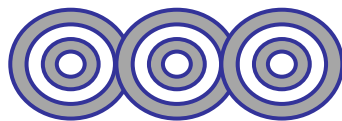




# Fundamentals of Analytical Chemistry



# Stoichiometric Calculations

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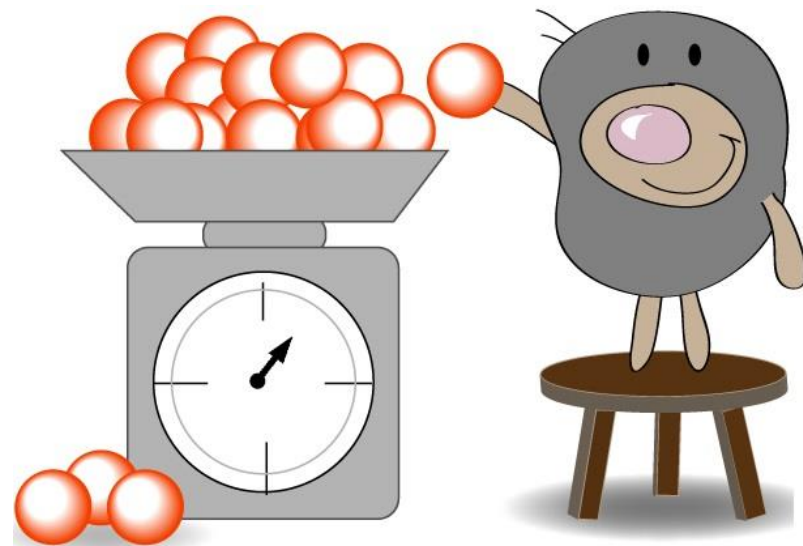
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# Amount of Substance – The Mole

The mole is the **SI** unit for the amount of a chemical substance. It is always associated with specific microscopic entities such as atoms, molecules, ions, electrons or other particles.

It is the amount of the specified substance that contains the same number of particles as the number of carbon atoms in exactly 12 grams of  $^{12}\text{C}$ .



$6.022 \times 10^{23}$  atoms

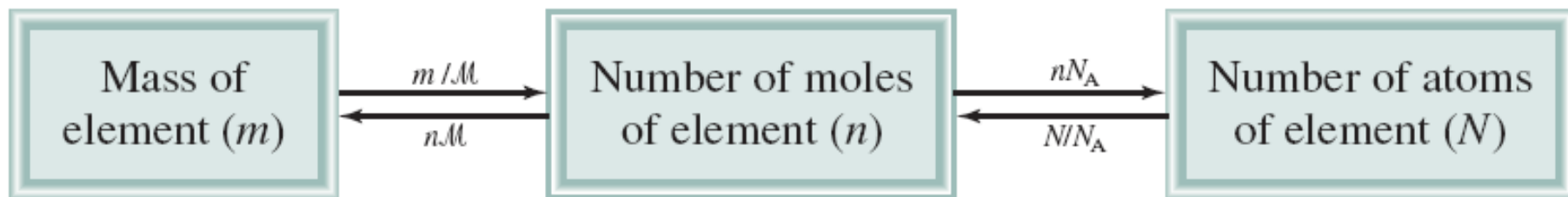
This important number is Avogadro's number:

$$N_A = 6.022 \times 10^{23}$$

The definition was adopted in November 2018 as one of the seven SI base units; It is defined as exactly  $6.022 \times 10^{23}$  constitutive particles, which may be atoms, molecules, ions or electrons.

The molar mass  $\mathcal{M}$  of a substance is the mass in grams of 1 mole of that substance.

The notions of Avogadro's number and molar mass enable us to carry out conversions between mass and moles of atoms and between moles and number of atoms



$$n = \frac{m}{\mathcal{M}} \quad N_A = \frac{N}{n}$$

$N_A$ : Avogadro's no. =  $6.022 \times 10^{23} \text{ mol}^{-1}$

$n$ : no. of moles

$N$ : no. of atoms, molecules, ions or particles

$\mathcal{M}$ : molar mass (g/mol)

$m$ : mass (g)



Water



Iron



Oxygen



Table Salt



Gold



Helium

$$\text{Moles} = \frac{\text{grams}}{\text{formula weight (g/mol)}}$$

Since many experiments deal with very small quantities, a more convenient form of measurement is the millimole.

$$\text{Millimoles} = \frac{\text{milligrams}}{\text{formula weight (mg/mmol)}}$$

Note that...

g/mol is the same as mg/mmol

g/L is the same as mg/mL

mol/L is the same as mmol/mL

## Example

Calculate the number of moles in 500 mg  $\text{Na}_2\text{WO}_4$  (sodium tungstate).

## Solution

$\mathcal{M}$  of the  $\text{Na}_2\text{WO}_4 = 293.8 \text{ g/mol}$

$n = 1.7 \times 10^{-3} \text{ mol}$

## Example

What is the weight, in milligrams, of 0.250 mmol  $\text{Fe}_2\text{O}_3$  (ferric oxide)?

## Solution

$\mathcal{M}$  of the  $\text{Fe}_2\text{O}_3 = 159.7 \text{ g/mol}$

mass = 39.9 mg

## Example

Sulfur (S) is a nonmetallic element that is present in coal. When coal is burned, sulfur is converted to sulfur dioxide and eventually to sulfuric acid that gives rise to the acid rain phenomenon. How many atoms are in 16.3 g of S?

## Solution

1 mol S = 32.07 g S

the conversion factor is  $\frac{1 \text{ mol S}}{32.07 \text{ g S}}$

1 mol =  $6.022 \times 10^{23}$  particles (atoms)

the conversion factors are  $\frac{6.022 \times 10^{23} \text{ S atoms}}{1 \text{ mol S}}$  and  $\frac{1 \text{ mol S}}{6.022 \times 10^{23} \text{ S atoms}}$

$$16.3 \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} \times \frac{6.022 \times 10^{23} \text{ S atoms}}{1 \text{ mol S}} = 3.06 \times 10^{23} \text{ S atoms}$$

## Example

How many hydrogen atoms are present in 25.6 g of urea  $[(\text{NH}_2)_2\text{CO}]$ , which is used as a fertilizer, in animal feed, and in the manufacture of polymers? The molar mass of urea is 60.06 g/mol.

## Solution

$$25.6 \text{ g } (\text{NH}_2)_2\text{CO} \times \frac{1 \text{ mol } (\text{NH}_2)_2\text{CO}}{60.06 \text{ g } (\text{NH}_2)_2\text{CO}} \times \frac{4 \text{ mol H}}{1 \text{ mol } (\text{NH}_2)_2\text{CO}} \times \frac{6.022 \times 10^{23} \text{ H atoms}}{1 \text{ mol H}}$$

$$= 1.03 \times 10^{24} \text{ H atoms}$$

# How Do We Express Concentrations of Solutions?

**Solutions** are **homogeneous** mixtures of two or more pure substances.

In a solution; the **solute** is dispersed uniformly throughout the **solvent**.

Component 1 (solute)	Component 2 (solvent)	State of Resulting solution	Examples
Gas	Gas	Gas	Air (N <sub>2</sub> , O <sub>2</sub> , Ar, CO <sub>2</sub> ...)
Gas	Liquid	Liquid	Soda water (CO <sub>2</sub> in water), O <sub>2</sub> in water
Gas	Solid	Solid	H <sub>2</sub> gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Liquid	Solid	Solid	Mercury in silver
Solid	Liquid	Liquid	Salt in water
Solid	Solid	Solid	Brass (Cu/Zn), Solder (Sn/Pb), Silver in gold

Solvent presents in the greater quantities and is used to dissolve the solute. All other substances are solutes. solutes present in smallest amount and is the substance dissolved in the solvent.



# Ways of Expressing Concentration

The **concentration** of a solution is the amount of solute present in a given amount of solvent, or a given amount of solution.

The concentration of a solution can be expressed either:

- **Qualitatively**
- **Quantitatively**

The terms **dilute** and **concentrated** are used to describe a solution qualitatively (unsaturated, saturated and supersaturated solution).

Chemists use several different concentration units (different expressions), each of which has advantages as well as limitations;

- **Mass percentage**
- **Mole fraction**
- **Molarity**
- **Molality**

# Mass Percentage, ppm and ppb

$$\text{Mass \% of component} = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 100$$

A solution of hydrochloric acid with 36% **HCl** by mass contains 36 g of **HCl** for each 100 g of solution.

Solute weight = 36 g

Solvent weight = 64 g

Total solution weight = 100 g

The concentrations of very dilute solution often express in parts per million (**ppm**) or part per billion (**ppb**).

**1 ppm = 1000 ppb**

$$\text{ppm of component} = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 10^6$$

A solution whose solute concentration is 1 ppm contains 1 g of solute for each million ( $10^6$ ) grams of solution.

This equivalent 1 mg of solute per kilogram of solution (**mg / kg**).

For aqueous solutions, because the density of water is 1 g/mL, this equivalent 1 mg of solute per liter of solution (**mg / L**).

The acceptable maximum concentrations of toxic or carcinogenic substances in the environment are often expressed in ppm or ppb. e.g., the maximum allowable concentration of arsenic in drinking water in USA is 0.010 ppm; that is 0.010 mg of arsenic per liter of water, this corresponds to 10 ppb.

**ppm and ppb expressions are very useful in trace and ultra-trace analyses.**



## National Ambient Air Quality Standards

Pollutant	Primary Standards		Secondary Standards	
	Level	Averaging Time	Level	Averaging Time
Carbon Monoxide	9 ppm (10 mg/m <sup>3</sup> )	8-hour <sup>(1)</sup>	None	
	35 ppm (40 mg/m <sup>3</sup> )	1-hour <sup>(1)</sup>	None	
Lead	0.15 µg/m <sup>3</sup> <sup>(2)</sup>	Rolling 3-Month Average	Same as Primary	
	1.5 µg/m <sup>3</sup>	Quarterly Average	Same as Primary	
Nitrogen Dioxide	53 ppb <sup>(3)</sup>	Annual (Arithmetic Average)	Same as Primary	
	100 ppb	1-hour <sup>(4)</sup>	None	
Particulate Matter (PM <sub>10</sub> )	150 µg/m <sup>3</sup>	24-hour <sup>(5)</sup>	Same as Primary	
Particulate Matter (PM <sub>2.5</sub> )	15.0 µg/m <sup>3</sup>	Annual <sup>(6)</sup> (Arithmetic Average)	Same as Primary	
	35 µg/m <sup>3</sup>	24-hour <sup>(7)</sup>	Same as Primary	
Ozone	0.075 ppm (2008 std)	8-hour <sup>(8)</sup>	Same as Primary	
	0.08 ppm (1997 std)	8-hour <sup>(9)</sup>	Same as Primary	
	0.12 ppm	1-hour <sup>(10)</sup>	Same as Primary	
Sulfur Dioxide	0.03 ppm	Annual (Arithmetic Average)	0.5 ppm	3-hour <sup>(1)</sup>
	0.14 ppm	24-hour <sup>(1)</sup>	None	
	75 ppb <sup>(11)</sup>	1-hour	None	

Trace analysis is usually analytical methods used to detect and/or quantify trace (very small amounts) of substances.

## Common Units for Expressing Trace Concentrations

Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million	ppm	mg/kg μg/g	mg/L μg/mL	μL/L nL/mL
Parts per billion	ppb	μg/kg ng/g	μg/L ng/mL	nL/L pL/mL
Milligram percent	mg%	mg/100g	mg/100mL	

Sometimes for this reason, these concentrations are written as ppmv or ppbv, and so on, indicating “by volume”.

# Mole Fraction

$$\text{Mole fraction of component} = \frac{\text{moles of component}}{\text{total moles of all components}}$$

The symbol  $X$  is commonly used for mole fraction, with a subscript to indicate the component of interest.

$$X_A = \frac{\text{moles of A}}{\text{total moles in solution}}$$

For example; a solution containing 1.00 mol of HCl (36.5 g) and 8.00 mol water (144 g) has a mole fraction of HCl and water:

$$X_{\text{HCl}} = (1.00 \text{ mol}) / (1.00 \text{ mol} + 8.00 \text{ mol}) = 0.111$$

$$X_{\text{H}_2\text{O}} = (8.00 \text{ mol}) / (1.00 \text{ mol} + 8.00 \text{ mol}) = 0.889 \text{ or } 1.00 - 0.111 = 0.889$$

Mole fraction has no unit (the units in the numerator and the denominator cancel). The sum of the mole fractions of all components of a solution must equal 1.

# Molarity and Molality

The Molarity  $M$  of a solute in a solution is defined as:

$$\text{Molarity} = \frac{\text{moles solute}}{\text{liters soln}}$$

Molarity is the most widely used

Since volume is temperature-dependent, molarity can change with temperature.

The Molality  $m$  of a solution, defined as:

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

Since both moles and mass do not change with temperature, molality (unlike molarity) is *not* temperature-dependent. Thus molality is often the concentration unit of choice when a solution is to be used over a range of temperatures.

## Example

A sample of 0.892 g of potassium chloride (KCl) is dissolved in 54.6 g of water. What is the percent by mass of KCl in the solution?

## Solution

$$\begin{aligned}\text{percent by mass of KCl} &= \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\% \\ &= \frac{0.892 \text{ g}}{0.892 \text{ g} + 54.6 \text{ g}} \times 100\% \\ &= 1.61\%\end{aligned}$$



## Example

**(a)** A solution is made by dissolving 13.5 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in 0.100 kg of water. What is the mass percentage of solute in this solution?

**(b)** A 2.5 g sample of groundwater was found to contain 5.4  $\mu\text{g}$  of  $\text{Zn}^{2+}$ . What is the concentration of  $\text{Zn}^{2+}$  in ppm?

## Solution

**(a)** The mass percentage of water in this solution is  $(100 - 11.9)\% = 88.1\%$ .

$$\text{Solve: Mass \% of glucose} = \frac{\text{mass glucose}}{\text{mass soln}} \times 100 = \frac{13.5 \text{ g}}{13.5 \text{ g} + 100 \text{ g}} \times 100 = 11.9\%$$

**(b)** In this case we are given the number of micrograms of solute. Because 1  $\mu\text{g}$  is  $1 \times 10^{-6}$  g,  $5.4 \mu\text{g} = 5.4 \times 10^{-6}$  g.

$$\text{Solve: ppm} = \frac{\text{mass of solute}}{\text{mass of soln}} \times 10^6 = \frac{5.4 \times 10^{-6} \text{ g}}{2.5 \text{ g}} \times 10^6 = 2.2 \text{ ppm}$$

## Example

Calculate the molar concentrations of 1 ppm solutions each of  $\text{Li}^+$  and  $\text{Pb}^{2+}$ .

## Solution

1 ppm = 1 mg/L

$$M_{\text{Li}} = \frac{1.00 \text{ mg Li/L} \times 10^{-3} \text{ g/mg}}{6.94 \text{ g Li/mol}} = 1.44 \times 10^{-4} \text{ mol/L Li}$$

$$M_{\text{Pb}} = \frac{1.00 \text{ mg Pb/L} \times 10^{-3} \text{ g/mg}}{207 \text{ g Pb/mol}} = 4.83 \times 10^{-6} \text{ mol/L Pb}$$

Because lead is much heavier than lithium, a given weight contains a smaller number of moles and its molar concentration is less

## Example

Calculate the molality of a sulfuric acid solution containing 24.4 g of sulfuric acid in 198 g of water. The molar mass of sulfuric acid is 98.09 g.

## Solution

$$\begin{aligned}\text{moles of H}_2\text{SO}_4 &= 24.4 \text{ g } \cancel{\text{H}_2\text{SO}_4} \times \frac{1 \text{ mol H}_2\text{SO}_4}{98.09 \text{ g } \cancel{\text{H}_2\text{SO}_4}} \\ &= 0.249 \text{ mol H}_2\text{SO}_4\end{aligned}$$

$$\begin{aligned}m &= \frac{0.249 \text{ mol H}_2\text{SO}_4}{0.198 \text{ kg H}_2\text{O}} \\ &= 1.26 \text{ m}\end{aligned}$$

## Example

Calculate the molality of a 35.4 percent (by mass) aqueous solution of phosphoric acid ( $\text{H}_3\text{PO}_4$ ). The molar mass of phosphoric acid is 97.99 g.

## Solution

Suppose that you start with a 100.0 g of the solution, then the mass of phosphoric acid is 35.4 percent, or 35.4 g, and mass of water must be  $100.0\% - 35.4\% = 64.6\%$  or 64.6 g.

$$\begin{aligned}\text{moles of H}_3\text{PO}_4 &= 35.4 \text{ g } \cancel{\text{H}_3\text{PO}_4} \times \frac{1 \text{ mol H}_3\text{PO}_4}{97.99 \text{ g } \cancel{\text{H}_3\text{PO}_4}} \\ &= 0.361 \text{ mol H}_3\text{PO}_4\end{aligned}$$

The mass of water is 64.6 g, or 0.0646 kg.

$$\begin{aligned}\text{molality} &= \frac{0.361 \text{ mol H}_3\text{PO}_4}{0.0646 \text{ kg H}_2\text{O}} \\ &= 5.59 \text{ m}\end{aligned}$$

## Example

The density of a 2.45 *M* aqueous solution of methanol (CH<sub>3</sub>OH) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

## Solution

The total mass of 1 L of a 2.45 *M* solution of methanol is

$$1 \text{ L soln} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \times \frac{0.976 \text{ g}}{1 \text{ mL soln}} = 976 \text{ g}$$

Because this solution contains 2.45 moles of methanol, the amount of water (solvent) in the solution is

$$\begin{aligned} \text{mass of H}_2\text{O} &= \text{mass of soln} - \text{mass of solute} \\ &= 976 \text{ g} - \left( 2.45 \text{ mol CH}_3\text{OH} \times \frac{32.04 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} \right) \end{aligned}$$

$$= 898 \text{ g}$$

$$\begin{aligned} \text{molality} &= \frac{2.45 \text{ mol CH}_3\text{OH}}{0.898 \text{ kg H}_2\text{O}} \\ &= 2.73 \text{ m} \end{aligned}$$

## Example

An aqueous solution of hydrochloric acid contains 36% HCl by mass. **(a)** Calculate the mole fraction of HCl in the solution. **(b)** Calculate the molality of HCl in the solution.

## Solution

(a) To calculate the mole fraction of HCl, we convert the masses of HCl and H<sub>2</sub>O to moles:

$$\text{Moles HCl} = (36 \text{ g HCl}) \left( \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \right) = 0.99 \text{ mol HCl}$$

$$\text{Moles H}_2\text{O} = (64 \text{ g H}_2\text{O}) \left( \frac{1 \text{ mol H}_2\text{O}}{18 \text{ g H}_2\text{O}} \right) = 3.6 \text{ mol H}_2\text{O}$$

$$X_{\text{HCl}} = \frac{\text{moles HCl}}{\text{moles H}_2\text{O} + \text{moles HCl}} = \frac{0.99}{3.6 + 0.99} = \frac{0.99}{4.6} = 0.22$$

(b) To calculate the molality of HCl in the solution, We use the calculated number of moles of HCl in part (a), and the mass of solvent is 64 g = 0.064 kg:

$$\text{Molality of HCl} = \frac{0.99 \text{ mol HCl}}{0.064 \text{ kg H}_2\text{O}} = 15 \text{ } m$$

## Example

A solution with a density of 0.876 g/mL contains 5.0 g of toluene (C<sub>7</sub>H<sub>8</sub>) and 225 g of benzene. Calculate the molarity and the molality of the solution.

## Solution

The volume of the solution is obtained from the mass of the solution (mass of solute + mass of solvent = 5.0 g + 225 g = 230 g) and its density.

$$\text{Moles C}_7\text{H}_8 = (5.0 \text{ g C}_7\text{H}_8) \left( \frac{1 \text{ mol C}_7\text{H}_8}{92 \text{ g C}_7\text{H}_8} \right) = 0.054 \text{ mol}$$

The density of the solution is used to convert the mass of the solution to its volume:

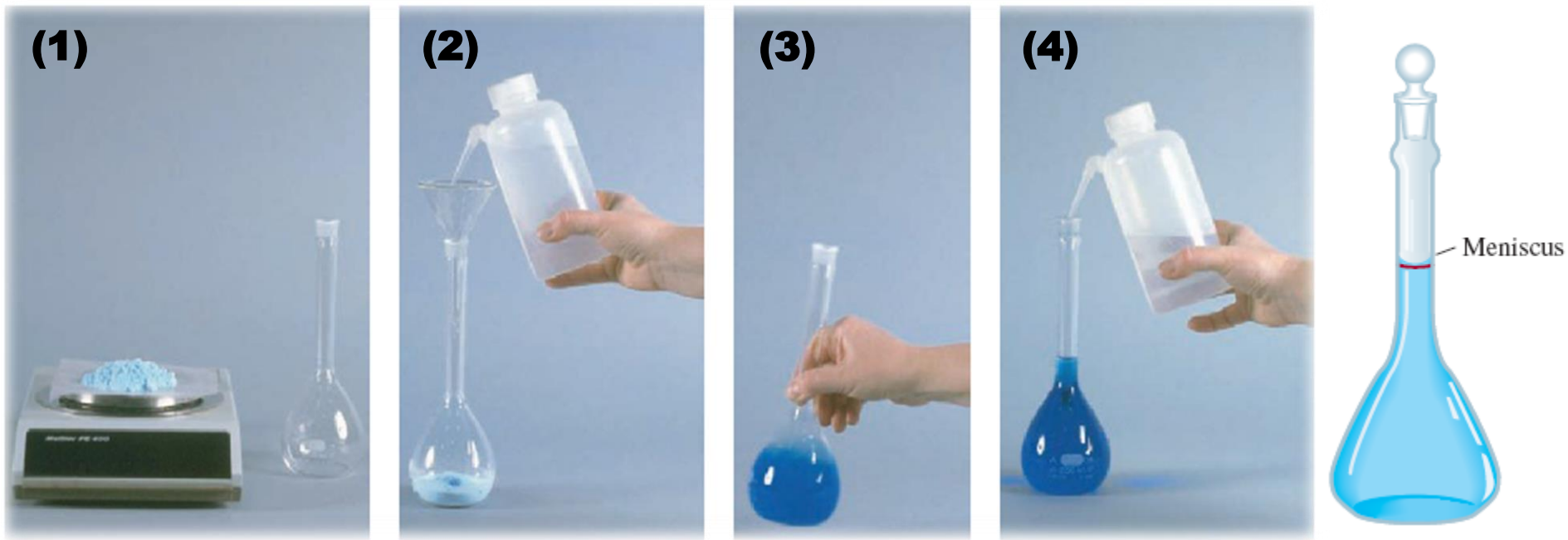
$$\text{Milliliters soln} = (230 \text{ g}) \left( \frac{1 \text{ mL}}{0.876 \text{ g}} \right) = 263 \text{ mL}$$

$$\text{Molarity} = \left( \frac{\text{moles C}_7\text{H}_8}{\text{liter soln}} \right) = \left( \frac{0.054 \text{ mol C}_7\text{H}_8}{263 \text{ mL soln}} \right) \left( \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \right) = 0.21 \text{ M}$$

Molality:

$$(0.054 \text{ mol C}_7\text{H}_8) / (0.225 \text{ kg solvent}) = 0.24 \text{ m}$$

# Preparation of Standard Solution



Procedure for preparation of 250 mL of 1.00 M solution of  $\text{CuSO}_4$  ( $\mathcal{M}=159.5$  g/mol).

0.25 mole of  $\text{CuSO}_4$  (39.9 g) is weighed out and placed in the volumetric flask. Water is added to dissolve the salt, and the resultant solution is diluted to a total volume of 0.250 L. The molarity of the solution is:

$$M = (0.250 \text{ mol CuSO}_4) / (0.250 \text{ L soln}) = 1.00 \text{ M}$$



## Example

How many grams of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) are required to prepare a 250 mL solution whose concentration is 2.16  $M$ ?

## Solution

moles of solute = molarity  $\times$  V soln. (L)

$$\begin{aligned}\text{moles of } \text{K}_2\text{Cr}_2\text{O}_7 &= \frac{2.16 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ L soln}} \times 0.250 \text{ L soln} \\ &= 0.540 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7\end{aligned}$$

The molar mass of  $\text{K}_2\text{Cr}_2\text{O}_7$  is 294.2 g, so

$$\begin{aligned}\text{grams of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ needed} &= 0.540 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7 \times \frac{294.2 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7} \\ &= 159 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7\end{aligned}$$

## Example

In a biochemical assay, a chemist needs to add 3.81 g of glucose to a reaction mixture. Calculate the volume in milliliters of a 2.53 *M* glucose solution that should use for the addition.

## Solution

The molar mass of  $\text{C}_6\text{H}_{12}\text{O}_6$  is 180.2 g, so

$$3.81 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} = 2.114 \times 10^{-2} \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6$$

$$\begin{aligned} V &= \frac{n}{M} \\ &= \frac{2.114 \times 10^{-2} \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}{2.53 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6/\text{L soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ &= 8.36 \text{ mL soln} \end{aligned}$$

# Dilution of Solutions

Concentrated solutions are often stored in the laboratory for use as needed; “**stock**” solutions are frequently diluted before working with them.

**Dilution** is the procedure for preparing a less concentrated solution from a more concentrated one.



Two potassium permanganate ( $\text{KMnO}_4$ ) solutions of different concentrations

moles of solute before dilution = moles of solute after dilution

$$\begin{array}{ccc} M_i V_i & = & M_f V_f \\ \text{moles of solute} & & \text{moles of solute} \\ \text{before dilution} & & \text{after dilution} \end{array}$$

where  $M_i$  and  $M_f$  are the initial and final concentrations of the solution in molarity and  $V_i$  and  $V_f$  are the initial and final volumes of the solution, respectively.

The units of  $V_i$  and  $V_f$  must be the same (mL or L) for the calculation to work.

$M_i > M_f$  and  $V_f > V_i$

## Example

Describe how you would prepare  $5.00 \times 10^2$  mL of a  $1.75 \text{ M H}_2\text{SO}_4$  solution, starting with an  $8.61 \text{ M}$  stock solution of  $\text{H}_2\text{SO}_4$ .

## Solution

$$\begin{array}{ll} M_i = 8.61 \text{ M} & M_f = 1.75 \text{ M} \\ V_i = ? & V_f = 5.00 \times 10^2 \text{ mL} \end{array}$$

$$\begin{aligned} (8.61 \text{ M})(V_i) &= (1.75 \text{ M})(5.00 \times 10^2 \text{ mL}) \\ V_i &= \frac{(1.75 \text{ M})(5.00 \times 10^2 \text{ mL})}{8.61 \text{ M}} \\ &= 102 \text{ mL} \end{aligned}$$

Thus, we must dilute 102 mL of the  $8.61 \text{ M H}_2\text{SO}_4$  solution with sufficient water to give a final volume of  $5.00 \times 10^2$  mL in a 500-mL volumetric flask to obtain the desired concentration.

## Example

How many milliliters of 3.0 M H<sub>2</sub>SO<sub>4</sub> are needed to make 450 mL of 0.10 M H<sub>2</sub>SO<sub>4</sub>?

## Solution

Calculating the moles of H<sub>2</sub>SO<sub>4</sub> in the dilute solution:

$$\begin{aligned}\text{moles H}_2\text{SO}_4 \text{ in dilute solution} &= (0.450 \text{ L soln}) \left( \frac{0.10 \text{ mol H}_2\text{SO}_4}{1 \text{ L soln}} \right) \\ &= 0.045 \text{ mol H}_2\text{SO}_4\end{aligned}$$

Calculating the volume of the concentrated solution that contains 0.045 mol H<sub>2</sub>SO<sub>4</sub>:

$$\text{L conc soln} = (0.045 \text{ mol H}_2\text{SO}_4) \left( \frac{1 \text{ L soln}}{3.0 \text{ mol H}_2\text{SO}_4} \right) = 0.015 \text{ L soln}$$

Converting liters to milliliters gives 15 mL.

If we apply dilution law, we get the same result:

$$\begin{aligned}(3.0 \text{ M})(V_{\text{conc}}) &= (0.10 \text{ M})(450 \text{ mL}) \\ (V_{\text{conc}}) &= \frac{(0.10 \text{ M})(450 \text{ mL})}{3.0 \text{ M}} = 15 \text{ mL}\end{aligned}$$

Either way, we see that if we start with 15 mL of 3.0 M H<sub>2</sub>SO<sub>4</sub> and dilute it to a total volume of 450 mL, the desired 0.10 M solution will be obtained.

## Example

You wish to prepare a calibration curve for the spectrophotometric determination of permanganate. You have a stock 0.100 M solution of  $\text{KMnO}_4$  and a series of 100 mL volumetric flasks. What volumes of the stock solution will you have to pipet into the flasks to prepare standards of 1.00, 2.00, 5.00, and  $10.0 \times 10^{-3}$  M  $\text{KMnO}_4$  solutions?

## Solution

$$C_1V_1 = C_2V_2$$

$$0.100 \text{ M} \times V_1 \text{ mL} = 1.00 \times 10^{-3} \text{ M} \times 100 \text{ mL}$$

$$V_1 = 1.00 \text{ mL}$$

Similarly, for the other solutions we will need 2.00, 5.00, and 10.0 mL of the stock solution, which will be diluted to 100 mL

# p-Functions

Scientists frequently express the concentration of a species in terms of its p-function, or p-value. The p-value is the negative logarithm (to the base 10) of the molar concentration of that species. Thus, for the species X,

$$\mathbf{pX = -\log [X]}$$

p-Values offer the advantage of allowing concentrations that vary over ten or more orders of magnitude to be expressed in terms of small positive numbers.

The best-known p-function is pH, which is the negative logarithm of  $[H^+]$ .

$$\mathbf{pH = -\log [H^+]}$$

## Example

Calculate the p-value for each ion in a solution that is  $2.00 \times 10^{-3}$  M in NaCl and  $5.4 \times 10^{-4}$  M in HCl.

## Solution

$$\text{pH} = -\log [\text{H}^+] = -\log (5.4 \times 10^{-4}) = 3.27$$

To obtain pNa, we write

$$\text{pNa} = -\log[\text{Na}^+] = -\log (2.00 \times 10^{-3}) = -\log (2.00 \times 10^{-3}) = 2.699$$

The total  $\text{Cl}^-$  concentration is given by the sum of the concentrations of the two solutes:

$$\begin{aligned} [\text{Cl}^-] &= (2.00 \times 10^{-3}) + (5.4 \times 10^{-4}) \\ &= 2.54 \times 10^{-3} \text{ M} \end{aligned}$$

$$\text{pCl} = -\log[\text{Cl}^-] = -\log (2.54 \times 10^{-3}) = 2.595$$



## Example

Calculate the molar concentration of  $\text{Ag}^+$  in a solution that has a pAg of 6.372.

## Solution

$$\text{pAg} = -\log [\text{Ag}^+] = 6.372$$

$$\log [\text{Ag}^+] = -6.372$$

anti-log

$$[\text{Ag}^+] = 4.25 \times 10^{-7} \text{ M}$$

# Density and Specific Gravity of Solutions

**Density** expresses the mass of a substance per unit volume. Density is expressed in units of kg/L or alternatively g/mL.

**Specific gravity** is the ratio of the mass of a substance to the mass of an equal volume of water.

Specific Gravities of Commercial Concentrated Acids and Bases

Reagent	Concentration, % (w/w)	Specific Gravity
Acetic acid	99.7	1.05
Ammonia	29.0	0.90
Hydrochloric acid	37.2	1.19
Hydrofluoric acid	49.5	1.15
Nitric acid	70.5	1.42
Perchloric acid	71.0	1.67
Phosphoric acid	86.0	1.71
Sulfuric acid	96.5	1.84

## Example

Calculate the molar concentration of  $\text{HNO}_3$  (63.0 g/mol) in a solution that has a specific gravity of 1.42 and is 70.5%  $\text{HNO}_3$  (w/w).

## Solution

70.5%  $\text{HNO}_3$  mass by mass

Suppose the mass of solution = 100 g

Mass  $\text{HNO}_3$  = 70.5 g,

mole  $\text{HNO}_3$  =  $70.5 / 63.0 = 1.119$  mole

Mass  $\text{H}_2\text{O}$  (solvent) = 63 g

$m = n$  (solute) / kg (solvent) =  $1.015 / 0.063 = 16.111$  m

To calculate M

Mass of solution = 100g

$d = m / v$  then,  $v = 100 / 1.42 = 70.42$  mL

$M = n$  (solute) /  $v$  (soln, L) =  $1.119 / 0.07042 = 15.89$  M

Or directly,,,

$M = (\text{assay} \times \text{density} \times 10) / \text{molar mass} = 70.5 \times 1.42 \times 10 / 63.0 = 15.89$  mol/L

## Example

Describe the preparation of 100 mL of 6.0 M HCl from a concentrated solution that has a specific gravity of 1.18 and is 37% (w/w) HCl (36.5 g/mol).

**2.5L** **9535-03**

**Hydrochloric Acid, 36.5-38.0%**

BAKER ANALYZED® A.C.S. Reagent  
HCl  
FW 36.460  
Batch No: XXXXXXXXXX  
Manufactured Date: 2012/06/28 (yyyy/mm/dd)  
Retest Date: 2012/06/25 (yyyy/mm/dd)  
Meets ACS Reagent Chemical Requirements  
For Laboratory/Research/Manufacturing Use

Appearance	Passes Test
Assay (as HCl) (by acid-base titrn)	36.5 - 38.0 %
Color (APHA)	≤ 10
Extractable Organic Substances	≤ 5 ppm
Free Chlorine (as Cl <sub>2</sub> )	≤ 1 ppm
Residue after ignition	≤ 3 ppm
Specific Gravity at 60°/60°F	1.185 - 1.192
Bromide (Br)	≤ 0.005 %
Phosphate (PO <sub>4</sub> )	≤ 1.0 ppm
Sulfate (SO <sub>4</sub> )	≤ 0.5 ppm
Sulfite (SO <sub>3</sub> )	≤ 0.8 ppm
Ammonium (NH <sub>4</sub> )	≤ 3 ppm
Arsenic and Antimony (as As)	≤ 5.0 ppb
Heavy Metals (as Pb)	≤ 100.00 ppb

Complete specifications at [avantormaterials.com](http://avantormaterials.com)

**J.T. Baker**

Avantor Performance Materials, Inc.  
3417 Corporate Parkway, Suite 200  
Center Valley, PA 18034  
610-573-2500  
[www.avantormaterials.com](http://www.avantormaterials.com)

Label from a bottle of reagent-grade hydrochloric acid.

## Solution

The concentration of the reagent,

$$c_{\text{HCl}} = \frac{1.18 \times 10^3 \text{ g reagent}}{\text{L reagent}} \times \frac{37 \text{ g HCl}}{100 \text{ g reagent}} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} = 12.0 \text{ M}$$

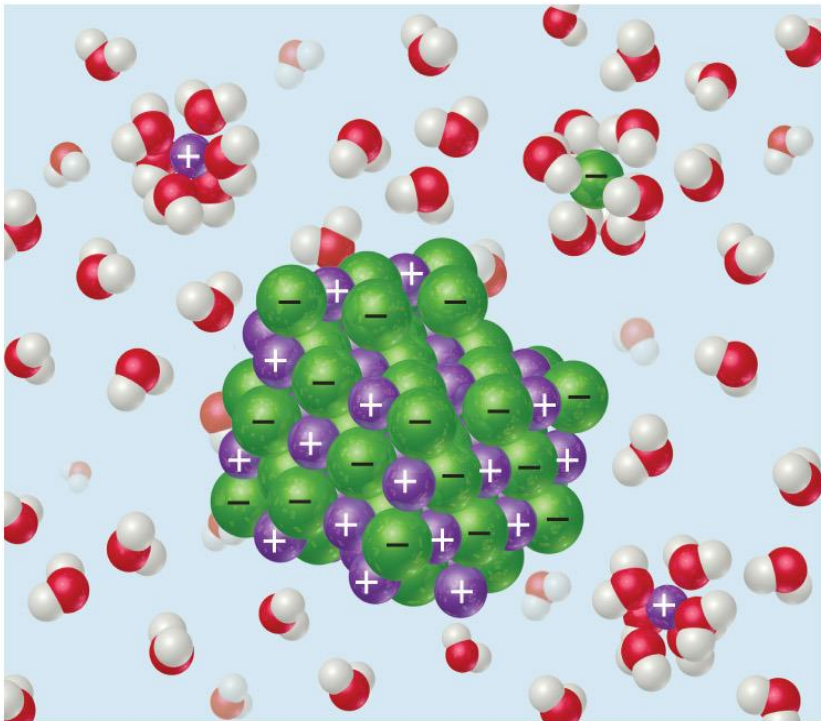
The volume of concentrated reagent,

$$M_1 V_1 = M_2 V_2$$

$$12 \times V_1 = 6 \times 100$$

$$V_1 = 50 \text{ mL}$$

# Expressing the Concentration of an Electrolyte



-When an ionic substance dissolves in water, the solvent pulls the individual ions from the crystal and solvates them.

-This process is called **dissociation**.

-An **electrolyte** is a substance that dissociates into ions when dissolved in water.

-A **nonelectrolyte** may dissolve in water, but it does not dissociate into ions when it does so.

# Strong and Weak Electrolytes

A **strong electrolyte** dissociates completely when dissolved in water (soluble ionic salts, strong acids and strong bases).

For example:



A **weak electrolyte** only dissociates partially when dissolved in water (produce a small concentration of ions when they dissolve, these ions exist in *equilibrium* with the unionized substance).

For example:

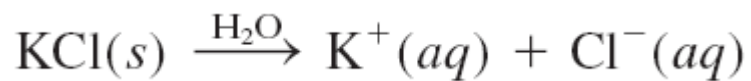


When an ionic compound dissolves, the relative concentrations of the ions introduced into the solution depend on the chemical formula of the compound.

For example, a 1.0 M solution of NaCl is 1.0 M in Na<sup>+</sup> ions and 1.0 M in Cl<sup>-</sup> ions. Similarly, a 1.0 M solution of Na<sub>2</sub>SO<sub>4</sub> is 2.0 M in Na<sup>+</sup> ions and 1.0 M in SO<sub>4</sub><sup>-2</sup> ions

Molarity refers only to the amount of solute originally dissolved in water and does not take into account any **subsequent processes**, such as the **dissociation** of a salt or the ionization of an acid.

Consider what happens when a sample of potassium chloride (KCl) is dissolved in enough water to make a 1 *M* solution:



Because KCl is a **strong electrolyte**, it undergoes complete dissociation in solution. Thus, a 1 *M* KCl solution contains 1 mole of K<sup>+</sup> ions and 1 mole of Cl<sup>-</sup> ions, and no KCl units are present.

The concentrations of the ions can be expressed as [K<sup>+</sup>] = 1 *M* and [Cl<sup>-</sup>] = 1 *M*.

Similarly, in a 1 *M* barium nitrate [Ba(NO<sub>3</sub>)<sub>2</sub>] solution



we have [Ba<sup>2+</sup>] = 1 *M* and [NO<sub>3</sub><sup>-</sup>] = 2 *M* and no Ba(NO<sub>3</sub>)<sub>2</sub> units at all.

## Example

What are the molar concentrations of each of the ions present in a 0.025 *M* aqueous solution of calcium nitrate? ( $\text{Ca}(\text{NO}_3)_2$ )

## Solution

$\text{Ca}(\text{NO}_3)_2$  composed of two  $\text{NO}_3^-$  ions for each  $\text{Ca}^{2+}$  ion in the compound, each mole of  $\text{Ca}(\text{NO}_3)_2$  that dissolves dissociates into 1 mol of  $\text{Ca}^{2+}$  and 2 mol of  $\text{NO}_3^-$ .

Thus, a solution that is 0.025 *M* in  $\text{Ca}(\text{NO}_3)_2$  is 0.025 *M* in  $\text{Ca}^{2+}$  and  $2 \times 0.025 \text{ M} = 0.050 \text{ M}$  in  $\text{NO}_3^-$ :

$$\frac{\text{mol NO}_3^-}{\text{L}} = \left( \frac{0.025 \text{ mol } \text{Ca}(\text{NO}_3)_2}{\text{L}} \right) \left( \frac{2 \text{ mol NO}_3^-}{1 \text{ mol } \text{Ca}(\text{NO}_3)_2} \right) = 0.050 \text{ M}$$

The concentration of  $\text{NO}_3^-$  ions is twice that of  $\text{Ca}^{2+}$  ions, as the subscript 2 after the  $\text{NO}_3^-$  in the chemical formula  $\text{Ca}(\text{NO}_3)_2$  suggests it should be.



# Chemical Stoichiometry

How much product will be formed from specific amounts of starting materials (reactants)?

How much starting material must be used to obtain a specific amount of product?

**Stoichiometry** is the quantitative study of reactants and products in a chemical reaction.

To interpret a reaction quantitatively, we need to apply our knowledge of molar masses and the mole concept.

**Mole method** means that the stoichiometric coefficients in a chemical equation can be interpreted as the number of moles of each substance.

Stoichiometry deals with the ratios in which chemicals reacts

# Law of Conservation of Mass

“We may lay it down as an incontestable axiom that, in all the operations of art and nature, nothing is created; an equal amount of matter exists both before and after the experiment. Upon this principle, the whole art of performing chemical experiments depends.”

-- **Antoine Lavoisier.**

Atoms are neither created nor destroyed during any chemical reaction. The changes that occur during any reaction merely rearrange the atoms. The same collection of atoms is present both before and after the reaction.

-- **Dalton's atomic theory.**



**Log**

10 kg

+



**Fire**

0.5 kg



**Ashes**

9 kg

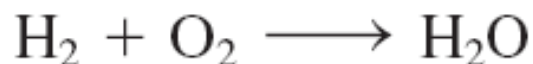
+



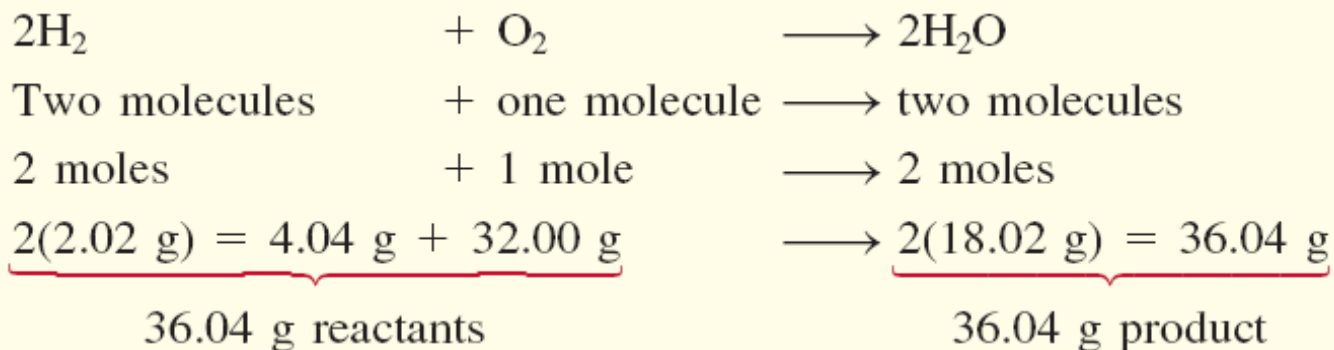
**Smoke**

1.5 kg

What happens when hydrogen gas ( $\text{H}_2$ ) burns in air (which contains oxygen,  $\text{O}_2$ ) to form water ( $\text{H}_2\text{O}$ ). This reaction can be represented by the chemical equation

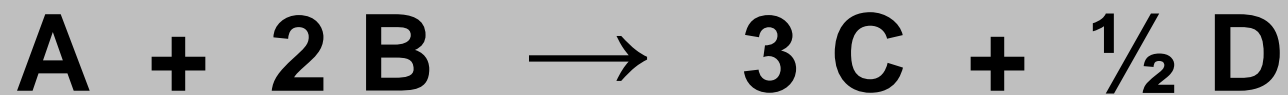


To conform with the **law of conservation of mass**, there must be the same number of each type of atom on both sides of the arrow (we should balance the equation).



# Stoichiometric Calculations

For the following general reaction:



$$\mathbf{\text{mol A} = \frac{\text{mol B}}{2} = \frac{\text{mol C}}{3} = 2 \text{ mol D}}$$

Note...

Limiting reactant criteria should be applied

## Example

The food we eat is degraded, or broken down, in our bodies to provide energy for growth and function. A general overall equation for this very complex process represents the degradation of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) to carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ):



If 856 g of  $\text{C}_6\text{H}_{12}\text{O}_6$  is consumed by a person over a certain period, what is the mass of  $\text{CO}_2$  produced?

grams of  $\text{C}_6\text{H}_{12}\text{O}_6$   $\longrightarrow$  moles of  $\text{C}_6\text{H}_{12}\text{O}_6$   $\longrightarrow$  moles of  $\text{CO}_2$   $\longrightarrow$  grams of  $\text{CO}_2$

$$856 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \text{ mol } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}}{180.2 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} = 4.750 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6$$

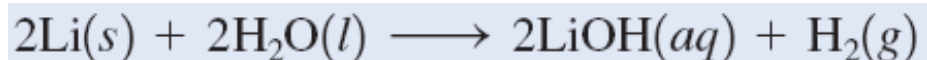
$$4.750 \text{ mol } \cancel{\text{C}_6\text{H}_{12}\text{O}_6} \times \frac{6 \text{ mol } \text{CO}_2}{1 \text{ mol } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} = 28.50 \text{ mol } \text{CO}_2$$

$$28.50 \text{ mol } \cancel{\text{CO}_2} \times \frac{44.01 \text{ g } \text{CO}_2}{1 \text{ mol } \cancel{\text{CO}_2}} = 1.25 \times 10^3 \text{ g } \text{CO}_2$$

$$\begin{aligned} \text{mass of } \text{CO}_2 &= 856 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \text{ mol } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}}{180.2 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} \times \frac{6 \text{ mol } \cancel{\text{CO}_2}}{1 \text{ mol } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} \times \frac{44.01 \text{ g } \text{CO}_2}{1 \text{ mol } \cancel{\text{CO}_2}} \\ &= 1.25 \times 10^3 \text{ g } \text{CO}_2 \end{aligned}$$

## Example

All alkali metals react with water to produce hydrogen gas and the corresponding alkali metal hydroxide. A typical reaction is that between lithium and water:



How many grams of Li are needed to produce 9.89 g of  $\text{H}_2$ ?

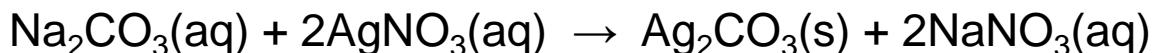
grams of  $\text{H}_2$   $\longrightarrow$  moles of  $\text{H}_2$   $\longrightarrow$  moles of Li  $\longrightarrow$  grams of Li

$$9.89 \text{ g } \cancel{\text{H}_2} \times \frac{1 \cancel{\text{ mol H}_2}}{2.016 \text{ g } \cancel{\text{H}_2}} \times \frac{2 \cancel{\text{ mol Li}}}{1 \cancel{\text{ mol H}_2}} \times \frac{6.941 \text{ g Li}}{1 \cancel{\text{ mol Li}}} = 68.1 \text{ g Li}$$

## Example

- (a) What mass of  $\text{AgNO}_3$  (169.9 g/mol) is needed to convert 2.33 g of  $\text{Na}_2\text{CO}_3$  (106.0 g/mol) to  $\text{Ag}_2\text{CO}_3$ ?
- (b) What mass of  $\text{Ag}_2\text{CO}_3$  (275.7 g/mol) will be formed?

## Solution



$$\begin{aligned} \text{(a)} \quad \text{amount Na}_2\text{CO}_3 &= n_{\text{Na}_2\text{CO}_3} = 2.33 \text{ g Na}_2\text{CO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{106.0 \text{ g Na}_2\text{CO}_3} \\ &= 0.02198 \text{ mol Na}_2\text{CO}_3 \end{aligned}$$

$$\begin{aligned} \text{amount AgNO}_3 &= n_{\text{AgNO}_3} = 0.02198 \text{ mol Na}_2\text{CO}_3 \times \frac{2 \text{ mol AgNO}_3}{1 \text{ mol Na}_2\text{CO}_3} \\ &= 0.04396 \text{ mol AgNO}_3 \end{aligned}$$

$$\text{mass AgNO}_3 = 0.04396 \text{ mol AgNO}_3 \times \frac{169.9 \text{ g AgNO}_3}{\text{mol AgNO}_3} = 7.47 \text{ g AgNO}_3$$

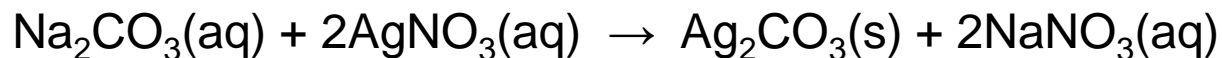
$$\text{(b)} \quad \text{amount Ag}_2\text{CO}_3 = \text{amount Na}_2\text{CO}_3 = 0.02198 \text{ mol}$$

$$\text{mass Ag}_2\text{CO}_3 = 0.02198 \text{ mol Ag}_2\text{CO}_3 \times \frac{275.7 \text{ g Ag}_2\text{CO}_3}{\text{mol Ag}_2\text{CO}_3} = 6.06 \text{ g Ag}_2\text{CO}_3$$

## Example

What mass of  $\text{Ag}_2\text{CO}_3$  (275.7 g/mol) is formed when 25.0 mL of 0.200 M  $\text{AgNO}_3$  are mixed with 50.0 mL of 0.0800 M  $\text{Na}_2\text{CO}_3$ ?

## Solution



The initial amounts of reactants are:

$$\begin{aligned} \text{amount AgNO}_3 = n_{\text{AgNO}_3} &= 25.0 \text{ mL AgNO}_3 \times \frac{1 \text{ L AgNO}_3}{1000 \text{ mL AgNO}_3} \\ &\times \frac{0.200 \text{ mol AgNO}_3}{1 \text{ L AgNO}_3} = 5.00 \times 10^{-3} \text{ mol AgNO}_3 \end{aligned}$$

$$\begin{aligned} \text{amount Na}_2\text{CO}_3 = n_{\text{Na}_2\text{CO}_3} &= 50.0 \text{ mL Na}_2\text{CO}_3 \text{ soln} \times \frac{1 \text{ L Na}_2\text{CO}_3}{1000 \text{ mL Na}_2\text{CO}_3} \\ &\times \frac{0.0800 \text{ mol Na}_2\text{CO}_3}{1 \text{ L Na}_2\text{CO}_3} = 4.00 \times 10^{-3} \text{ mol Na}_2\text{CO}_3 \end{aligned}$$

Because 1 mole of  $\text{Na}_2\text{CO}_3$  is only needed to react with 2 mole  $\text{AgNO}_3$ ,  $\text{AgNO}_3$  is the limiting reactant

$$\begin{aligned} \text{mass Ag}_2\text{CO}_3 &= 5.00 \times 10^{-3} \text{ mol AgNO}_3 \times \frac{1 \text{ mol Ag}_2\text{CO}_3}{2 \text{ mol AgNO}_3} \times \frac{275.7 \text{ g Ag}_2\text{CO}_3}{1 \text{ mol Ag}_2\text{CO}_3} \\ &= 0.689 \text{ g Ag}_2\text{CO}_3 \end{aligned}$$



