

*SECTION 10***CHEMICAL 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

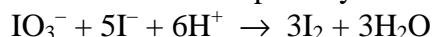
of mol L⁻¹

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

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

$$\text{reaction, } xX \quad aA \quad \text{so that } n(A) = \frac{an(X)}{x} = \frac{am(X)}{xM(X)}.$$

[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:

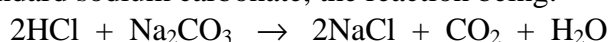
$$\frac{n_t(\text{B})}{b} = \frac{n_t(\text{A})}{a} \quad \text{and} \quad c(\text{B}) = \frac{n_t(\text{B})}{V_t(\text{B})}$$

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

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

$m_t(\text{A})$ 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 $c(\text{B}) = n_t(\text{B})/V_t(\text{B})$

$$\text{and } n_t(\text{B}) = \frac{bn_t(\text{A})}{a} = \frac{V}{a}$$

(A) (A)

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.

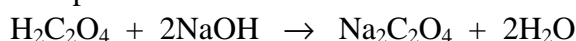
[e.g. Calculate the concentration of a solute, with $\epsilon = 1200 \text{ L mol}^{-1} \text{ cm}^{-1}$, for which the absorbance is 0.450 when measured in a 1.0 cm cell.

$$c = \frac{A}{\epsilon b} = \frac{0.450}{1200 \text{ L mol}^{-1} \text{ cm}^{-1} \times 1.0 \text{ cm}} = 3.75 \times 10^{-4} \text{ mol L}^{-1} = 375 \mu\text{mol L}^{-1} \quad]$$

EXERCISES

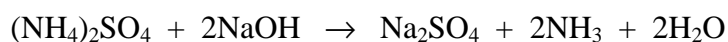
From the masses of the compounds dissolved in the given volumes in questions 1-3 calculate the concentrations of the solutions in units of (a) g L^{-1} and (b) mol L^{-1} .

- 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

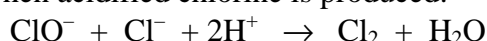


Determine the concentration of the sodium hydroxide solution.

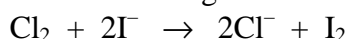
- The standardised NaOH solution of question 4 was used to determine the percentage purity of a sample of ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$. 0.8548 g of the ammonium sulfate was weighed into a conical flask and titrated with the NaOH solution according to the equation below, the titre being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



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

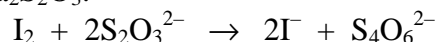


The concentration of the bleach is often given as grams of "available chlorine" per litre. In measuring this an aliquot of the bleach solution is pipetted into a conical flask containing a solution of potassium iodide and some acid added slowly. The chlorine formed reacts with the iodide to give iodine:



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.

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

(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.