	

limiting reactant is consumed completely

To find the amount of remaining excess reactant, we first find the amount consumed, again based on the amount of limiting reactant

$$0.500\ \text{mol B} \times \frac{1\ \text{mol A}}{3\ \text{mol B}} \times \frac{10.0\ \text{g A}}{1\ \text{mol A}} = 1.67\ \text{g of A is consumed}$$

remaining A = (Initial A) − (A consumed)
= 10.0 g − 1.67 g = 8.33 g of A remaining

Percent Yield

An important indicator of the efficiency of a particular laboratory or industrial reaction.

$$\text{percent yield} = \frac{\text{Actual amount of product}}{\text{Ideal amount of product}} \times 100\%$$

Ideal (theoretical) yield:

The amount of product calculated according to the desired chemical equation and the limiting reactant amount.

For calculations, we typically work with the fractional (out of 1) form of percent (e.g. 0.93 instead of 93%).

$$\text{Fractional yield} = \frac{\text{Actual amount of product}}{\text{Ideal amount of product}}$$

Algebraic rearrangement gives:

$$\text{Ideal amount of product} = \frac{\text{Actual amount of product}}{\text{Fractional yield}}$$

$$\left[\begin{array}{c}\text{Actual amount}\\ \text{of product}\end{array}\right] = \left[\text{Fractional yield}\right]\left[\begin{array}{c}\text{Ideal amount}\\ \text{of product}\end{array}\right]$$

Why would we get less than 100% yield?

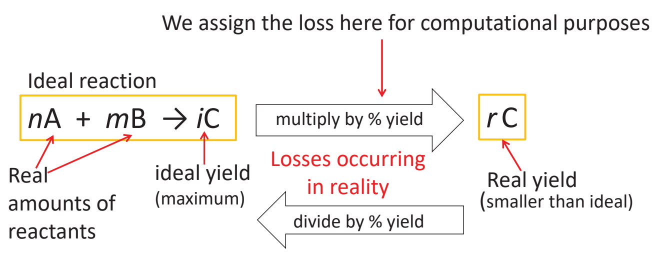
Some possible reasons:

- Reaction may not go to completion in the time allowed
- Reactants may undergo different reactions, producing other, unwanted products
- Some product may be lost while being recovered from the reaction mixture

Remember:

- A reaction equation can only be used to relate “ideal” quantities of products and reactants
- The product amount calculated from the reaction equation alone is the “ideal” amount. We then calculate the actual yield using the % yield
- An “actual” yield needs to be converted to the “ideal” yield (using the % yield) before we can work backward to calculate the required reactant amount

- The coefficients in a reaction equation are “ideal”
- They relate moles of reactants and products in an “ideal” reaction



To find **reactant** amount(s) needed:

- go from real to ideal yield first
- use the ratios in the ideal reaction as usual

Practice

For the following reaction:

$$P_4(s) + 6F_2(g) \longrightarrow 4PF_3(g)$$

What mass of P_4 is needed to produce 85.0 g of PF_3 if the reaction has a 64.9% yield?

Steps:

1. $P_4(s)$ is implied to be the limiting reactant
2. 85.0 g is the “actual amount of product” (actual yield)
3. We know the % yield, so we can find the “ideal” yield
4. Ideal yield comes from the limiting reactant amount and reaction equation
5. Work back to the amount of $P_4(s)$

Practice (cont.)

$$P_4(s) + 6\,F_2(g) \longrightarrow 4\,PF_3(g)$$

130.97 g ← ÷0.649 ← Real yield 85.0 g @ 64.9% yield

Ideal yield *(Can be used to calculate the reactant amounts)*

Ideal yield *Calculated from actual yield*

$$130.97\text{ g } PF_3 \times \frac{1\text{ mol } PF_3}{87.97\text{ g } PF_3} \times \frac{1\text{ mol } P_4}{4\text{ mol } PF_3} \times \frac{123.88\text{ g } P_4}{1\text{ mol } P_4} = 46.1\text{ g of } P_4\text{ needed}$$

For the actual yield