## *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* $1^\circ C$ *?*

| 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.

An atom with a mass number of $A$ consist of a nucleus with a positive charge of $+Z\,e$ containing $Z$ protons (each with charge $+e$ and mass $\approx 1.0\,\mathrm{u}$) and $(A-Z)$ neutrons (each with zero charge and mass $\approx 1.0\,\mathrm{u}$), surrounded by a cloud of $Z$ electrons (each with charge $-e$ and mass $\approx 1/1823\,\mathrm{u}$).

**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 ${}^{A}_{Z}(\mathit{name})$, as in ${}^{74}_{32}\mathrm{Ge}$ or ${}^{37}_{17}\mathrm{Cl}$. 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 ${}^{A}(\mathit{name})$, as in ${}^{74}\mathrm{Ge}$ or ${}^{18}\mathrm{O}$ or ${}^{37}\mathrm{Cl}$

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 $75.770\%$ ${}^{35}\mathrm{Cl}$ (mass 34.968 852 u) and $24.230\%$ ${}^{37}\mathrm{Cl}$ (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.

## *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 $\left\{ \begin{array}{l} \\ \\ \\ \\ \\ \end{array} \right.$

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 $12.\dot{0}$ 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 {*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?**

| 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 ($\mu$)[a] |
| $10^{-9}$ | nano (n) |
| $10^{-12}$ | pico (p) |
| $10^{-15}$ | femto (f) |
| $10^{-18}$ | atto (a) |

[a]The Greek letter $\mu$ (pronounced "mew").

Useful Prefixes for big/small amounts.

We assume that you *know* them!!

Common examples:

2.3 mmol =

7.73 $\mu$mol =

0.0188 pmol =

## *Empirical Formula 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:**

**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 89.10and 10.6% carbon by mass. What is its empirical formula?

## *Stoichiometry & Chemical Equations*

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*

$$C_4H_8 \;+\; \quad O_2 \;\longrightarrow\; \quad H_2O \;+\; \quad CO_2$$

**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 it traveling at a speed of 54.4 miles per hour, *what is its speed in meters per second*?

---

**Exercise 5:** For our reactions $C_4H_8 \ + \quad O_2 \longrightarrow \quad H_2O \ + \quad CO_2$
*how many grams* of $O_2$ are required to consume 5.20 g of $C_4H_8$ ?

## *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

$$C_4H_8 + O_2 \longrightarrow H_2O + CO_2 \qquad (1)$$

vs.

$$C_4H_8 + O_2 \longrightarrow H_2O + CO \qquad (2)$$

or compare

$$C_2H_2 + O_2 \longrightarrow H_2O + CO_2 \qquad (3)$$

vs.

$$C_2H_4 + O_2 \longrightarrow H_2O + CO_2 \qquad (4)$$

vs.

$$C_2H_6 + O_2 \longrightarrow H_2O + CO_2 \qquad (5)$$

---

**Exercise 6:** How many grams of oxygen are present in 6.21 g of ferric sulphate [iron(III) sulphate] $Fe_2(SO_4)_3$?

## *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 ...

**For a pure liquid or solid component** we must also know the *density* of the substance – the conversion factor which relates volume to mass.

---

**Exercise 7.** Metallic aluminum has a density of 2.70 g/cm$^3$. If a $10.25\,\mathrm{cm} \times 5.50\,\mathrm{cm}$ piece of aluminum foil of thickness $0.606\,\mathrm{mm}$ is dissolved in excess aqueous HCl according to the reaction $2\,\mathrm{Al(s)} + 6\,\mathrm{HCl(aq)} \longrightarrow 2\,\mathrm{AlCl_3(aq)} + 3\,\mathrm{H_2(g)}$ , *what mass* of $H_2$(g) is produced?

---

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

---

**Exercise 8.** For the reaction $\mathrm{KClO_3(s)} \longrightarrow \mathrm{KCl(s)} + \mathrm{O_2(g)}$ how many grams of $KClO_3$ are required to produce 650 cm$^3$ of $O_2$(g) at STP?

**For mixtures or solutions** we must know the mole fraction or the mass % composition.

---

**Exercise 9.** One particularly useful alloy of aluminum has a composition of 93.7% Al and 6.3% Cu (by mass) and a density of $2.85\,\mathrm{g/cm^3}$. 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 be dissolved to produce $3.55\,\mathrm{g}$ of $H_2$ ?

---

***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 (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).

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

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

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

---

**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 ?

$$Al_2(SO_4)_3\,(s) \xrightarrow{H_2O(l)} 2\,Al^{3+}(aq) \;+\; 3\,SO_4^{2-}(aq)$$

---

**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 it 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, $O_2(g)$ is the *excess reagent* and the stuff being burned is the *limiting reagent*.

---

**Exercise 13.** If equal masses of Zn(s) and $Br_2(l)$ are brought together and allowed to react: $Zn(s) + Br_2(l) \longrightarrow ZnBr_2(s)$ , 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 the actual amount of reaction product obtained.

***% Yield*** is the ratio of {Actual Yield} to {% Yield} , expressed as a percentage.

## *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

$$\mathrm{HBr} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{HOOBr} \tag{1}$$

$$\mathrm{HOOBr} + \mathrm{HBr} \xrightarrow{k_2} 2\,\mathrm{HOBr} \tag{2}$$

$$\mathrm{HOBr} + \mathrm{HBr} \xrightarrow{k_3} \mathrm{H_2O} + \mathrm{Br_2} \tag{3}$$

---

Overall reaction: $\quad (1) + (2) + 2 \times (3)$

---

*Simultaneous reactions* occur independently, so it makes no sense to add them together.

---

**Exercise 14.** A mixture of NaBr and KBr weighing 0.560 g is dissolved in water, the resulting mixed with a solution containing excess $AgNO_3$(aq) (all $Ag^+$(aq) and $NO_3^-$(aq)) which precipitates all of the $Br^-$(aq) as a solid sample of AgBr(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 $Na^+$(aq), $Br^-$(aq) and $K^+$(aq). Why not write the reaction as (??)

$$\mathrm{NaBr(aq)} + \quad \mathrm{KBr(aq)} + \quad \mathrm{Ag^+(aq)} \longrightarrow \quad \mathrm{AgBr(s)} + \quad \mathrm{Na^+(aq)} + \quad \mathrm{K^+(aq)}$$

---

**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 $O_2$ is 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 $Br_2$?

$$\begin{array}{rcll} Fe + Br_2 & \longrightarrow & FeBr_2 & \quad \text{efficiency } 92.5\% \\ 3\,FeBr_2 + Br_2 & \longrightarrow & Fe_3Br_8 & \quad \text{efficiency } 82.0\% \end{array}$$

---

**Exercise 18.** A "stock" solutionof 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