

SECTION 10

CHEMICAL ANALYSIS

A large number of professional chemists are *analysts*. They determine things like "how much of a particular compound is in a sample of a substance", or "the amount of a particular element in a compound or mixture", or "the concentration of compound or ion in a water sample". When a chemist makes what is believed to be a new compound, an elemental analysis is carried out, i.e. the percentage by mass of each element in the compound is determined and compared with the theoretical figure for the compound. Chemical analysis is central to the practice of chemistry.

Three main quantities that are measured in analysis are mass, volume, and intensity of a beam of electromagnetic radiation, giving rise respectively to gravimetric, volumetric and spectrophotometric methods of analysis. In this section, after you have been given the definitions of ways the composition of a system can be expressed, you are introduced to these three classes of analysis.

Analysis: The determination of the **composition** of a substance.

Composition: The composition of a substance or of a mixture can be expressed in many ways. In **elemental analysis** it is usually expressed as the percentage by mass of each element in the substance. For solutions or mixtures common terms are **concentration, mole fraction, molality, percentage composition, and parts per million**.

Concentration: Symbol c , the "amount" of solute per unit volume of the solution. The "amount" may be given as mass, and $c = m/V$, where m is the mass of solute and V the volume of the solution (common unit g L^{-1}), or using the formal definition of amount of substance as

$c = n/V$, (common unit mol L^{-1}). For a given solute, concentration in one set of units may be converted to the other using $m = nM$ or $n = \frac{m}{M}$ [e.g. 5.50 g of sodium chloride was dissolved in water to give 200 mL of solution. Determine the concentration.

$$c(\text{NaCl}) = \frac{m(\text{NaCl})}{V(\text{NaCl})} = \frac{5.50 \text{ g}}{200 \times 10^{-3} \text{ L}} = 27.5 \text{ g L}^{-1}$$

$$\text{or } c(\text{NaCl}) = \frac{n(\text{NaCl})}{V(\text{NaCl})} = \frac{m(\text{NaCl})}{M(\text{NaCl})V(\text{NaCl})} = \frac{5.50 \text{ g}}{(23.0 + 35.5) \text{ g mol}^{-1} \times 200 \times 10^{-3} \text{ L}}$$

$$= 0.470 \text{ mol L}^{-1}$$

This example may be written in the following one line format:

$$c(\text{NaCl}) = m(\text{NaCl})/V(\text{NaCl}) = 5.50 \text{ g}/(200 \times 10^{-3} \text{ L}) = 27.5 \text{ g L}^{-1}$$

$$n(\text{NaCl})/V(\text{NaCl}) = m(\text{NaCl})/M(\text{NaCl})V(\text{NaCl})$$

$$= 5.50 \text{ g}/\{(23.0 + 35.5) \text{ g mol}^{-1} \times 200 \times 10^{-3} \text{ L}\} = 0.470 \text{ mol L}^{-1}$$

This format is only used for simple equations in the remainder of this section.

The term **molarity**, symbol M , is an old term no longer approved by the International Union of Pure and Applied Chemistry (the body which determines the rules on the language of chemistry), but unfortunately often still used by analytical chemists for concentration in units

of mol L⁻¹. [e.g. The molarity of the above NaCl solution is 0.470; it is a 0.470 M solution of NaCl; in speech it may be described as a 0.470 molar solution. Here **molar** means mol L⁻¹, not per mole. This is an example of chemists having two different meanings for the same word. The meaning is made clear by the context in which the word is used.]

Mole fraction: Symbol x , the amount of a substance or entity (molecules, atoms or ions) in a mixture as a fraction of the total amounts of substances or entities in the mixture. [e.g. 1.0 g of sodium chloride is dissolved in 10 g of water. What is the mole fraction of NaCl in the solution?

$$x = \frac{n(\text{NaCl})}{n(\text{NaCl}) + n(\text{H}_2\text{O})}$$

$$n(\text{NaCl}) = \frac{m(\text{NaCl})}{M(\text{NaCl})} = \frac{1.0 \text{ g}}{58.5 \text{ g mol}^{-1}} = 0.017 \text{ mol}$$

$$n(\text{H}_2\text{O}) = \frac{m(\text{H}_2\text{O})}{M(\text{H}_2\text{O})} = \frac{10 \text{ g}}{18 \text{ g mol}^{-1}} = 0.555 \text{ mol}$$

$$x = \frac{0.017 \text{ mol}}{(0.017 + 0.555) \text{ mol}} = 0.030 \quad]$$

Molality: The amount of solute per kilogram of solvent. (units: mol kg⁻¹)

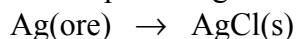
Percentage composition: There are various forms of this. %w/w is percentage by mass of the substance relative to the total mass. %w/V is the mass of substance in grams divided by the volume of the solution in millilitres and multiplied by 100. (Chemists here use w for mass, originating from the loose use of the word weight.) %V/V is the percentage by volume of the substance relative to the total volume.

Parts per million: Symbol ppm: a ratio. For a gaseous mixture, the mole ratio, (mol/mol). For solutions, normally calculated from mg of substance per kg of solution, but for dilute aqueous solutions as mg of substance per litre of solution. For solids, the mass ratio.

This section will cover three classes of chemical analysis, **gravimetric**, **volumetric**, and **spectrophotometric**.

Gravimetric analysis: Analysis by measurement of mass.

[e.g. The silver in a 100 g ore sample was recovered as 4.55 g of pure silver chloride. Determine the percentage mass of silver in the sample.



Silver chloride is AgCl. Identify the quantities known and to be determined: $m(\text{AgCl})$ and $m(\text{Ag})$ respectively. From the stoichiometry determine the relationship between them: $n(\text{Ag}) = n(\text{AgCl})$.

$$n(\text{Ag}) = n(\text{AgCl}) = \frac{m(\text{AgCl})}{M(\text{AgCl})} = \frac{4.55 \text{ g}}{(107.9 + 35.5) \text{ g mol}^{-1}} = 0.0317 \text{ mol}$$

$$m(\text{Ag}) = n(\text{Ag})M(\text{Ag}) = 0.0317 \text{ mol} \times 107.9 \text{ g mol}^{-1} = 3.42 \text{ g}$$

$$\% \text{ mass} = \frac{m(\text{Ag})}{m(\text{sample})} \times 100 = \frac{3.42 \text{ g}}{100 \text{ g}} \times 100 = 3.42 \quad]$$

It can be useful to derive the overall expression between the required unknown and known quantities and put all the numerical values into this expression at the end.

[e.g. In the above example:

$$\begin{aligned} m(\text{Ag}) &= n(\text{Ag})M(\text{Ag}) = n(\text{AgCl})M(\text{Ag}) = \frac{m(\text{AgCl})M(\text{Ag})}{M(\text{AgCl})} = \frac{4.55 \text{ g} \times 107.9 \text{ g mol}^{-1}}{(107.9 + 35.5) \text{ g mol}^{-1}} \\ &= 3.42 \text{ g} \end{aligned}$$

Volumetric analysis: Analysis by measurement of volume.

Volumetric analysis involves **titration**. In titration one reactant, A (the **analyte**), is in solution in a flask (usually a conical flask) and a second reactant, B (the **titrant**), in solution is added from a **burette** (a graduated glass tube with a tap at the bottom).

Equivalence point or **stoichiometric point:** The stage of a titration where the volume added from the burette (the **titre**) contains the exact amount of B required to react with all of A according to the chemical equation for the reaction

$$\text{For } aA + bB \rightarrow cC + dD \quad \text{it is where } \frac{n(A)}{a} = \frac{n(B)}{b} .$$

This stoichiometric relationship is at the centre of all volumetric analysis calculations.

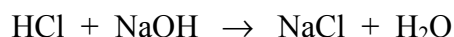
In titration there are commonly two scenarios.

I $c_t(\text{B})$ is known, (i.e. B is a **standard solution**), and $n_t(\text{A})$ is to be determined. Here the subscript t has been used to emphasise these are quantities in the actual titration step. The amount of A in the conical flask is determined from the titre, the volume of solution B, $V_t(\text{B})$, delivered from the burette:

$$n_t(\text{A}) = \frac{an_t(\text{B})}{b} = \frac{ac_t(\text{B})V_t(\text{B})}{b} .$$

From $n_t(\text{A})$, the amount of A in the flask, information such as the concentration of a solution of A, the amount of A in a mixture, or the percentage purity of a substance may be determined.

[e.g. A 25.0 mL **aliquot** (a small known volume of solution) of hydrochloric acid was transferred with a **pipette** (device which delivers a fixed known volume of solution) to a conical flask and titrated with 0.150 mol L⁻¹ sodium hydroxide solution, the reaction being



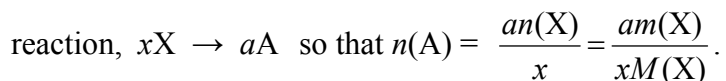
The titre was 23.4 mL. Determine the concentration of the HCl solution.

Stoichiometry: $n_t(\text{HCl}) = n_t(\text{NaOH}) = c_t(\text{NaOH})V_t(\text{NaOH})$

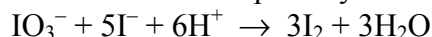
$$c_t(\text{HCl}) = \frac{n_t(\text{HCl})}{V_t(\text{HCl})} = \frac{c_t(\text{NaOH})V_t(\text{NaOH})}{V_t(\text{HCl})} = \frac{0.150 \text{ mol L}^{-1} \times 23.4 \text{ mL}}{25.0 \text{ mL}} = 0.140 \text{ mol L}^{-1}$$

II $n_t(\text{A})$ is known, and $c(\text{B})$ is determined. This is called **standardising** the solution of

B. The amount of A may be obtained (a) from the mass of a very pure substance A (known as a **primary standard**) determined by weighing and calculating $n(A)$ from $n(A) = m(A)/M(A)$, or, (b) if A does not have the properties of necessary for a primary standard, weighing out some other primary standard substance, X, that gives A in a stoichiometric



[e.g. Potassium iodate, KIO_3 , a primary standard reacts with excess iodide to produce a known amount of iodine which is not a primary standard. The chemical equation is



$$\text{Here X is } \text{IO}_3^- \text{ and A is } \text{I}_2 \text{ and } n(\text{I}_2) = 3n(\text{IO}_3^-) = \frac{3m(\text{KIO}_3)}{M(\text{KIO}_3)}]$$

(a) By weighing a primary standard A directly into the conical flask:

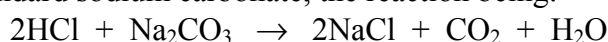
$$\frac{n_t(\text{B})}{b} = \frac{n_t(\text{A})}{a} \text{ and } c(\text{B}) = \frac{n_t(\text{B})}{V_t(\text{B})}$$

$$n_t(\text{B}) = \frac{bn_t(\text{A})}{a} = \frac{bm_t(\text{A})}{aM(\text{A})} \quad (\text{because } n = m/M)$$

$$c(\text{B}) = \frac{bm_t(\text{A})}{aM(\text{A})V_t(\text{B})}$$

$m_t(\text{A})$ and $V_t(\text{B})$ are the quantities measured in the experiment.

[e.g. A solution of hydrochloric acid was standardised by titration against 0.200 g of the primary standard sodium carbonate, the reaction being:



The titre was 19.7 mL. Determine the concentration of HCl.

$$\text{Stoichiometry: } n_t(\text{HCl}) = 2n_t(\text{Na}_2\text{CO}_3) = \frac{2m_t(\text{Na}_2\text{CO}_3)}{M(\text{Na}_2\text{CO}_3)}$$

$$\begin{aligned} c(\text{HCl}) &= \frac{n_t(\text{HCl})}{V_t(\text{HCl})} = \frac{2m_t(\text{Na}_2\text{CO}_3)}{M(\text{Na}_2\text{CO}_3)V_t(\text{HCl})} \\ &= \frac{2 \times 0.200 \text{ g}}{\{(2 \times 23.0 + 12.0 + 3 \times 16.0) \text{ g mol}^{-1} \times 19.7 \times 10^{-3} \text{ L}\}} = 0.192 \text{ mol L}^{-1} \end{aligned}$$

(b) By weighing a larger mass of primary standard A into a **volumetric flask** (a stoppered flask with a graduation mark on the neck) of fixed volume V_f , dissolving it in the solvent (usually water), then adding more solvent until the level of the solution is on the graduation mark, and then shaking thoroughly. An aliquot of the solution is transferred from the volumetric flask to the conical (titration) flask using a pipette of volume V_p . In this case the concentration of A in the volumetric flask is

$$c_f(\text{A}) = \frac{n_f(\text{A})}{V_f(\text{A})} = \frac{m(\text{A})}{M(\text{A})V_f(\text{A})}$$

where the _f refers to the volumetric flask. The amount of A used in the titration is

$$n_t(\text{A}) = c_f(\text{A})V_p(\text{A}) \quad (\text{because } c = n/V)$$

$$= \frac{m(\text{A})V_p(\text{A})}{M(\text{A})V_f(\text{A})}$$

As in (a), for the titration $n_t(\text{B})/b = n_t(\text{A})/a$ and $c(\text{B}) = n_t(\text{B})/V_t(\text{B})$

$$\text{and } n_t(\text{B}) = \frac{bn_t(\text{A})}{a} = \frac{bc_f(\text{A})V_p(\text{A})}{a} = \frac{bm(\text{A})V_p(\text{A})}{aM(\text{A})V_f(\text{A})}$$

$$\text{and } c(\text{B}) = n_t(\text{B})/V_t(\text{B}) = \frac{bm(\text{A})V_p(\text{A})}{aM(\text{A})V_f(\text{A})V_t(\text{B})}$$

Again $m(\text{A})$ and $V_t(\text{B})$ are measured in the experiment, the molar mass of A and the volumes of the flask and pipette being known.

[e.g. A second solution of hydrochloric acid was standardised against sodium carbonate, but this time 23.7 g of sodium carbonate was dissolved in water and made up to the mark in a 250 mL volumetric flask. A 10 mL aliquot was titrated with the hydrochloric acid solution. The titre of HCl was 12.6 mL. Determine the concentration of this HCl solution.

$$\begin{aligned} c_f(\text{Na}_2\text{CO}_3) &= \frac{n_f(\text{Na}_2\text{CO}_3)}{V_f} = \frac{m_f(\text{Na}_2\text{CO}_3)}{M(\text{Na}_2\text{CO}_3)V_f} \\ &= \frac{23.7 \text{ g}}{106.0 \text{ g mol}^{-1} \times 0.250 \text{ L}} = 0.894 \text{ mol L}^{-1} \end{aligned}$$

$$n_t(\text{Na}_2\text{CO}_3) = c_f(\text{Na}_2\text{CO}_3)V_p$$

$$\begin{aligned} c(\text{HCl}) &= \frac{n_t(\text{HCl})}{V_t(\text{HCl})} = \frac{2n_t(\text{Na}_2\text{CO}_3)}{V_t(\text{HCl})} = \frac{2c_f(\text{Na}_2\text{CO}_3)V_p}{V_t(\text{HCl})} = \frac{2 \times 0.894 \text{ mol L}^{-1} \times 10 \text{ mL}}{12.6 \text{ mL}} \\ &= 1.42 \text{ mol L}^{-1} \end{aligned}$$

(Note: The subscripts t, f and p, are introduced to help understanding - they would not normally be used in doing a calculation.)

Spectroscopic analysis: Analysis involving the absorption (or emission) of light.

In ultraviolet-visible spectroscopy the absorbance of a solution in a **spectrophotometric cell** (a container with flat transparent walls) is measured.

Absorbance: Symbol A , $\log_{10}(I^0/I)$, where I^0 is the intensity of the light beam entering the solution and I the intensity leaving it. [e.g. If 90% of the incident light is absorbed by the solution, $A=1$.] **Optical density** is an older term for absorbance.

Beer's law (Beer-Lambert law): $A = \epsilon cb$. This states that the absorbance, A , of a solution is proportional to the concentration of the absorbing solute, c , and the pathlength, b , of the light. ϵ is the proportionality constant. (l is sometimes used in place of b .)

Molar absorptivity: The value of ϵ when the concentration of the solute is measured in mol L^{-1} . (**Extinction coefficient** is an older term for this.) The value of ϵ varies with the wavelength, λ , of the light.

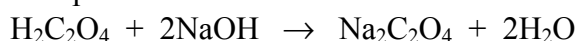
[e.g. Calculate the concentration of a solute, with $\epsilon = 1200 \text{ L mol}^{-1} \text{ cm}^{-1}$, for which the absorbance is 0.450 when measured in a 1.0 cm cell.

$$c = \frac{A}{\epsilon b} = \frac{0.045}{1200 \text{ L mol}^{-1} \text{ cm}^{-1} \times 1.0 \text{ cm}} = 3.75 \times 10^{-4} \text{ mol L}^{-1} = 375 \text{ } \mu\text{mol L}^{-1} \quad]$$

EXERCISES

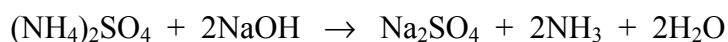
From the masses of the compounds dissolved in the given volumes in questions 1-3 calculate the concentrations of the solutions in units of (a) g L^{-1} and (b) mol L^{-1} .

- 1 kg of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, in 5 L
- 48.6 mg of KF in 100 mL
- 5.234 g of the primary standard oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, made up to the mark in a 100 mL volumetric flask
- A sodium hydroxide solution was standardised by titrating against the above oxalic solution (question 3). A 10 mL aliquot of the oxalic acid took 18.52 mL of NaOH to reach the equivalence point for the reaction

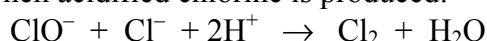


Determine the concentration of the sodium hydroxide solution.

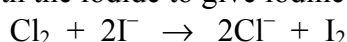
- The standardised NaOH solution of question 4 was used to determine the percentage purity of a sample of ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$. 0.8548 g of the ammonium sulfate was weighed into a conical flask and titrated with the NaOH solution according to the equation below, the titre being 26.75 mL. Determine the percentage purity.



- Household chlorine bleaches are aqueous solutions of sodium hypochlorite and sodium chloride. When acidified chlorine is produced:

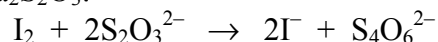


The concentration of the bleach is often given as grams of "available chlorine" per litre. In measuring this an aliquot of the bleach solution is pipetted into a conical flask containing a solution of potassium iodide and some acid added slowly. The chlorine formed reacts with the iodide to give iodine:



The amount of iodine formed is measured by titration against a standard solution of

sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$:



Sodium thiosulfate is not a primary standard, and its solution is standardised by titration with a known amount of iodine formed by the reaction of a known amount of potassium iodate, KIO_3 , with excess iodide in an acidified solution:



In such an analysis 1.187 g of KIO_3 was transferred to a 250 mL volumetric flask, dissolved in water and made up to the mark. 25.0 mL aliquots of this solution were transferred to conical flasks, excess KI solution and acid added, and the iodine formed titrated against the sodium thiosulfate solution to standardise it. The average titre was 23.48 mL. Then 10.0 mL aliquots of the bleach solution were pipetted into conical flasks containing aqueous excess KI and acid slowly added. The released iodine was titrated against the standard thiosulfate solution. The average titre was 34.70 mL. Determine the concentration of the bleach solution in terms of grams of available chlorine per litre.

$M/\text{g mol}^{-1}$: $\text{KIO}_3 = 214.0$ $\text{Cl}_2 = 70.90$

(Hint: You will have to calculate the concentration of the standard potassium iodate solution from the weighing, then that of the standard thiosulfate solution from the first titrations, and then use this figure to determine the mass of chlorine from the second titrations.)

7. A solution of an azo dye with a molar absorptivity of $17\,500 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 560 nm wavelength had an absorbance of 0.528 when measured in a 0.50 cm cell at this wavelength. Determine the concentration of the dye. If the relative molecular mass of the dye was 468 calculate the mass of dye in a 20 litre vat.