

Atoms, Molecules and Stoichiometry

01 · RELATIVE MASSES

A_r — weighted mean mass of an atom relative to ^{12}C taken as exactly 12. M_r — the same for a molecule or formula unit. Both are ratios, so no units.

$A_r = \Sigma(\text{isotopic mass} \times \% \text{abundance}) \div 100$.
Read abundances off a mass spectrum (x-axis m/z , y-axis relative abundance).

02 · THE MOLE

$$n = m \div M$$

$$N = n \times L \quad (L = 6.02 \times 10^{23} \text{ mol}^{-1})$$

One mole is the amount containing as many particles as there are atoms in 12 g of ^{12}C . Always state *what* the particles are — atoms, molecules or ions.

03 · SOLUTIONS AND GASES

$$n = c \times V(\text{dm}^3) \quad c = n \div V$$

$$pV = nRT \quad V_m = 24.0 \text{ dm}^3 \text{ at r.t.p.}$$

Ideal-gas units: p in Pa, V in m^3 ($1 \text{ dm}^3 = 1 \times 10^{-3} \text{ m}^3$), T in K, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$. $\text{cm}^3 \div 1000 = \text{dm}^3$.

04 · EMPIRICAL AND MOLECULAR FORMULAE

Empirical — simplest whole-number ratio of atoms. **Molecular** — the actual number in one molecule; it is a whole-number multiple of the empirical formula.

Method. % or mass $\rightarrow \div A_r \rightarrow$ divide by the smallest $\rightarrow \times 2$ or $\times 3$ to clear halves and thirds.

C 40.0 %, H 6.7 %, O 53.3 %:
 $3.33 : 6.7 : 3.33 \rightarrow 1 : 2 : 1 \rightarrow \text{CH}_2\text{O}$
If $M_r = 180$, $180 \div 30 = 6 \rightarrow \text{C}_6\text{H}_{12}\text{O}_6$

05 · BALANCING AND STATE SYMBOLS

Balance atoms first, then charge. Every equation needs **(s)** **(l)** **(g)** **(aq)**. Ionic equations show only the species that change — cancel the spectator ions.

Half-equations: balance atoms, then O with H_2O , then H with H^+ , then charge with e^- .

06 · REACTING-MASS CALCULATIONS

The route every time:
mass or volume $\rightarrow$ **moles** $\rightarrow$ mole ratio from the equation $\rightarrow$ moles of the wanted species $\rightarrow$ mass or volume.

Never compare masses directly across an equation — only moles carry the ratio.

07 · WORKED EXAMPLE — LIMITING REACTANT

4.00 g Mg reacts with 100 cm^3 of 2.00 mol dm^{-3} HCl.
 $\text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2$
 $n(\text{Mg}) = 4.00 \div 24.3 = 0.165 \text{ mol}$
 $n(\text{HCl}) = 2.00 \times 0.100 = 0.200 \text{ mol}$
HCl needed for all the Mg = $2 \times 0.165 = 0.329 \text{ mol} > 0.200$
 $\rightarrow$ **HCl is limiting**

$n(\text{H}_2) = 0.200 \div 2 = 0.100 \text{ mol}$
 $V(\text{H}_2) = 0.100 \times 24.0 = \mathbf{2.40 \text{ dm}^3}$ at r.t.p.

08 · WORKED EXAMPLE — REACTING MASSES

What mass of CaO forms from 25.0 g of CaCO_3 ?
 $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
 $n(\text{CaCO}_3) = 25.0 \div 100.1 = 0.250 \text{ mol}$
ratio 1 : 1 $\rightarrow n(\text{CaO}) = 0.250 \text{ mol}$
 $m(\text{CaO}) = 0.250 \times 56.1 = \mathbf{14.0 \text{ g}}$
Check by difference: the 11.0 g lost is the CO_2 .

09 · TYPES OF FORMULA

Type	Ethanoic acid
empirical	CH_2O
molecular	$\text{C}_2\text{H}_4\text{O}_2$
structural	CH_3COOH
displayed	every bond drawn

An ionic compound has only an empirical formula — the lattice has no molecules.

10 · WORKED EXAMPLE — COMBUSTION DATA

0.150 g of a hydrocarbon burns to give 0.440 g CO_2 and 0.270 g H_2O .
 $n(\text{C}) = 0.440 \div 44.0 = 0.0100 \text{ mol}$
 $n(\text{H}) = 2 \times (0.270 \div 18.0) = 0.0300 \text{ mol}$
ratio C : H = 1 : 3 $\rightarrow \text{CH}_3$
If $M_r = 30$, molecular formula = C_2H_6

11 · AVOGADRO'S LAW

Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. So for gases the **volume ratio equals the mole ratio** — no need to convert.

$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$: 10 cm^3 of N_2 needs 30 cm^3 of H_2 and gives 20 cm^3 of NH_3 , all measured under the same conditions.

12 · PERCENTAGE COMPOSITION

$$\% \text{ by mass} = (n \times A_r) \div M_r \times 100$$

% N in NH_4NO_3 ($M_r = 80.0$):
 $(2 \times 14.0) \div 80.0 \times 100 = \mathbf{35.0 \%}$

Compare fertilisers this way — urea $\text{CO}(\text{NH}_2)_2$ is 46.7 % N.

13 · THE FOUR ROUTES TO MOLES

From mass — $n = m \div M$

From solution — $n = c \times V(\text{dm}^3)$

From gas volume — $n = V \div 24.0 \text{ dm}^3$ at r.t.p., or $n = pV \div RT$

From particles — $n = N \div 6.02 \times 10^{23}$

14 · WORKED EXAMPLE — GAS VOLUMES

50 cm^3 of C_3H_8 burns in 300 cm^3 of O_2 , all volumes at the same conditions.
 $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}(\text{l})$
 O_2 needed = $5 \times 50 = 250 \text{ cm}^3 \rightarrow 50 \text{ cm}^3 \text{ O}_2$ left over
 CO_2 formed = $3 \times 50 = 150 \text{ cm}^3$
Water is a liquid at r.t.p., so it adds no volume.

Final gas volume = $150 + 50 = \mathbf{200 \text{ cm}^3}$

15 · YIELD AND ATOM ECONOMY

% yield = $\text{actual} \div \text{theoretical} \times 100$
atom economy = $M_r(\text{desired}) \div$

$\Sigma M_r(\text{products}) \times 100$

Theoretical yield comes from the limiting reactant. Losses come from side reactions, reversible reactions and transfer losses. An addition reaction has 100 % atom economy.

Titrations and Gas Calculations

16 · STANDARD SOLUTIONS

Dissolve a weighed mass, transfer with washings to a volumetric flask, make up to the mark, invert to mix. Concentration in mol dm^{-3} or g dm^{-3} ; **$\text{g dm}^{-3} = \text{mol dm}^{-3} \times M$** .

Dilution: $c_1V_1 = c_2V_2$. Moles are unchanged by dilution.

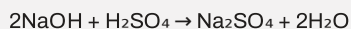
17 · TITRATION TECHNIQUE

Pipette the aliquot, rinse the burette with the titrant, record initial and final readings to **0.05 cm^3** , discard the rough titre and average only **concordant** titres (within 0.10 cm^3).

Rinse the conical flask with distilled water only. Adding more water does not change the moles present, so it does not affect the titre.

18 · WORKED EXAMPLE — TITRATION

25.0 cm^3 of NaOH needs 22.40 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$.



$$\begin{aligned} n(\text{H}_2\text{SO}_4) &= 0.100 \times 0.02240 = 2.24 \times 10^{-3} \text{ mol} \\ n(\text{NaOH}) &= 2 \times 2.24 \times 10^{-3} = 4.48 \times 10^{-3} \text{ mol} \\ c(\text{NaOH}) &= 4.48 \times 10^{-3} \div 0.0250 = \mathbf{0.179 \text{ mol dm}^{-3}} \end{aligned}$$

Give 3 s.f. — the data limits it.

19 · BACK TITRATION

Used when the sample is insoluble or reacts slowly (an impure carbonate, an antacid). React with a **known excess** of acid, then titrate the leftover acid with standard alkali.

$$n \text{ reacted with sample} = n \text{ added} - n \text{ left over}$$

20 · WORKED EXAMPLE — GAS LAW

0.240 g of a gas occupies 240 cm^3 at 100 kPa and 300 K . Find M_r .

$$\begin{aligned} V &= 240 \times 10^{-6} \text{ m}^3, p = 1.00 \times 10^5 \text{ Pa} \\ n &= pV \div RT = (1.00 \times 10^5 \times 2.40 \times 10^{-4}) \div (8.31 \times 300) \\ n &= 24.0 \div 2493 = 9.63 \times 10^{-3} \text{ mol} \\ M &= 0.240 \div 9.63 \times 10^{-3} = \mathbf{24.9 \text{ g mol}^{-1}} \end{aligned}$$

21 · IDEAL GASES

Assumptions: negligible molecular volume, no intermolecular forces, elastic collisions, random rapid motion.

Real gases deviate most at **high pressure and low temperature**, where molecules are close together and attractions matter. Behaviour is most ideal at high T and low p.

22 · WATER OF CRYSTALLISATION

For $\text{MX} \cdot x\text{H}_2\text{O}$, find moles of the anhydrous salt and moles of water lost on heating, then take the ratio.

$$\begin{aligned} 2.50 \text{ g CuSO}_4 \cdot x\text{H}_2\text{O} &\rightarrow 1.60 \text{ g CuSO}_4 \\ n(\text{CuSO}_4) &= 1.60 \div 159.6 = 0.01003 \text{ mol} \\ n(\text{H}_2\text{O}) &= 0.90 \div 18.0 = 0.0500 \text{ mol} \\ \text{ratio } 1 : 4.99 &\rightarrow \mathbf{x = 5} \end{aligned}$$

23 · APPARATUS AND UNCERTAINTY

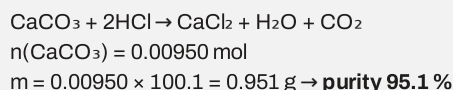
Apparatus	Uncertainty
burette (per reading)	$\pm 0.05 \text{ cm}^3$
pipette 25.0 cm^3	$\pm 0.06 \text{ cm}^3$
balance (per reading)	$\pm 0.001 \text{ g}$

A titre needs **two** burette readings, so the total uncertainty is $\pm 0.10 \text{ cm}^3$. % uncertainty = uncertainty $\div$ measurement $\times 100$; reduce it by using a larger titre or a bigger sample mass.

24 · WORKED EXAMPLE — BACK TITRATION

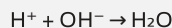
1.00 g of impure CaCO_3 is added to 30.0 cm^3 of $1.00 \text{ mol dm}^{-3} \text{ HCl}$. The excess needs 22.0 cm^3 of $0.500 \text{ mol dm}^{-3} \text{ NaOH}$.

$$\begin{aligned} n(\text{HCl}) \text{ added} &= 0.0300 \text{ mol} \\ n(\text{HCl}) \text{ left} &= 0.0220 \times 0.500 = 0.0110 \text{ mol} \\ n(\text{HCl}) \text{ reacted} &= 0.0190 \text{ mol} \end{aligned}$$

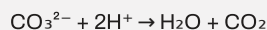


25 · IONIC EQUATIONS TO KNOW

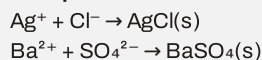
Neutralisation



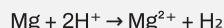
Carbonate + acid



Precipitation



Metal + acid



26 · WORKED EXAMPLE — DILUTION

What volume of $2.00 \text{ mol dm}^{-3} \text{ HCl}$ is needed to make 250 cm^3 of $0.150 \text{ mol dm}^{-3}$ acid?

$$\begin{aligned} c_1V_1 &= c_2V_2 \\ V_1 &= (0.150 \times 250) \div 2.00 \\ V_1 &= \mathbf{18.8 \text{ cm}^3} \end{aligned}$$

Pipette this into a 250 cm^3 volumetric flask and make up to the mark.

27 · SOURCES OF ERROR IN A TITRATION

Rinsing the burette with water rather than the titrant dilutes it and the titre reads high. An air bubble in the jet leaves the same false high reading when it clears.

Overshooting the end point, misreading the meniscus, and swirling too little all shift the titre. Read the bottom of the meniscus at eye level against a white tile.

Repeat until two titres agree within 0.10 cm^3 , and average only those.

28 · WORKED EXAMPLE — PURITY

2.50 g of impure Na_2CO_3 is dissolved and made up to 250 cm^3 . A 25.0 cm^3 portion needs 20.0 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ HCl}$.

$$\begin{aligned} \text{Na}_2\text{CO}_3 + 2\text{HCl} &\rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \\ n(\text{HCl}) &= 2.00 \times 10^{-3} \text{ mol} \\ n(\text{Na}_2\text{CO}_3) \text{ in } 25 \text{ cm}^3 &= 1.00 \times 10^{-3} \text{ mol} \\ \text{in } 250 \text{ cm}^3 &= 0.0100 \text{ mol} \\ m &= 0.0100 \times 106.0 = 1.06 \text{ g} \\ \text{purity} &= 1.06 \div 2.50 \times 100 = \mathbf{42.4 \%} \end{aligned}$$

MARKS LOST HERE

— Leaving volumes in cm^3 inside $n = cV$, or in dm^3 inside $sc\text{-camel-p-v} = nRT$.

— Ignoring the mole ratio and assuming 1 : 1.

— Forgetting to test which reactant is limiting.

— Rounding mid-calculation, or quoting more significant figures than the data allows.

— Omitting state symbols, or leaving spectator ions in an ionic equation.