

Why Take Chemistry

- The quantitative reasoning & problem solving skills you learn is valuable in *any* profession or discipline.
- It provides a quantitative intuitive understanding of the molecular nature of the physical world which is an essential basis for further study in all fields of science & technology.

What in the world isn't chemistry?

- The fundamental concepts of mass/material conservation and equilibrium balance learned here are key to any real understanding of the physical world around us.

The molecular viewpoint simplifies/rationalizes otherwise disparate collections of facts: **e.g.**, *how much heat energy is required to raise the temperature of a fixed amount of metal by 1°C?*

metal	Li	Mg	Al	Fe	Ag	Pb	Hg	...
specific heat [J/(g K)]	3.85	1.05	0.88	0.46	0.23	0.13	0.14	...
heat capacity [J/(mol K)]	26.4	25.5	23.8	25.5	25.1	26.8	27.6	...

Recall Basic Assumptions of Atomic Theory

1. A given amount of any pure chemical element consists of an integer number of indestructible atoms which cannot be created or destroyed.
2. All atoms of a given chemical element are identical.
3. All distinct chemical substances are formed by combining atoms of different kinds in precise integer ratios which are a defining property of that substance.
4. A “molecule” is the smallest unit of a given chemical substance which can exist and still retain the fundamental physical characteristics defining that substance.
5. Equal volumes of gases at the same temperature and pressure contain the same numbers of molecules, independent of their chemical identity.

Of course (as with virtually any scientific theory), these assumptions require some qualifications or corrections! In particular:

1. Atoms are not really “indestructible”.

High energy nuclear reactions can occur to create new atoms or split atoms into smaller atomic fragments. Fortunately, however, this does not occur in the context of ‘normal’ chemistry.

2. Atoms of a given species are not all identical, since they usually can exist in more than one stable isotopic form.

Each atomic species is formally identified with the label $\frac{A}{Z}(\text{name})$, as in ${}_{32}^{74}\text{Ge}$ or ${}_{17}^{37}\text{Cl}$. However, since both the name and the chemical properties of a given type of atom are defined by the value of Z , it is redundant to use both, so we normally use the label ${}^A(\text{name})$, as in ${}^{74}\text{Ge}$ or ${}^{18}\text{O}$ or ${}^{37}\text{Cl}$

However, the relative abundances of different isotopic forms of different elements are fairly uniform (in terrestrial samples), and the conventional atomic weight (or more correctly, atomic mass), for each element is the average of the isotopic masses, weighted by their relative abundance.

e.g., normal atomic chlorine is 75.770% ${}^{35}\text{Cl}$ (mass 34.968 852 u) and 24.230% ${}^{37}\text{Cl}$ (mass 36.965 902 u). Hence, the atomic weight of chlorine is:

$$0.75770 \times 34.968\,852 + 0.24230 \times 36.965\,902 = 35.452\,737\,22 = \mathbf{35.453\,u}$$

Exercise 1. Germanium has five stable isotopic forms with mass numbers $A = 70, 72, 73, 74$ & 76 . Look up the isotope masses and abundances (see e.g., the *Handbook of Chemistry and Physics*) and calculate the “atomic weight” of germanium.

4. Many chemical substances do not exist as independent molecules, but as extended arrays which may be
- covalent
 - ionic
5. This ‘ideal gas’ composition ‘law’ is an approximation which neglects the fact that molecules have finite (not negligible!) size, and that intermolecular forces cause them to attract and/or repel one another.

ASIDE

Uncertainties in Arithmetic: Significant Digits

Determining a property of physical interest from an experimental measurement often involves calculations. It is common sense that a result obtained in this way can be no more precise than the least-precise piece of information which went into the calculation. This is where rules for *significant digits* come in. They provide a zeroth order estimate of the propagation of uncertainty (or error) in a calculation. While better methods will be discussed later, it is appropriate to review the basic rules governing significant digits in arithmetic.

Rule 1. First of all – what do we mean by ‘significant digits’?

In a given recorded number:

- all non-zero digits and any zeros surrounded by non-zero digits are significant
e.g., 1.235, 1.035 and 1.005 all have four significant digits
- all zeros recorded which lie to the right of the last non-zero digit are significant
e.g., 1.2350 and 1200.0 both have five significant digits
- no zeros appearing before the first non-zero digit count as significant digits
e.g., 0.00012350 and 1235.3 both have five significant digits
- it is a common convention that in a number with no decimal point showing, trailing zeros do *not* count as significant digits, but for the same number, trailing zeros appearing before a decimal point *do* count as significant digits
e.g., 123000 has three significant digits, but 123000. has six and 123000.00 has eight
- exact conversion factors have an infinite number of significant digits, independent of whether or not a decimal point is shown
e.g., the factor 100 cm/m and the numbers denoted as π or e have an infinite number of significant digits

Rule 2. When adding or subtracting two numbers, the number of decimal places in the answer is equal to the number of decimal places in the one with the fewest significant digits after the decimal.

e.g.,

Rule 3. In multiplication or division of two numbers, the number of significant digits in the answer is the smaller of the numbers of significant digits in the two numbers.

e.g.,

Rule 4. When rounding off, round up or down to whichever value is closest.

Rule 5. In practical work, input known physical constants to *at least* two more significant digits than are associated with measured numbers, and retain intermediate results to at least that precision (or better yet, to the full precision of your calculator!), and perform appropriate rounding only when reporting the final answer(s).

Note, that while the above rules are a useful first zeroth order treatment, but they do not take account of the accumulation of uncertainty in repetitive additions or multiplications. For that, more quantitative ‘propagation-of-errors’ techniques are required.

The “Mole” is a Name for a (really big!!) Number

Just as we use the names $\left\{ \begin{array}{l} \text{a couple} \\ \text{a dozen} \\ \text{a score} \\ \text{a thousand} \\ \text{a million} \end{array} \right\}$ for the numbers $\left\{ \right\}$

so we use the name mole for the number of objects which is called Avogadro’s number $6.022\,141\,5(10) \times 10^{23}$. This is defined as the number of atoms in exactly 12.0 g of ^{12}C . However, like the name for any other number (dozen, thousand) it *has no units*, so when we use it, we *must always* specify the number of moles of $\{\text{some specific item/substance}\}$.

Where did this odd number ($6.022\,141\,5(10) \times 10^{23}$) and the mass unit amu (or u) come from?

Useful Prefixes for big/small amounts.

We assume that you *know* them!!

Common examples:

2.3 mmol =

7.73 μmol =

0.0188 pmol =

TABLE 1.2 SI Prefixes	
Multiple	Prefix
10^{18}	exa (E)
10^{15}	peta (P)
10^{12}	tera (T)
10^9	giga (G)
10^6	mega (M)
10^3	kilo (k)
10^2	hecto (h)
10	deca (da)
10^{-1}	deci (d)
10^{-2}	centi (c)
10^{-3}	milli (m)
10^{-6}	micro (μ) ^a
10^{-9}	nano (n)
10^{-12}	pico (p)
10^{-15}	femto (f)
10^{-18}	atto (a)

^aThe Greek letter μ (pronounced “mew”).

Stoichiometry & Composition: Empirical vs. Molecular Formula

Analytic chemical methods can determine the % composition by weight of the different types of elements forming a particular substance. We can use this information to determine the “empirical formula” for that substance.

empirical formula:

molecular formula:

They are *not* the same: e.g., acetylene C_2H_2 (MW 26) and benzene C_6H_6 (MW 78) both have the same ‘empirical formula’: C_1H_1 (formula weight 13)

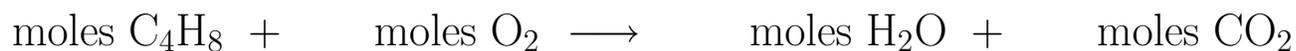
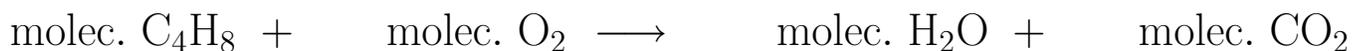
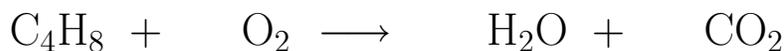
Exercise 2. The artificial sweetener “sorbital” has a % composition by mass of 39.56% carbon (C), 7.74% H and 52.70% O. *What is its empirical formula?*
If another experiment shows that the molecular weight of sorbital is approximately 182 u, *what is its molecular formula?*

Exercise 3. Chloroform is found to be 89.10% chlorine, 0.84% hydrogen and 10.6% carbon by mass. What is its empirical formula?

Stoichiometry & Chemical Reactions

A chemical equation shows how atoms rearrange in a chemical reaction.

- it is a **conservation law** (when properly balanced), as we have exactly the same amounts of each atomic species on each side
- the “stoichiometric coefficients” (the number in front of each molecular formula) indicate the *relative* molar/molecular amounts of the various species, but *have no absolute significance!*



Stoichiometry Problems are concerned with the “bookkeeping” of chemical reactions – relating an amount of one reagent (expressed in some particular units: mass, moles, volume) to that of another. Often very convenient to treat them as *unit conversion* problems – converting an *amount of reaction* from one set of units (amount of one component) to a precisely equivalent amount of another.

How are unit conversion problems solved?

Multiply the *amount*, given in the original units, by one or more factors in each of which (numerator) = (denominator), which allow us to cancel out the original units and express the *same amount of “stuff”, or of reaction*, in the desired units.

Exercise 4: If a car is traveling at a speed of 54.4 miles per hour, *what is its speed in meters per second?*

Exercise 5: For our reaction $\text{C}_4\text{H}_8 + \text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{CO}_2$
how many grams of O₂ are required to consume 5.20 g of C₄H₈?

To solve stoichiometry problems:

1. convert amount of known component to units *moles*
2. use the (usually integer) stoichiometric coefficients of (balanced) chemical equations and/or molecular formula subscripts to relate molar amount of known component to those of other species
3. convert result of step 2 to desired units!

Note the stoichiometric coefficient ratio can differ for the same reagents if the net reactions differ!

e.g., compare



vs.



or compare



vs.



vs.



Exercise 6: How many grams of oxygen are present in 6.21 g of ferric sulphate [iron(III) sulphate] $\text{Fe}_2(\text{SO}_4)_3$?

Other Measures of “Amount of Reaction”

To define the “amount of reaction” for a given chemical process, we need to know the (balanced) chemical reaction equation and the amount of at least one of the reagent or product species. They are often specified using the mass or number of moles of a species. However, one can also use the volume of a component, but to do this ...

If the **volume of a pure liquid or solid component** is given/requested we must also know the *density* of the substance – the conversion factor relating volume to mass.

Exercise 7. Metallic aluminum has a density of 2.70 g/cm³. If a 10.25 cm × 5.50 cm piece of aluminum foil of thickness 0.606 mm is dissolved in excess aqueous HCl according to the reaction $2 \text{Al(s)} + 6 \text{HCl(aq)} \longrightarrow 2 \text{AlCl}_3\text{(aq)} + 3 \text{H}_2\text{(g)}$, *what mass* of H₂(g) is produced?

Ans: {amount of reaction} =

For a pure gas the volume at a given temperature & pressure is uniquely related to the number of moles via the ideal gas law $PV = nRT$. Thus, volume can be related to no. moles of gas under *any* conditions.

At “standard temperature and pressure (STP) [defined as $T = 0^\circ\text{C} = 273.15 \text{ K}$ and $P = 1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ Torr} = 101.325 \text{ kPa} = 1.01325 \text{ bar}$] one mole of *any* gas occupies 22.413 996(39) L (more in Chapt. 6).

Exercise 8. For the reaction $\text{KClO}_3\text{(s)} \longrightarrow \text{KCl(s)} + \text{O}_2\text{(g)}$ how many grams of KClO₃ are required to produce 650 cm³ of O₂(g) at STP?

Ans: {amount of reaction} = {650 cm³ of O₂ at STP} =

For mixtures or solutions we must know *the mole fraction*,
or *the mass % composition*, or *the concentration*: {amount} per {unit volume}.

Exercise 9. One useful alloy of aluminum has a composition of 93.7% Al and 6.3% Cu (by mass) and a density of 2.85 g/cm^3 . If placed in excess acid HCl solution the Cu does not react, but the Al reacts according to the equation given in Exercise 7. What volume of this alloy must dissolve to produce 3.55 g of H_2 ?

Ans: {amount of reaction} = {3.55 [g H_2]}

A solution is a homogeneous mixture in which one or more atomic/molecular/ionic species is uniformly dispersed in a (usually much larger) sample of another species. It may be gaseous, liquid or solid (in which case it is called an alloy).

The **solvent** is the component which determines the physical *phase* of the solution (solid vs. liquid vs. gas), and is usually (but not always!) the dominant component.

The **solute(s)** is/are the other components of the solution, usually the ones of interest w.r.t. reactions.

For **liquid solutions** we describe the amount of reagent by a combination of the volume of the sample with the solution concentration, usually expressed in *molarity*, or moles per litre (M).

$$\text{Molarity} \equiv \frac{\# \text{ moles solute}}{\# \text{ litres solution}}$$

In a solution $\{ \text{No. moles of solute reagent} \} = \text{Volume} \times \text{concentration}$

On dilution or mixing $M_{\text{init.}} \times V_{\text{init.}} = M_{\text{final}} \times V_{\text{final}}$

Exercise 10. If 93.4 g of aluminum sulphate are dissolved in water and diluted to yield exactly 250. mL of solution, *what is the solution concentration?*



Exercise 11. A nitric acid (HNO_3) solution with a density of 1.424 g/mL is 70.9% acid by mass. What is its molarity?

Note: on combining, mixing or diluting solutions, must be careful to account for

- final total # of moles of each distinct component
- final total volume

Dilution \Rightarrow does not change the molar amount of a chemical species

\Rightarrow but does change its concentration by distributing it over a larger volume!

$$(\text{concentration after mixing}) = M_2 = \frac{\text{total No. moles}}{\text{total volume}} = \frac{M_1 V_1}{V_2}$$

Exercise 12. What is the final molarity of chloride ion Cl^- (aq) in the solution obtained on mixing 255. mL of 0.125 M MgCl_2 solution with 855. mL of 0.350 M FeCl_3 solution?

Limiting vs. Excess Reagents

Reacting species are rarely measured out and mixed together in *exactly* the molar ratio defined by the stoichiometric coefficients of a reaction. *Usually* when a reaction is “complete” and stops, one component reagent species is completely used up (making it the “*limiting reagent*”) while amounts of others are left over (making them “*excess reagents*”). The amount of the *limiting reagent* present determines how much reaction occurs and how much product has been produced.

e.g., in any combustion reaction open to the atmosphere, $\text{O}_2(\text{g})$ is the *excess reagent* and the stuff being burned is the *limiting reagent*.

Exercise 13. If equal masses of $\text{Zn}(\text{s})$ and $\text{Br}_2(\text{l})$ are brought together and allowed to react: $\text{Zn}(\text{s}) + \text{Br}_2(\text{l}) \longrightarrow \text{ZnBr}_2(\text{s})$, which is the excess reagent, and what fraction (by mass) of it is left over?

Theoretical Yield vs. Actual Yield vs. % Yield

(or ... nobody's perfect - not even chemists!)

Theoretical Yield is the amount of reaction product generated in a reaction assuming that the process was “stoichiometrically exact” – that absolutely none of the product was lost and the measured amount of reagent did not include impurities,

Actual Yield is

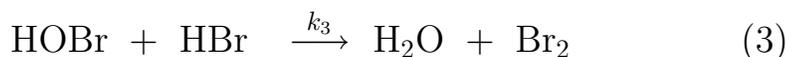
% Yield is

Simultaneous vs. Consecutive Reactions

The difference here is whether the reaction can proceed at the same time, completely independently (**simultaneous reactions**), or whether the product of one reaction is required as reagent for a subsequent one (**consecutive reactions**).

With *consecutive reactions*, one can add the reactions together to describe a single, meaningful, quantitatively correct overall reaction.

e.g., a proposed mechanism for the oxidation of HBr is

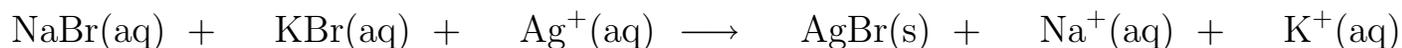


Overall reaction: (1) + (2) + 2 × (3)

Simultaneous reactions occur independently, so adding them together makes no sense.

Exercise 14. A mixture of NaBr and KBr weighing 0.560 g is dissolved in water, the resulting mixed with a solution containing excess $\text{AgNO}_3(\text{aq})$ (all $\text{Ag}^+(\text{aq})$ and $\text{NO}_3^-(\text{aq})$) which precipitates all of the $\text{Br}^-(\text{aq})$ as a solid sample of $\text{AgBr}(\text{s})$ weighing 0.970 g. *What fraction* of the original mixture was KBr?

Ans. Both NaBr and KBr are very highly soluble, as is AgNO_3 , so the species present in our original solution are $\text{Na}^+(\text{aq})$, $\text{Br}^-(\text{aq})$ and $\text{K}^+(\text{aq})$. Why not write the reaction as (??)

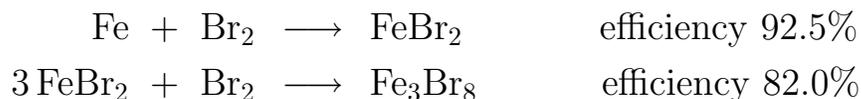


Exercise 15. A sample of gaseous compound made up only of B and H weighing 0.596 g occupies 484 mL at STP. Then burned in excess O_2 it yields 1.17 g of H_2O , and all of the boron is converted to B_2O_3 .

What are: (a) its empirical formula? (b) its molecular weight?
(c) its molecular formula? (d) the weight of B_2O_3 produced?

Exercise 16. A 4.22 g sample of a mixture of $CaCl_2$ and $NaCl$ was dissolved, and then treated to precipitate all of the Ca as $CaCO_3(s)$, which was then heated to drive off $CO_2(g)$, leaving a sample of pure $CaO(s)$ which was found to weigh 0.969 g. What percentage of the original mixture was $CaCl_2$?

Exercise 17. If Fe_3Br_8 is produced by the following mechanism, where the two reactions have the indicated efficiencies, what mass of Fe_3Br_8 is produced from 10.0 g of Fe and excess Br_2 ?



Exercise 18. A “stock” solution of $HCl(aq)$ is 36% HCl by mass, and the density of this solution is 1.18 g/mL.

(a) What is the molarity of this stock solution?

(b) What volume of this stock solution is required to make 0.750 L of a 0.250 M solution of $HCl(aq)$?

Glossary: (see the “Key Terms” list at the end of each chapter)

You should recognize & understand the meaning of and how to use these terms!

mole molar mass

empirical formula molecular formula

stoichiometric coefficients

binary compound ternary compound

cation anion

significant digits

organic vs. inorganic

molarity

alcohol

theoretical yield vs. actual yield vs. % yield

solute solvent solution

limiting reagent excess reagent

simultaneous reactions consecutive reactions

alkane

isomer