

SHORT NOTES ON PHYSICAL CHEMISTRY



The physical chemistry of Class 11 and Class 12 in NCERT order — formulae, graphs, short-cuts, traps and 124 solved numerical examples

Some Basic Concepts of Chemistry (Mole Concept) · Structure of Atom · Gaseous State · Thermodynamics and Thermochemistry · Chemical Equilibrium · Ionic Equilibrium · Redox Reactions and Equivalent Concept · The Solid State · Solutions · Electrochemistry · Chemical Kinetics · Surface Chemistry · Nuclear Chemistry and Radioactivity

Short Notes on Physical Chemistry

for IIT-JEE Advanced, JEE Main, NEET (UG),
Class 11 and 12

MTA Team

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Numerical answers to the solved examples have been checked a second time by computer; the book is not printed if any of these checks fails. If you still find a mistake, please write to us.

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How to use these notes

These are revision notes: short, exact and complete. They are not a first textbook. Read a chapter of NCERT first; come here to fix every result in memory and to see how each one is used in a JEE question.

Order. Part I follows the physical chemistry chapters of the NCERT Class 11 textbooks, in the same order; Part II does the same for Class 12. Solid state, surface chemistry and nuclear chemistry (radioactivity) are kept in Part II: they are still asked in JEE Advanced and in many State and Board examinations, and they are needed to understand the rest.

Numericals. Physical chemistry is mostly calculation. Every formula is followed by the ways it is used; every solved example shows each step with units, and the final number was worked out again by computer before printing.

In every chapter:

- **boxed** — key definitions and results, to be learnt by heart;
- **red** — shortcuts, traps and common mistakes;
- **Solved examples** — questions of the NEET and JEE type, each with a complete solution. Cover the solution, try the question, then check.

In the last week before the examination, reading only the boxes of every chapter is a complete revision of the syllabus.

MTA Team

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PART I

Class 11

CHAPTER 1

Some Basic Concepts of Chemistry (Mole Concept)

Every calculation in physical chemistry starts here: counting particles by weighing them. The chapter fixes the units (amu, mole, molar mass), the ways of expressing concentration, and the two working tools — stoichiometry with the limiting reagent, and the principle of atom conservation (POAC) — that are used again in redox, solutions, equilibrium and electrochemistry.

1.1 Sub-atomic particles and atoms

Fundamental particles

	Proton	Neutron	Electron	
Mass	1.672×10^{-27} kg	1.674×10^{-27} kg	9.1×10^{-31} kg	$e = 1.6 \times 10^{-19}$ C
Charge	$+1e$	0	$-1e$	

Representation of an atom: ${}^A_ZX$, where A = mass number = (number of protons + number of neutrons) and Z = atomic number = number of protons.

Important definitions

- Isotopes:** atoms with the same atomic number (Z) but different mass number (A): ${}^1_1\text{H}$, ${}^2_1\text{H}$, ${}^3_1\text{H}$; ${}^{35}_{17}\text{Cl}$, ${}^{37}_{17}\text{Cl}$.
- Molecule:** a particle that contains two or more atoms bonded chemically: H_2 , CO_2 , $\text{C}_6\text{H}_{12}\text{O}_6$.
- Atomicity:** the total number of atoms in one molecule (defined only for molecules). H_2 : 2; NH_3 : 4; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$: $1 + 1 + 4 + 5(3) = 21$.
- Element:** a pure substance that contains only one type of atom. All elements have different atomic numbers; some have two or more isotopes; some exist as atoms (He , C), others as molecules (H_2 , N_2 , O_2 , halogens X_2 , P_4 , S_8).
- Compound:** a pure substance containing two or more elements in a fixed ratio by mass: H_2O , $\text{C}_6\text{H}_{12}\text{O}_6$, NH_2CONH_2 . All molecules of a particular compound are identical.

1.2 Laws of chemical combination

The five laws (NCERT)

- Conservation of mass** (Lavoisier): matter is neither created nor destroyed in a chemical reaction.
- Definite proportions** (Proust): a given compound always contains the same elements in the same proportion by mass, whatever its source.
- Multiple proportions** (Dalton): when two elements form more than one compound, the masses of one element that combine with a fixed mass of the other are in a simple whole-number ratio (H_2O and H_2O_2 : $16 : 32 = 1 : 2$ of O per 2 g H).
- Gay-Lussac's law of gaseous volumes:** gases combine (and gaseous products form) in a simple ratio by volume at the same T and p : $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$, $1 : 1 : 2$.
- Avogadro's law:** equal volumes of all gases at the same T and p contain equal numbers of molecules.

1.3 The mole

Mole and Avogadro's number

One mole of any substance contains as many unit particles as there are atoms in exactly 12 g of the ^{12}C isotope:

$$1 \text{ mol} = 6.023 \times 10^{23} = N_A \text{ (Avogadro's number, } N_0\text{)}$$

(The 2019 SI definition fixes $N_A = 6.022\,140\,76 \times 10^{23} \text{ mol}^{-1}$ exactly; 6.022 or 6.023×10^{23} is used in questions.)

$$\text{Number of moles } n = \frac{\text{number of unit particles}}{6.023 \times 10^{23}} \implies \boxed{\text{Number of unit particles} = n \times N_A}$$

Example 1.1 Find the total number of atoms in $\frac{3}{4}$ mol of CO_2 .

Solution. 1 mol CO_2 contains $3N_A$ atoms, so $\frac{3}{4}$ mol contains $\frac{3}{4} \times 3N_A = \frac{9}{4}N_A = 2.25 \times 6.023 \times 10^{23} = 1.355 \times 10^{24}$ atoms.

Answer: $\frac{9}{4}N_A \approx 1.36 \times 10^{24}$ atoms

Gram-atom, gram-molecule, gram-ion

These are older names for a mole of the particle named: 5 gram-ion $\text{Na}^+ = 5 \text{ mol Na}^+$; 5 gram-atom He = 5 mol He; 5 gram-molecule $\text{NH}_3 = 5 \text{ mol NH}_3$.

1.4 Atomic mass, molecular mass and molar mass

Relative atomic and molecular mass (unitless)

“Atomic mass” and “relative atomic mass” mean the same thing and are unitless:

$$\text{Atomic mass} = \frac{\text{mass of 1 atom of the element}}{\frac{1}{12}(\text{mass of 1 atom of C-12})} \quad \text{Molecular mass} = \frac{\text{mass of 1 molecule}}{\frac{1}{12}(\text{mass of 1 C-12 atom})}$$

Atomic mass unit (amu, u)

A unit of mass used for very small masses: $1 \text{ amu} = \frac{1}{12}(\text{mass of 1 atom of C-12}) = \frac{1}{12}(1.99 \times 10^{-23} \text{ g})$

$$\boxed{1 \text{ amu} = 1.66 \times 10^{-24} \text{ g} = \frac{1}{6.023 \times 10^{23}} \text{ g} = \frac{1}{N_A} \text{ g}} \quad (\text{relation between amu and } N_A)$$

Since atomic mass = $\frac{\text{mass of 1 atom}}{1 \text{ amu}}$: mass of 1 atom = (atomic mass of that element) amu; mass of 1 molecule = (molecular mass) amu.

Molar mass (M)

The molar mass of a substance is the mass of 1 mol of it, i.e. the mass of N_A particles. Mass of 1 molecule $\text{H}_2\text{O} = 18 \text{ amu}$, so mass of N_A molecules = $18 (N_A \times \text{amu}) = 18 \text{ g mol}^{-1}$. **Unit of molar mass:** g mol^{-1} .

Calculation of moles

$$\text{Number of unit particles} \xrightarrow[\times N_A]{\div N_A} \text{Moles} \xrightarrow[\div M]{\times M} \text{Mass of substance (g)}$$

$$n = \frac{N}{N_A} = \frac{w}{M} = \frac{V_{\text{gas at STP}}}{22.4 \text{ L}} \text{ (old STP)} = \frac{pV}{RT}$$

1.5 Ideal gas equation and STP

Ideal gas

A gas that obeys $pV = nRT$ (p pressure, V volume of gas/container, n moles, T in kelvin, R universal gas constant).

Values of R : $0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \approx \frac{1}{12}$; $8.314 \text{ J K}^{-1} \text{ mol}^{-1} \approx \frac{25}{3}$; $2 \text{ cal K}^{-1} \text{ mol}^{-1}$ (more exactly 1.987).

Different forms: $pV = nRT$; $pM = dRT$ (M molar mass, d density); $p = CRT$ (C concentration of gas in mol L^{-1}).

Unit conversions

Volume: $1 \text{ L} = 10^{-3} \text{ m}^3 = 1 \text{ dm}^3 = 1000 \text{ mL} = 1000 \text{ cc} = 1000 \text{ cm}^3$ (cc = mL = cm^3).

Pressure: $1 \text{ atm} = 1.01325 \times 10^5 \text{ N m}^{-2} = 1.01325 \text{ bar} = 760 \text{ torr} = 760 \text{ mm Hg}$; $1 \text{ Pa} = 9.869 \times 10^{-6} \text{ atm}$; $1 \text{ bar} = 10^5 \text{ Pa}$.

Useful values of RT ($R = 0.0821$, in L atm mol^{-1}): at 0°C 22.4; at 25°C 24.46; at 27°C 24.6.

STP/NTP for an ideal gas

Old convention: $T = 0^\circ\text{C}$, $p = 1 \text{ atm}$ New (IUPAC) convention: $T = 0^\circ\text{C}$, $p = 1 \text{ bar}$

$V_{1\text{mol}} = 22.4 \text{ L}$

$V_{1\text{mol}} = 22.7 \text{ L}$

$V_{\text{gas}} = (n \times 22.4) \text{ L}$

$V_{\text{gas}} = (n \times 22.7) \text{ L}$

(n = moles of gas at STP)

$V/22.4$ is only for gases

The relation $n = V/22.4$ holds only for a gas at STP. For a liquid or solid use mass = volume $\times$ density, then $n = w/M$.

Example 1.2 Calculate the number of moles in 11.2 L of $\text{H}_2\text{O}(\text{l})$.

Solution. Water is a liquid, so $n = V/22.4$ is not valid. $V = 11.2 \times 1000 = 11\,200 \text{ mL}$; generally $d_{\text{water}} = 1 \text{ g mL}^{-1}$, so mass = $V \times d = 11\,200 \text{ g}$ and

$$n = \frac{11\,200}{18} = 622.22 \text{ mol.}$$

Answer: 622.22 mol (not 0.5 mol)

1.6 Specific gravity, vapour density and average masses

Specific gravity (solids and liquids only)

$$(\text{SG})_{\text{substance}} = \frac{\text{density of substance}}{\text{density of water at } 4^\circ\text{C}}$$

Unitless. Since $\rho_{\text{H}_2\text{O}}$ at $4^\circ\text{C} = 1 \text{ g mL}^{-1}$, SG is numerically equal to the density in g mL^{-1} .

Vapour density (gases only)

$$(\text{VD})_{\text{gas}} = \frac{\text{density of gas at some } T, p}{\text{density of H}_2 \text{ gas at the same } T, p}$$

Unitless. For an ideal gas $pM = dRT$, so $\text{Molar mass of gas} = 2 \times (\text{VD}) \text{ g mol}^{-1}$.

Average molar mass of a gaseous mixture

Defined only for a gaseous mixture (which is always homogeneous). For n_1 mol of A and n_2 mol of B:

$$M_{\text{mix}} = \frac{(\text{given mass})_{\text{mix}}}{n_{\text{mix}}} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}, \quad n_{\text{mix}} = n_1 + n_2.$$

Air ($\approx 80\% \text{ N}_2$, $20\% \text{ O}_2$ by moles): $M \approx 0.8(28) + 0.2(32) = 28.8 \text{ g mol}^{-1}$.

Average atomic mass

Defined for elements that have two or more isotopes with *comparable* abundance in nature:

$$M_{\text{avg}} = \frac{m_1 x_1 + m_2 x_2 + \cdots + m_n x_n}{100}$$

$m_1, m_2, \dots$ masses of the isotopes; $x_1, x_2, \dots$ their percentage abundances. ^1H ($\approx 99\%$), ^2H ($\approx 1\%$): not comparable, the average is simply ≈ 1 . ^{35}Cl ($\approx 75\%$), ^{37}Cl ($\approx 25\%$), ratio 3 : 1: comparable.

Example 1.3 Find the average atomic mass of chlorine (^{35}Cl 75%, ^{37}Cl 25%).

Solution. $M_{\text{avg}} = \frac{75(35) + 25(37)}{100} = 35.5 \text{ g mol}^{-1}$.

Answer: 35.5

Example 1.4 Boron has two isotopes, ^{10}B and ^{11}B , and an average atomic mass of 10.81. Find the percentage of ^{10}B .

Solution. Let $x\%$ be ^{10}B : $10x + 11(100 - x) = 1081 \Rightarrow x = 19\%$.

Answer: 19% ^{10}B , 81% ^{11}B

1.7 Percentage composition, empirical and molecular formula

Definitions

Mass per cent of an element = $\frac{\text{mass of that element in 1 mol of compound}}{\text{molar mass of compound}} \times 100$.

Molecular formula (MF): shows the exact number of atoms of each element in one molecule. **Empirical formula (EF):** shows the simplest ratio of atoms. H_2O_2 : MF; HO: EF. $\text{C}_6\text{H}_{12}\text{O}_6$: MF; CH_2O : EF. The MF and EF may or may not be the same.

$$\text{MF} = (\text{EF})_x, \quad x = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

Finding the EF: (1) convert the given amount of every element into moles of its atoms; (2) find the simplest whole-number ratio of these moles. (If a ratio ends in .5, .33 or .25, multiply all by 2, 3 or 4.)

Example 1.5 6.4 g of a compound of H and N contains 0.8 g of hydrogen. Determine its empirical formula.

Solution. $(\text{mass})_{\text{H}} = 0.8 \text{ g}$, $(\text{mass})_{\text{N}} = 6.4 - 0.8 = 5.6 \text{ g}$. $n_{\text{H}} = 0.8/1 = 0.8 \text{ mol}$, $n_{\text{N}} = 5.6/14 = 0.4 \text{ mol}$. $n_{\text{H}} : n_{\text{N}} = 0.8 : 0.4 = 2 : 1$.

Answer: NH_2

Example 1.6 In a compound C, H and N are present in the ratio 9 : 1 : 3.5 by weight. Its molecular mass is 108. Find its molecular formula.

Solution. C: $9/12 = 0.75$; H: $1/1 = 1$; N: $3.5/14 = 0.25$. Dividing by 0.25: C : H : N = 3 : 4 : 1. EF = C_3H_4N , EF mass = $36 + 4 + 14 = 54$. $x = 108/54 = 2$, so MF = $C_6H_8N_2$.

Answer: $C_6H_8N_2$

Example 1.7 The ratio of mass per cent of C and H in an organic compound $C_xH_yO_z$ is 6 : 1. If one molecule of the compound contains half as much oxygen as is required to burn one molecule of C_xH_y completely to CO_2 and H_2O , find the empirical formula. [JEE Main 2018]

Solution. $C_xH_y + (x + y/4)O_2 \longrightarrow xCO_2 + y/2 H_2O$. Oxygen atoms required to burn $C_xH_y = 2(x + \frac{y}{4})$; oxygen present in the compound $z = \frac{1}{2} \cdot 2(x + \frac{y}{4}) = x + \frac{y}{4}$.

Mass ratio $\frac{12x}{y} = \frac{6}{1} \Rightarrow y = 2x$. Taking $x = \frac{1}{2}$: $y = 1$ and $z = \frac{1}{2} + \frac{1}{4} = \frac{3}{4}$. So C : H : O = $\frac{1}{2} : 1 : \frac{3}{4} = 2 : 4 : 3$ (multiplying by 4).

Answer: $C_2H_4O_3$

1.8 Concentration terms

Ways of expressing concentration		
Term	Formula	Unit / remark
1. Mole fraction	$x_A = \frac{n_A}{n_A + n_B + n_C}$ (and so on)	$x_A + x_B + x_C = 1$; mole % = $x_A \times 100$
2. % w/w (mass %)	$\frac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 100$	unitless
3. % v/v	$\frac{\text{vol. of solute (mL)}}{\text{vol. of solution (mL)}} \times 100$	unitless
4. % w/v	$\frac{\text{mass of solute (g)}}{\text{vol. of solution (mL)}} \times 100$	g per 100 mL
5. ppm	$\frac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 10^6$	very dilute solutions
6. ppb	$\frac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 10^9$	
7. Molarity M	$\frac{n_{\text{solute}}}{V_{\text{solution (in L)}}$	mol L^{-1} , molar, M
8. Molality m	$\frac{n_{\text{solute}}}{\text{mass of solvent (in kg)}}$	mol kg^{-1} , molal

What each statement tells you

- Solution with $x_{\text{solute}} = 0.3$: 3 mol solute with $(10 - 3) = 7$ mol solvent.
- 20% H_2SO_4 solution by mass: 20 g H_2SO_4 in 100 g solution, i.e. $100 - 20 = 80$ g solvent.
- 30% v/v $FeSO_4$ solution: 30 mL $FeSO_4$ and 70 mL solvent in 100 mL.
- 20% w/v HNO_3 : 100 mL solution has 20 g HNO_3 ; you can say nothing about the amount of solvent.
- Molarity changes with temperature (volume changes); molality, mole fraction and mass % do not.

Inter-conversions (learn these)

For a solution of density d (g mL^{-1}), molar mass of solute M_B , of solvent M_A :

$$M = \frac{10 \times (\% w/w) \times d}{M_B}, \quad m = \frac{1000 M}{1000 d - M M_B}, \quad x_B = \frac{m M_A}{1000 + m M_A} \iff m = \frac{1000 x_B}{(1 - x_B) M_A}.$$

Example 1.8 Find the molarity of HNO_3 in a sample of density 1.4 g mL^{-1} and mass per cent 63%.

Solution. 100 g solution has 63 g HNO_3 . Volume = $\frac{\text{mass}}{d} = \frac{100}{1.4} \text{ mL}$.

$$M = \frac{n_{\text{HNO}_3}}{V_{\text{soln}} (\text{L})} = \frac{63/63}{\frac{100}{1.4} \times \frac{1}{1000}} = 14 \text{ mol L}^{-1}.$$

Shortcut: $M = \frac{10 \times 63 \times 1.4}{63} = 14$.

Answer: 14 M

Example 1.9 Find the molality and mole fraction of glucose in a 1 M aqueous solution of density 1.2 g mL^{-1} .

Solution. 1 L solution: mass 1200 g, glucose 1 mol = 180 g, water 1020 g. $m = \frac{1}{1.020} = 0.98 \text{ mol kg}^{-1}$. $x_{\text{glucose}} = \frac{1}{1 + 1020/18} = \frac{1}{57.67} = 0.0173$.

Answer: 0.98 m, $x = 0.0173$

1.9 Dilution and mixing of solutions

Dilution

Adding extra solvent is dilution. As the amount of solvent changes, all the concentration terms change. The best approach is to convert all concentration terms into molarity and then use the relation. Since the moles of solute do not change on dilution,

$$M_1 V_1 = M_2 V_2 \quad M_1, V_1 \text{ before; } M_2, V_2 \text{ after dilution.}$$

Mixing of solutions

For solutions 1, 2, ... mixed to give the final solution: $V_f = V_1 + V_2 + V_3 + \dots$ (only for non-reacting ideal solutions); $W_f = W_1 + W_2 + W_3 + \dots$ (always). For any component

$$[X] = \frac{(n_X)_{\text{total}}}{V_{\text{final}}}, \quad \text{e.g. } M_f = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2} \text{ (same solute).}$$

Example 1.10 10 L of 0.1 M NaOH solution is mixed with 20 L of 0.2 M $\text{Ba}(\text{OH})_2$ solution. Find the final molarity of OH^- .

Solution. NaOH: $n_{\text{OH}^-} = 1 \times (10 \times 0.1) = 1 \text{ mol}$. $\text{Ba}(\text{OH})_2$: $n_{\text{OH}^-} = 2 \times (20 \times 0.2) = 8 \text{ mol}$. $(n_{\text{OH}^-})_{\text{total}} = 9 \text{ mol}$, $V = 30 \text{ L}$, $[\text{OH}^-] = 9/30 = 0.3 \text{ M}$.

Answer: 0.3 M

1.10 Stoichiometry

Mole ratio

For a particular reaction, e.g. $A + 2B \longrightarrow 3C + 4D$, the ratio of the stoichiometric coefficients is fixed. This ratio is also the **molar ratio** in which reactants react and products are formed: $\frac{n_A}{1} = \frac{n_B}{2} = \frac{n_C}{3} = \frac{n_D}{4}$ (amounts reacted or formed).

Example 1.11 25 mL of a solution of Ba(OH)_2 on titration with 0.1 M HCl gave a titre value of 35 mL. Find the molarity of Ba(OH)_2 .

Solution. Titre value = volume used for complete titration. $\text{Ba(OH)}_2 + 2\text{HCl} \longrightarrow \text{BaCl}_2 + 2\text{H}_2\text{O}$: 2 mol HCl consume 1 mol Ba(OH)_2 . $35 \times 0.1 = 3.5 \text{ mmol HCl}$ react with $\frac{1}{2} \times 3.5 = 1.75 \text{ mmol Ba(OH)}_2$. $[\text{Ba(OH)}_2] = \frac{35 \times 0.1}{2 \times 25} = 0.07 \text{ M}$.

Answer: 0.07 M

Example 1.12 Ammonia released on quantitative reaction of 0.6 g urea with NaOH can be neutralised by:

(a) 200 mL of 0.4 M HCl

(b) 200 mL of 0.2 M HCl

(c) 100 mL of 0.2 M HCl

(d) 100 mL of 0.1 M HCl

Solution. $\text{NH}_2\text{CONH}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{CO}_3 + 2\text{NH}_3$ ($\text{CO}_2 + \text{H}_2\text{O} + 2\text{NH}_3$ on hydrolysis). 1 mol = 60 g urea gives 2 mol NH_3 ; 0.6 g gives $\frac{2}{60} \times 0.6 = 0.02 \text{ mol NH}_3$, which needs 0.02 mol H^+ . Option (c): $0.1 \times 0.2 = 0.02 \text{ mol}$.

Answer: (c)

1.11 Limiting reagent and per cent yield

Limiting reagent (LR)

Applicable only to reactions with two or more reactants. The reactant that is used up first is the **limiting reagent**; it decides the amount of product.

Finding the LR: (1) balance the equation; (2) for every reactant calculate $\frac{\text{initial moles}}{\text{stoichiometric coefficient}}$; (3) the species with the least value of this ratio is the LR.

$$\% \text{ yield} = \frac{\text{observed (experimental) amount}}{\text{theoretical amount}} \times 100$$

Example 1.13 10 L of N_2 and 40 L of H_2 react to give NH_3 at constant T and p . Calculate the change in volume if the reaction goes to 50% (of the limiting reagent).

Solution. $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$. Ratios: N_2 $10/1 = 10$, H_2 $40/3 = 13.3$, so N_2 is the LR. At 100%: 0, 10, 20 L. At 50%: N_2 5 L, H_2 $40 - 15 = 25 \text{ L}$, NH_3 10 L; total 40 L. $\Delta V = 50 - 40 = 10 \text{ L}$ (decrease).

Answer: 10 L decrease

1.12 Problems involving mixtures

Method

If a mixture is treated with some external compound, analyse its reaction with each component separately. For $(A + C + D) + B$: $A+B$ reacts, $C+B$ no reaction, $D+B$ reacts — write one equation for each component that reacts and add the amounts.

Example 1.14 A 40 g sample of impure CaCO_3 gives 11 g CO_2 on strong heating. Find the mass per cent of CaCO_3 in the mixture.

Solution. Let x g be CaCO_3 (the rest does not give CO_2). $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$; $\frac{x}{100} = \frac{11}{44} = \frac{1}{4}$ mol, so $x = 25$ g and $\% \text{CaCO}_3 = \frac{25}{40} \times 100 = 62.5\%$.

Answer: 62.5%

Example 1.15 Some effervescent tablets containing sodium bicarbonate and oxalic acid release 0.25 mL of CO_2 at 298.15 K and 1 bar per tablet. If the molar volume of CO_2 is 25 L under these conditions, find the percentage of NaHCO_3 in each tablet (mass of a tablet 10 mg).

Solution. $2\text{NaHCO}_3 + \text{H}_2\text{C}_2\text{O}_4 \longrightarrow \text{Na}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2$. $n_{\text{CO}_2} = \frac{0.25}{25 \times 1000} = 1 \times 10^{-5} \text{ mol} = n_{\text{NaHCO}_3}$.
Mass of $\text{NaHCO}_3 = 84 \times 10^{-5} \text{ g}$; $\% = \frac{84 \times 10^{-5}}{10 \times 10^{-3}} \times 100 = 8.4\%$.

Answer: 8.4%

1.13 Principle of atom conservation (POAC)

POAC

In a chemical reaction the atoms of every element are conserved. Thus, for an element,

Moles of its atoms before reaction = Moles of its atoms after reaction

(moles of compound) $\times$ (atoms of the element per formula unit) = same, summed over the products

POAC lets you skip balancing: apply it to an element that ends up in a single product.

Example 1.16 x mol of O_2 is converted to O_3 . How many moles of O_3 are produced?

Solution. By POAC on O: $n_{\text{O}_2} \times 2 = n_{\text{O}_3} \times 3 \Rightarrow 2x = 3n_{\text{O}_3}$, $n_{\text{O}_3} = \frac{2x}{3}$.

Answer: $\frac{2x}{3}$ mol

Example 1.17 A 13.8 g sample of K_2CO_3 was treated so that all its carbon was captured in the compound $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$. Find the mass of this product. (K 39, Zn 65.4, Fe 56)

Solution. POAC on C: $n_{\text{K}_2\text{CO}_3} \times 1 = n_{\text{product}} \times 12$. $n_{\text{K}_2\text{CO}_3} = \frac{13.8}{138} = 0.1$, so $n_{\text{product}} = \frac{0.1}{12}$. Molar mass of $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 = 2(39) + 3(65.4) + 2(56) + 12(12) + 12(14) = 698.2 \text{ g mol}^{-1}$.

$$x = \frac{0.1}{12} \times 698.2 = 5.82 \text{ g.}$$

Answer: 5.82 g

Molar mass of the complex

Count every atom: $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ has 2 K, 3 Zn, 2 Fe, 12 C and 12 N. Its molar mass is about 698, not 638; using 638 gives the wrong answer 5.32 g.

Example 1.18 On complete combustion, 0.1 g of an organic compound gave 0.176 g CO_2 and 0.18 g H_2O . Find the percentage composition of C and H in the compound.

Solution. $\text{C}_x\text{H}_y \xrightarrow{\Delta} \text{CO}_2 + \text{H}_2\text{O}$. POAC on C: $\left(\frac{0.1}{M_w}\right)x = \left(\frac{0.176}{44}\right) \times 1 \Rightarrow \frac{x}{M_w} = 0.04$. POAC on H: $\left(\frac{0.1}{M_w}\right)y = \left(\frac{0.18}{18}\right) \times 2 \Rightarrow \frac{y}{M_w} = 0.20$. So $\frac{x}{y} = \frac{0.04}{0.20} = \frac{1}{5}$: by number of atoms C = $\frac{1}{6} \times 100 = 16.67\%$, H = $\frac{5}{6} \times 100 = 83.33\%$.

By mass (what “percentage composition” means): mass of C = $\frac{12}{44} \times 0.176 = 0.048$ g, i.e. 48%; mass of H = $\frac{2}{18} \times 0.18 = 0.02$ g, i.e. 20%. These add to 68% only, so the compound is not a hydrocarbon: the remaining 32% is another element (oxygen, found by difference).

Answer: C 48%, H 20% by mass (atom ratio C : H = 1 : 5)

Percentage of elements from combustion (Liebig)

$$\% \text{C} = \frac{12}{44} \times \frac{\text{mass of CO}_2}{\text{mass of compound}} \times 100, \quad \% \text{H} = \frac{2}{18} \times \frac{\text{mass of H}_2\text{O}}{\text{mass of compound}} \times 100$$

1.14 Volume strength of H_2O_2

Volume strength

The volume of $\text{O}_2(\text{g})$ (in L) produced at STP by complete decomposition of 1 L of H_2O_2 solution:

$$\text{VS} = \frac{\text{vol. of O}_2 \text{ produced (in L) at STP}}{\text{vol. of H}_2\text{O}_2 \text{ solution taken (in L)}} \quad (\text{unitless; used only for H}_2\text{O}_2)$$

From $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$: 1 L of M molar H_2O_2 gives $M/2$ mol O_2 :

$$\boxed{\text{VS} = 11.2 \times \text{Molarity}} \quad (\text{old STP}), \quad \boxed{\text{VS} = 11.35 \times \text{Molarity}} \quad (\text{new STP}).$$

Example 1.19 Find the molarity and the strength in g L^{-1} of “20 volume” H_2O_2 (old STP).

Solution. $M = \frac{20}{11.2} = 1.786 \text{ M}$; strength = $1.786 \times 34 = 60.7 \text{ g L}^{-1}$ (about 6% w/v).

Answer: 1.79 M, 60.7 g L^{-1}

1.15 Eudiometry (gas analysis)

Principle

Used for reactions having at least one gaseous component. Reactions are carried out at constant temperature and pressure; until something else is given, take room temperature (25°C) and atmospheric pressure (1 atm).

At constant T and p , $pV = nRT$ gives

$$n \propto V \quad \Rightarrow \quad \text{molar ratio} = \text{volume ratio.}$$

Assumptions: (1) $V_{\text{solid}} < V_{\text{liquid}} \ll V_{\text{gas}}$, so the volumes of solids and liquids are neglected and only the volume due to gases is considered; (2) air is taken as a mixture of N_2 and O_2 only; (3) unless given, N_2 is inert; (4) unless given, room temperature is assumed, so H_2O is always a liquid.

Balanced reaction for combustion: $\text{C}_x\text{H}_y + (x + y/4)\text{O}_2 \longrightarrow x\text{CO}_2 + y/2\text{H}_2\text{O}$

Absorbents: some substances absorb particular gases when the gas is passed through them.

Substance	Gas absorbed
aq. KOH / aq. NaOH	$\text{CO}_2(\text{g})$ (also SO_2)
alkaline pyrogallol	$\text{O}_2(\text{g})$
turpentine oil	$\text{O}_3(\text{g})$
$\text{H}_2\text{O}(\text{l})$	$\text{NH}_3(\text{g})$, $\text{HCl}(\text{g})$
anhydrous CaCl_2 or anhydrous CuSO_4	$\text{H}_2\text{O}(\text{g})$
ammoniacal Cu_2Cl_2	$\text{CO}(\text{g})$

Example 1.20 10 mL of a gaseous hydrocarbon is exploded with 80 mL O_2 . On cooling, the volume is 65 mL; on passing through KOH it falls to 45 mL. Find the formula of the hydrocarbon.

Solution. CO_2 formed = $65 - 45 = 20 \text{ mL} = 10x \Rightarrow x = 2$. Contraction on combustion (water condenses): $10 + 80 - 65 = 25 \text{ mL}$; for C_xH_y , contraction per mL = $1 + \frac{y}{4}$, so $10(1 + \frac{y}{4}) = 25 \Rightarrow y = 6$. O_2 used = $10(2 + 1.5) = 35 \text{ mL}$; left 45 mL, consistent.

Answer: C_2H_6