Chemistry Units 1 & 2

Chapter 6 — Quantifying atoms and compounds

Contents

Chapter 6 Quantifying atoms and compounds — 6A Relative atomic and isotopic mass

Theory

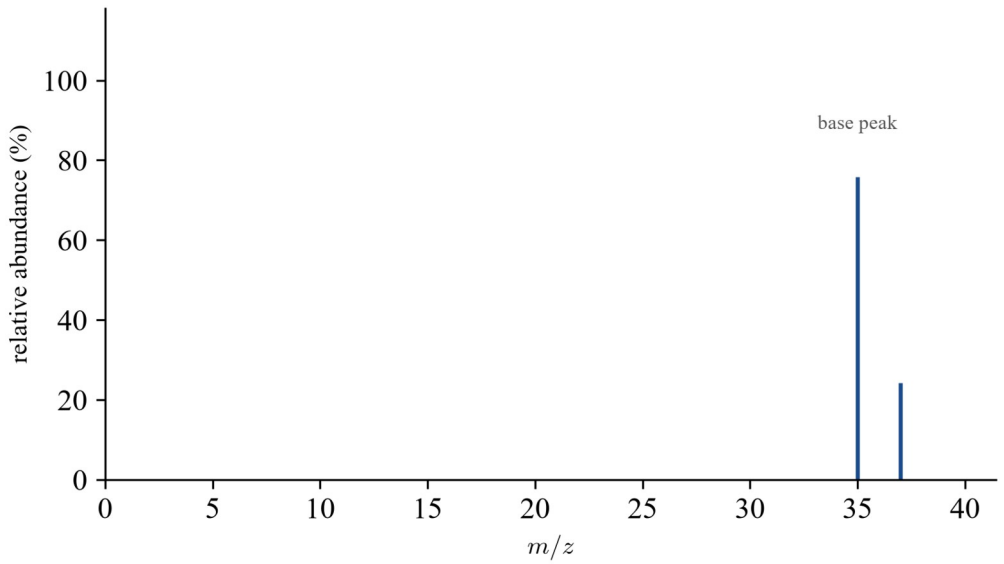
Atoms are far too small and far too light to weigh one at a time in grams — a single chlorine atom has a mass of about $5.8 \times 10^{-23}\,\text{g}$. Rather than work with such tiny numbers, chemists compare the masses of atoms with one another on a *relative* scale. This subtopic sets up that scale, shows how the instrument called a **mass spectrometer** reveals the isotopes present in an element, and uses the data it produces to calculate the **relative atomic mass** of an element as an abundance-weighted average.

The carbon-12 scale. The whole scale of atomic masses is fixed by a single agreement: one atom of the **carbon-12** isotope is assigned a mass of **exactly 12**. Every other atomic mass is then expressed *relative* to that reference. Because each value is really a ratio — the mass of an atom compared with one-twelfth of the mass of a carbon-12 atom — the numbers on this scale are **pure ratios and carry no units**. Carbon-12 is the *only* isotope whose value is a whole number by definition; the values for all other isotopes are measured against it.

Relative isotopic mass. The **relative isotopic mass** of an isotope is the mass of one atom of that isotope on the scale where carbon-12 is exactly 12. Its value is always *close to* the isotope's mass number, but — apart from carbon-12 itself, which is exactly 12 by definition — never exactly equal to it. For example, chlorine-35 has a relative isotopic mass of 34.97 (not exactly 35), and chlorine-37 has a relative isotopic mass of 36.97. In an introductory calculation the mass number is often used as a good approximation, but the more precise relative isotopic masses are what a mass spectrometer actually measures, and they are what we use here. Like every quantity on this scale, a relative isotopic mass has **no units**.

Isotopes and the mass of an element. Recall that the atoms of an element all have the same number of protons but may have different numbers of neutrons; these different versions are the element's **isotopes**. Most elements occur naturally as a *mixture* of isotopes present in fixed proportions. This raises a question: if a sample of chlorine is a mixture of chlorine-35 and chlorine-37 atoms, what single mass should we use for "chlorine"? The answer is an **average** — but an average that gives more weight to the isotopes that are more plentiful. That weighted average is the element's **relative atomic mass**, A_r. It is essential to keep the two terms apart: a *relative isotopic mass* describes **one** isotope, whereas the *relative atomic mass* describes the **element** as a whole.

The mass spectrometer and the mass spectrum. To find the proportions of the isotopes we need an instrument that can sort the atoms of a sample by mass and count how many there are of each. A **mass spectrometer** does exactly this: it separates the atoms of a sample according to their mass and records how many atoms of each mass are present (the working of the instrument itself is not required here). Its output is a **mass spectrum** — a stick graph in which **each peak corresponds to one isotope**, the *position* of the peak fixes that isotope's mass, and the *height* of the peak gives that isotope's **relative abundance**. The mass spectrum of chlorine below shows just two peaks, confirming that chlorine has two isotopes.



Reading a mass spectrum. The horizontal axis is the **mass-to-charge ratio**, m/z. The atoms are detected as ions carrying a single positive charge, so $z = 1$ and each peak's m/z value is numerically equal to the mass of that isotope; in the chlorine spectrum the peaks therefore sit at $m/z = 35$ and $m/z = 37$. The vertical axis is the **relative abundance**. The tallest peak in a spectrum is called the **base peak**; for an element, the base peak marks the *most abundant* isotope (here, chlorine-35). Abundances may be presented in two ways:

- as **percentage abundances** that add up to 100 (the chlorine peaks are 75.8% and 24.2%); or
- as **relative peak heights** measured against the tallest peak (which is set to 100), in which case the heights do **not** add to 100 and must first be converted.

To turn any set of peak heights into **fractional abundances**, divide each height by the *total* of all the heights. A percentage abundance is converted to a fraction simply by dividing by 100. The fractional abundances of all the isotopes always add up to 1.

Calculating the relative atomic mass. The relative atomic mass is the average of the relative isotopic masses, each weighted by how common that isotope is:

$$A_r = \sum(\text{relative isotopic mass} \times \text{fractional abundance})$$

Writing $m_1, m_2, \ldots$ for the relative isotopic masses and $f_1, f_2, \ldots$ for the matching fractional abundances,

$$A_r = m_1 f_1 + m_2 f_2 + \cdots$$

If the abundances are given as percentages $p_1, p_2, \ldots$ it is often tidier to weight by the percentages and divide by 100 at the end:

$$A_r = \frac{m_1 p_1 + m_2 p_2 + \cdots}{100}$$

For chlorine, $A_r = 34.97 \times 0.758 + 36.97 \times 0.242 = 35.45$. Two features of this result are worth noting and always hold. First, because it is a *weighted* average of two or more different masses, A_r is almost never a whole number. Second, the average is pulled towards the mass of the **most abundant** isotope: chlorine's value of 35.45 lies much nearer 35 than 37 because chlorine-35 makes up about three-quarters of all chlorine atoms. And, like everything on this scale, A_r has **no units**. These are the A_r values printed for each element on the periodic table.

Working backwards from a known A_r. The weighted-average relationship can also be used in reverse: if the relative atomic mass and the isotope masses are known, an *unknown abundance* can be found. For an element with just two isotopes, let the fractional abundance of the first be x; the second must then be $(1 - x)$, and

$$m_1 x + m_2(1 - x) = A_r$$

is a single linear equation that is solved for x. For an element with three isotopes, *two* unknown abundances can be found provided the third one is known: the weighted-average equation and the fact that the fractions add to 1 give the two equations needed, which are then solved together. (If two of the three abundances are already known, the third follows from the fractions summing to 1 on its own.) Setting up the weighted-average equation and solving for the missing fraction is the key skill in these "reverse" problems.

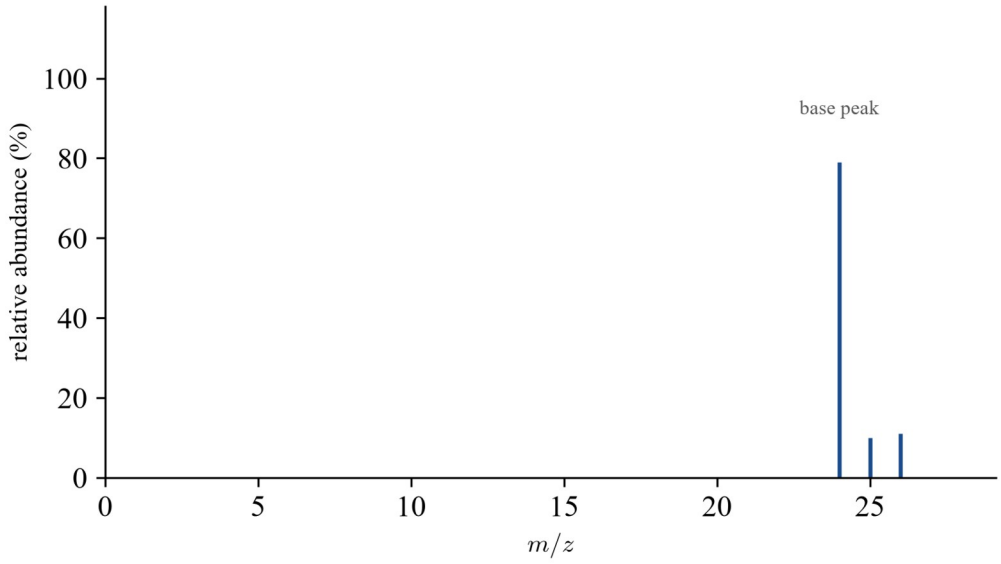
Worked examples

Worked Example 1 — The mass spectrum of chlorine (shown above) has two peaks: one at $m/z = 35$ with a relative abundance of 75.8%, and one at $m/z = 37$ with a relative abundance of 24.2%. The relative isotopic masses of the two isotopes are 34.97 (chlorine-35) and 36.97 (chlorine-37). Calculate the relative atomic mass of chlorine.

Working	Comment
Two peaks → two isotopes: chlorine-35 (mass 34.97, 75.8%) and chlorine-37 (mass 36.97, 24.2%).	Each peak is one isotope; its position gives the mass and its height gives the abundance.

Working	Comment
$f_{35} = \frac{75.8}{100} = 0.758,\ f_{37} = \frac{24.2}{100} = 0.242$	Convert each percentage to a fractional abundance by dividing by 100; the fractions sum to 1.
$A_r = (34.97 \times 0.758) + (36.97 \times 0.242)$	Weighted average: each relative isotopic mass multiplied by its fractional abundance.
$= 26.507 + 8.947 = 35.454$	Add the weighted contributions.
$A_r = 35.45$ (no units)	Quote to 4 significant figures; a ratio, so no units. The value lies near 35, the mass of the more abundant isotope.

Worked Example 2 — The mass spectrum of magnesium is shown below. Magnesium has three isotopes, with relative abundances of 78.99% at $m/z = 24$, 10.00% at $m/z = 25$ and 11.01% at $m/z = 26$. Taking the relative isotopic masses as 23.99, 24.99 and 25.98 respectively, calculate the relative atomic mass of magnesium.



Working	Comment
Three peaks → three isotopes (magnesium-24, -25 and -26).	The base peak at $m/z = 24$ is the most abundant isotope.
$f_{24} = 0.7899,\ f_{25} = 0.1000,\ f_{26} = 0.1101$	Divide each percentage by 100; check the fractions sum to $0.7899 + 0.1000 + 0.1101 = 1.0000$.
$A_r = (23.99 \times 0.7899) + (24.99 \times 0.1000) + (25.98 \times 0.1$	Weighted average over all three isotopes.
$= 18.950 + 2.499 + 2.860 = 24.309$	Sum the three weighted contributions.
$A_r = 24.31$ (no units)	4 significant figures; nearest to 24, the most abundant isotope.

Worked Example 3 — In the mass spectrum of bromine the two peaks, at $m/z = 79$ and $m/z = 81$, have relative peak heights of 100 and 97.3 (each measured against the taller peak). The relative isotopic masses are 78.92 (bromine-79) and 80.92 (bromine-81). Determine the relative atomic mass of bromine.

The peak heights are given relative to the tallest peak, so they do **not** add up to 100; they must first be converted to fractional abundances by dividing each height by the total height.

$$\text{total height} = 100 + 97.3 = 197.3$$

$$f_{79} = \frac{100}{197.3} = 0.5068,\ f_{81} = \frac{97.3}{197.3} = 0.4932$$

Now apply the weighted-average formula:

$$A_r = (78.92 \times 0.5068) + (80.92 \times 0.4932) = 40.00 + 39.91 = 79.91$$

$\therefore$ the relative atomic mass of bromine is 79.91 (no units). The two isotopes are almost equally abundant, so A_r sits roughly midway between 79 and 81.

Worked Example 4 — Antimony consists of two isotopes: antimony-121 (relative isotopic mass 120.90) and antimony-123 (relative isotopic mass 122.90). The relative atomic mass of antimony is 121.76. Determine the percentage abundance of each isotope.

Let the fractional abundance of antimony-121 be x; then the fractional abundance of antimony-123 is $(1 - x)$. Substituting into the weighted-average relationship,

$$120.90\,x + 122.90(1 - x) = 121.76$$

$$122.90 - 2.00\,x = 121.76$$

$$2.00\,x = 1.14 \Rightarrow x = 0.570$$

So antimony-121 has a fractional abundance of 0.570 and antimony-123 has $1 - 0.570 = 0.430$.

Check: $120.90 \times 0.570 + 122.90 \times 0.430 = 68.913 + 52.847 = 121.76$ ✓

$\therefore$ antimony-121 is **57.0%** abundant and antimony-123 is **43.0%** abundant.

Practice questions

Question 1 — This question is about the scale used for atomic masses.

a. State the isotope that defines the scale, and the value it is assigned.
b. Explain what is meant by the *relative isotopic mass* of an isotope.
c. Explain why a relative isotopic mass has no units.

Question 2 — Lithium has two isotopes: lithium-6 (relative isotopic mass 6.015, abundance 7.5%) and lithium-7 (relative isotopic mass 7.016, abundance 92.5%).

a. State the m/z value at which each isotope appears in the mass spectrum, and identify which peak is the base peak.
b. Calculate the relative atomic mass of lithium.
c. State the units of your answer to part b, and justify your statement.

Question 3 — Potassium has three isotopes. Their relative isotopic masses and percentage abundances are: potassium-39, 38.96, 93.26%; potassium-40, 39.96, 0.012%; potassium-41, 40.96, 6.73%.

a. Calculate the relative atomic mass of potassium.
b. State which isotope is the most abundant.
c. Explain why the relative atomic mass lies much closer to 39 than to 41.

Question 4 — Copper has two isotopes, copper-63 (relative isotopic mass 62.93) and copper-65 (relative isotopic mass 64.93). The relative atomic mass of copper is 63.55.

a. Taking the fractional abundance of copper-63 to be x, write an equation for the relative atomic mass in terms of x.
b. Solve your equation to find the percentage abundance of each isotope.
c. Verify your answer by using it to recalculate the relative atomic mass.

Question 5 — In the mass spectrum of gallium the peak at $m/z = 69$ has a relative height of 100 and the peak at $m/z = 71$ has a relative height of 65.8. The relative isotopic masses are 68.93 (gallium-69) and 70.92 (gallium-71).

a. Convert the two peak heights into fractional abundances.
b. Calculate the relative atomic mass of gallium.

c. State which isotope is the more abundant, and explain how the relative peak heights told you this.

Question 6 — Neon has three isotopes: neon-20 (relative isotopic mass 19.99, abundance 90.48%), neon-21 (relative isotopic mass 20.99, abundance 0.27%) and neon-22 (relative isotopic mass 21.99, abundance 9.25%).

a. Calculate the relative atomic mass of neon.
b. Explain why the value lies between 20 and 22 but very close to 20.
c. State what information the *height* of each peak in a mass spectrum provides.

Question 7 — Silver occurs as silver-107 (relative isotopic mass 106.91, abundance 51.84%) and silver-109 (relative isotopic mass 108.90, abundance 48.16%). Calculate the relative atomic mass of silver.

Question 8 — A mass spectrum of silicon shows three peaks corresponding to silicon-28 (relative isotopic mass 27.98, abundance 92.23%), silicon-29 (28.98, 4.67%) and silicon-30 (29.97, 3.10%). Calculate the relative atomic mass of silicon.

Question 9 — Rubidium has two isotopes, rubidium-85 (relative isotopic mass 84.91) and rubidium-87 (relative isotopic mass 86.91). The relative atomic mass of rubidium is 85.47. Determine the percentage abundance of each isotope.

Question 10 — A mass spectrum of an unknown element shows two peaks: $m/z = 113$ (relative isotopic mass 112.90, abundance 4.28%) and $m/z = 115$ (relative isotopic mass 114.90, abundance 95.72%). Calculate the relative atomic mass of the element, and use the periodic table to identify it.

Question 11 — The relative atomic mass of chlorine is 35.45, which is not a whole number. With reference to its mass spectrum, explain fully why the relative atomic mass of chlorine is not a whole number and why it lies closer to 35 than to 37.

Question 12 — A hypothetical element Q has three isotopes, appearing in its mass spectrum at $m/z = 63$, $m/z = 65$ and $m/z = 67$, with relative isotopic masses of 62.9, 64.9 and 66.9 respectively. The isotope at $m/z = 65$ makes up 20.0% of the atoms, and the relative atomic mass of element Q is 63.70. Determine the percentage abundance of the isotopes at $m/z = 63$ and $m/z = 67$.

Question 13 — Nitrogen has two isotopes: nitrogen-14 (relative isotopic mass 14.003, abundance 99.63%) and nitrogen-15 (relative isotopic mass 15.000, abundance 0.37%). Calculate the relative atomic mass of nitrogen, and explain why its value is so close to a whole number even though a relative atomic mass is usually not a whole number.

Question 14 — Argon has three isotopes, argon-36 (relative isotopic mass 35.97, abundance 0.337%), argon-38 (37.96, 0.063%) and argon-40 (39.96, 99.60%). Calculate the relative atomic mass of argon, and state which isotope its value lies closest to.

Question 15 — Europium consists of two isotopes, europium-151 (relative isotopic mass 150.92) and europium-153 (relative isotopic mass 152.92). Its relative atomic mass is 151.96. Determine the percentage abundance of each isotope.

Question 16 — A student claims that "the relative isotopic mass of carbon-12 is 12 grams, and every other isotope's mass is measured against it." Identify the two errors in this statement and rewrite it correctly, explaining in each case why the correction is needed.

Question 17 — The mass spectrum of an element M shows two peaks. The peak at $m/z = 84$ has a relative height of 100 and the peak at $m/z = 86$ has a relative height of 32.5. The relative isotopic masses are 83.9 and 85.9 respectively. Determine the relative atomic mass of element M, quoting it to an appropriate number of significant figures and stating its units.

Question 18 — The table below gives the relative abundance measured for each peak in the mass spectrum of thallium.

m/z	203	205
relative abundance (%)	29.5	70.5

The relative isotopic masses are 202.97 (thallium-203) and 204.97 (thallium-205).

a. State the m / z value of the base peak.
b. Calculate the relative atomic mass of thallium.
c. A classmate writes the answer to part b as a value in grams. Explain why this is incorrect.

Answers

1 a carbon-12, assigned a value of exactly 12; b the mass of one atom of that isotope on the scale where carbon-12 = 12 exactly; c it is a ratio (a comparison of masses), so the units cancel. **2** a lithium-6 at $m/z = 6$, lithium-7 at $m/z = 7$; base peak $m/z = 7$; b 6.94; c no units — it is a ratio. **3** a 39.10; b potassium-39; c potassium-39 is by far the most abundant (93.26%), and a weighted average sits near the mass of the dominant isotope. **4** a $62.93\,x + 64.93(1 - x) = 63.55$; b copper-63 69.0%, copper-65 31.0%; c $62.93 \times 0.690 + 64.93 \times 0.310 = 63.55$ ✓. **5** a $f_{69} = 0.6031$, $f_{71} = 0.3969$; b 69.72; c gallium-69 — its peak is taller, so more atoms have that mass. **6** a 20.18; b it is a weighted average of masses 20, 21 and 22, and neon-20 (90.48%) dominates, pulling the average close to 20; c the relative abundance of that isotope. **7** 107.87 (no units). **8** 28.09 (no units). **9** rubidium-85 72.0%, rubidium-87 28.0%. **10** 114.81; the element is indium (In). **11** chlorine is a mixture of two isotopes, so A_r is a weighted average of 34.97 and 36.97, which is not a whole number; chlorine-35 (75.8%) is much more abundant than chlorine-37 (24.2%), so the average is pulled towards 35. **12** $m/z = 63$: 70.0%; $m/z = 67$: 10.0%. **13** 14.01; nitrogen-14 makes up 99.63% of atoms, so the average is dominated by (and almost equal to) its mass. **14** 39.95; closest to argon-40. **15** europium-151 48.0%, europium-153 52.0%. **16** the mass has no units (not grams), and carbon-12 is exactly 12 by definition; corrected statement in the solutions. **17** $A_r = 84.4$ (3 significant figures); no units. **18** a $m/z = 205$; b 204.38; c a relative atomic mass is a ratio and has no units, so it cannot be quoted in grams.

Fully-worked solutions

Question 1 a. The scale is defined by the **carbon-12** isotope, which is assigned a relative isotopic mass of **exactly 12**. b. The relative isotopic mass of an isotope is the mass of one atom of that isotope expressed on the scale where a carbon-12 atom is taken to be exactly 12 — in effect, the mass of the atom compared with one-twelfth of the mass of a carbon-12 atom. c. It is defined as a *ratio* of one mass to another (the isotope's mass compared with the carbon-12 reference). Dividing a mass by a mass leaves a pure number, so the quantity has no units.

Question 2 a. Each singly charged ion has m/z equal to its mass, so lithium-6 appears at $m/z = 6$ and lithium-7 at $m/z = 7$. Lithium-7 is far more abundant (92.5%), so its peak is the tallest — the base peak at $m/z = 7$. b. $A_r = 6.015 \times 0.075 + 7.016 \times 0.925 = 0.451 + 6.490 = 6.94$. c. The answer has **no units**: a relative atomic mass is a ratio of masses on the carbon-12 scale, so the units cancel.

Question 3 a. Converting each percentage to a fraction and weighting,

$$A_r = 38.96 \times 0.9326 + 39.96 \times 0.00012 + 40.96 \times 0.0673 = 36.334 + 0.005 + 2.757 = 39.10.$$

b. Potassium-39 is the most abundant isotope (93.26%). c. The relative atomic mass is a *weighted* average. Potassium-39 accounts for over 93% of all potassium atoms, so it dominates the average and drags the value very close to 39; the small amounts of potassium-40 and potassium-41 shift it up only slightly, to 39.10.

Question 4 a. With fractional abundance x for copper-63 and $(1 - x)$ for copper-65,

$$62.93\,x + 64.93(1 - x) = 63.55.$$

b. Expanding: $64.93 - 2.00\,x = 63.55$, so $2.00\,x = 1.38$ and $x = 0.690$. Thus copper-63 is **69.0%** abundant and copper-65 is $100 - 69.0 = 31.0\,\%$ abundant. c. Check: $62.93 \times 0.690 + 64.93 \times 0.310 = 43.422 + 20.128 = 63.55$ ✓, which matches the stated relative atomic mass.

Question 5 a. The heights are measured against the tallest peak, so divide each by the total height, $100 + 65.8 = 165.8$:

$$f_{69} = \frac{100}{165.8} = 0.6031,\ f_{71} = \frac{65.8}{165.8} = 0.3969.$$

b. $A_r = 68.93 \times 0.6031 + 70.92 \times 0.3969 = 41.57 + 28.15 = 69.72$. c. Gallium-69 is the more abundant isotope. Its peak is the taller of the two, and the height of a peak is proportional to the number of atoms of that isotope, so the taller peak means more gallium-69 atoms.

Question 6 a. $A_r = 19.99 \times 0.9048 + 20.99 \times 0.0027 + 21.99 \times 0.0925 = 18.087 + 0.057 + 2.034 = 20.18$. b. The relative atomic mass is a weighted average of the masses 19.99, 20.99 and 21.99. Neon-20 makes up 90.48% of the atoms, so it overwhelmingly dominates the average and pulls it close to 20; the modest amount of neon-22 lifts it only a little above 20, giving 20.18. c. The height of each peak gives the **relative abundance** of that isotope — how common that isotope is compared with the others.

Question 7

$$A_r = 106.91 \times 0.5184 + 108.90 \times 0.4816 = 55.422 + 52.446 = 107.87 \,(\text{no units}).$$

Question 8

$$A_r = 27.98 \times 0.9223 + 28.98 \times 0.0467 + 29.97 \times 0.0310 = 25.806 + 1.353 + 0.929 = 28.09 \,(\text{no units}).$$

Question 9 Let the fractional abundance of rubidium-85 be x and that of rubidium-87 be $(1 - x)$:

$$84.91\,x + 86.91(1 - x) = 85.47.$$

$$86.91 - 2.00\,x = 85.47 \Rightarrow 2.00\,x = 1.44 \Rightarrow x = 0.720.$$

So rubidium-85 is **72.0%** abundant and rubidium-87 is **28.0%** abundant. (Check: $84.91 \times 0.720 + 86.91 \times 0.280 = 61.135 + 24.335 = 85.47$ ✓.)

Question 10

$$A_r = 112.90 \times 0.0428 + 114.90 \times 0.9572 = 4.832 + 109.982 = 114.81.$$

The element with a relative atomic mass of about 114.8 on the periodic table is **indium (In)**.

Question 11 A mass spectrum shows that chlorine is a *mixture* of two isotopes — chlorine-35 (relative isotopic mass 34.97) and chlorine-37 (relative isotopic mass 36.97) — present in fixed proportions. The relative atomic mass is the abundance-weighted average of these two masses. Averaging two different values (that are themselves not whole numbers) in unequal proportions gives a value that is **not** a whole number, which is why $A_r = 35.45$. The two peaks in the spectrum are unequal in height: the chlorine-35 peak (75.8%) is about three times as tall as the chlorine-37 peak (24.2%). Because a weighted average is pulled towards the mass of the more abundant isotope, and chlorine-35 is by far the more abundant, the average lies **closer to 35** than to 37.

Question 12 The isotope at $m/z = 65$ is 20.0% abundant (fraction 0.200). Let the fractional abundances of the $m/z = 63$ and $m/z = 67$ isotopes be x and z. Since the fractions sum to 1,

$$x + z = 1 - 0.200 = 0.800.$$

The weighted-average equation is

$$62.9\,x + 64.9(0.200) + 66.9\,z = 63.70 \Rightarrow 62.9\,x + 66.9\,z = 63.70 - 12.98 = 50.72.$$

Substituting $z = 0.800 - x$:

$$62.9\,x + 66.9(0.800 - x) = 50.72 \Rightarrow 53.52 - 4.0\,x = 50.72 \Rightarrow 4.0\,x = 2.80 \Rightarrow x = 0.700.$$

Then $z = 0.800 - 0.700 = 0.100$. So the isotope at $m/z = 63$ is **70.0%** abundant and the isotope at $m/z = 67$ is **10.0%** abundant. (Check: $62.9 \times 0.700 + 64.9 \times 0.200 + 66.9 \times 0.100 = 44.03 + 12.98 + 6.69 = 63.70$ ✓.)

Question 13

$$A_r = 14.003 \times 0.9963 + 15.000 \times 0.0037 = 13.951 + 0.056 = 14.01.$$

Although a relative atomic mass is a weighted average and is usually not a whole number, nitrogen-14 makes up 99.63% of all nitrogen atoms. The average is therefore almost entirely determined by the mass of nitrogen-14 (14.003), and the tiny 0.37% of nitrogen-15 shifts it upward by only about 0.004. The result, 14.01, is consequently very close to the whole number 14.

Question 14

$$A_r = 35.97 \times 0.00337 + 37.96 \times 0.00063 + 39.96 \times 0.9960 = 0.121 + 0.024 + 39.800 = 39.95.$$

Argon-40 accounts for 99.60% of argon atoms, so the relative atomic mass lies closest to **argon-40** (its value, 39.95, is only just below 40).

Question 15 Let the fractional abundance of europium-151 be x and that of europium-153 be $(1 - x)$:

$$150.92\,x + 152.92(1 - x) = 151.96.$$

$$152.92 - 2.00\,x = 151.96 \Rightarrow 2.00\,x = 0.96 \Rightarrow x = 0.480.$$

So europium-151 is **48.0%** abundant and europium-153 is **52.0%** abundant. (Check: $150.92 \times 0.480 + 152.92 \times 0.520 = 72.442 + 79.518 = 151.96$ ✓.)

Question 16 The statement contains two errors.

- **"12 grams" is wrong.** The relative isotopic mass of carbon-12 is **12 (no units)**, not 12 grams. It is a value on a *relative* scale — a ratio of masses — and ratios have no units. (The actual mass of a carbon-12 atom in grams is about 2×10^{-23} g, an entirely different quantity.)
- **"measured against it" understates the definition.** Carbon-12 is not merely a convenient reference; it is assigned the value **exactly 12 by definition**, and this single choice *defines* the whole scale. Every other isotopic mass is then expressed relative to it.

Corrected: "The relative isotopic mass of carbon-12 is **exactly 12** (a value on a relative scale, with no units), and every other isotope's relative isotopic mass is measured on that same scale."

Question 17 The peak heights are relative to the tallest peak, so convert them to fractional abundances using the total height $100 + 32.5 = 132.5$:

$$f_{84} = \frac{100}{132.5} = 0.7547,\ f_{86} = \frac{32.5}{132.5} = 0.2453.$$

$$A_r = 83.9 \times 0.7547 + 85.9 \times 0.2453 = 63.32 + 21.07 = 84.39.$$

The relative isotopic masses are given to only 3 significant figures, so the answer must be quoted to the same precision: $A_r = 84.4$ (3 significant figures). It has **no units**, being a ratio on the carbon-12 scale.

Question 18 a. The base peak is the tallest peak, which is the one with the greater relative abundance: $m/z = 205$ (thallium-205, 70.5%). b. $A_r = 202.97 \times 0.295 + 204.97 \times 0.705 = 59.876 + 144.504 = 204.38$. c. A relative atomic mass is defined on the carbon-12 *relative* scale — it is a ratio of one mass to another, so the units cancel and the quantity is a pure number. It therefore cannot correctly be written with the unit grams; the answer is simply 204.38.

Chapter 6 Quantifying atoms and compounds — 6B The mole

Theory

Atoms and molecules are far too small to see, and any weighable sample contains a staggering number of them: a single teaspoon of water holds roughly two hundred thousand billion billion molecules. Chemists cannot count these particles one at a time, but reactions happen *particle by particle* — one atom combining with another, one molecule reacting with the next. To connect the world we can measure (**mass**, in grams) with the world in which reactions actually occur (**numbers of particles**), chemistry uses a counting unit called the **mole**. This subtopic introduces the mole, Avogadro's constant and molar mass, and uses them to work out the **amount, in moles, of atoms or molecules in a pure sample of known mass** — and, from that, the number of particles the sample contains.

A counting unit. Everyday counting units group a fixed number of items so that large collections can be handled conveniently. A *dozen* always means 12 objects; a *ream* of paper always means 500 sheets. Whether the objects are eggs or nails, "one dozen" is the same count. The **mole** works in exactly the same way: it is the chemist's counting unit, and it always stands for the same very large number of particles, chosen so that laboratory-sized masses correspond to convenient numbers of moles.

Avogadro's constant. The number of particles in one mole is **Avogadro's constant**, given the symbol N_A:

$$N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$$

So **one mole of any substance contains** 6.02×10^{23} **particles** — atoms, molecules, ions or formula units, depending on what the substance is made of. One mole of helium contains 6.02×10^{23} helium atoms; one mole of water contains 6.02×10^{23} water molecules; one mole of sodium chloride contains 6.02×10^{23} NaCl formula units. The unit of N_A is mol^{-1} ("per mole"), because it counts *particles per mole*.

This particular number is not arbitrary. The size of the mole was set on the carbon-12 scale: historically, one mole was defined as the number of atoms in exactly 12 g of the carbon-12 isotope, and 6.02×10^{23} is that number. (The mole is now defined instead by fixing N_A at an exact value, chosen so that the mole keeps the same size.) Because of that choice, the mass of one mole of a substance, measured in grams, is numerically equal to the relative mass of its particles on the carbon-12 scale (subtopic 6A). That link is what makes the mole so useful: it lets us count particles simply by weighing.

The symbol for amount. The **amount of substance** — the number of moles — is given the symbol n and always has the unit **mol**. Saying "the amount of water is 0.500 mol" means the sample contains $0.500 \times N_A = 3.01 \times 10^{23}$ water molecules. "Amount", used in this precise sense, always means "number of moles"; it never means mass.

Molar mass. The **molar mass**, symbol M, is the mass of one mole of a substance. Its unit is **grams per mole**, g mol^{-1}. Because of that link with the carbon-12 scale, the molar mass of an element in g mol^{-1} is numerically equal to its **relative atomic mass** A_r, and the molar mass of a compound is numerically equal to its **relative molecular (or formula) mass** M_r. So a molar mass is found simply by **adding up the relative atomic masses** of all the atoms shown in the formula. The relative atomic masses used throughout this subtopic are:

Element	H	C	N	O	Na	Mg	Al	S	Cl	Ca	Fe	Cu	Zn
A_r	1.0	12.0	14.0	16.0	23.0	24.3	27.0	32.1	35.5	40.1	55.8	63.5	65.4

For example, the molar mass of water, H_2O, adds two hydrogen atoms and one oxygen atom:

$$M(\text{H}_2\text{O}) = 2 \times 1.0 + 16.0 = 18.0\ \text{g mol}^{-1}$$

and the molar mass of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, is

$$M(\text{C}_6\text{H}_{12}\text{O}_6) = 6 \times 12.0 + 12 \times 1.0 + 6 \times 16.0 = 180.0\ \text{g mol}^{-1}.$$

Each element's relative atomic mass is multiplied by its **subscript** in the formula before the values are added.

The first relationship: mass and amount. Because M is the mass of one mole, a sample of mass m contains

$$n = \frac{m}{M}$$

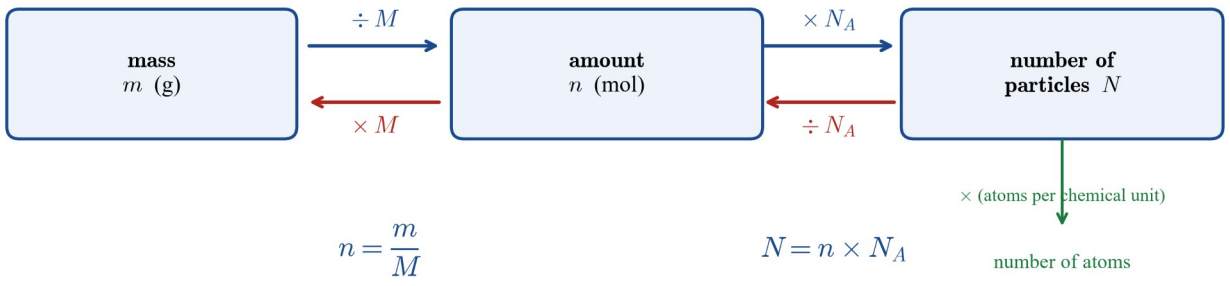
moles. This is the central relationship of the subtopic: divide the mass (in grams) by the molar mass (in g mol^{-1}) to get the amount (in moles). Rearranged, it also gives the mass of a known amount, $m = n \times M$, and the molar mass of a sample of known mass and amount, $M = m / n$.

The second relationship: amount and number of particles. Once the amount in moles is known, the actual **number of particles**, N, follows by multiplying by Avogadro's constant:

$$N = n \times N_A$$

and, in reverse, $n = N / N_A$. Together these two relationships let us move freely between the three quantities — **mass**, **amount** and **number of particles** — in either direction. This is summarised in the *mole map*:

The mole map — converting for a pure sample of known mass

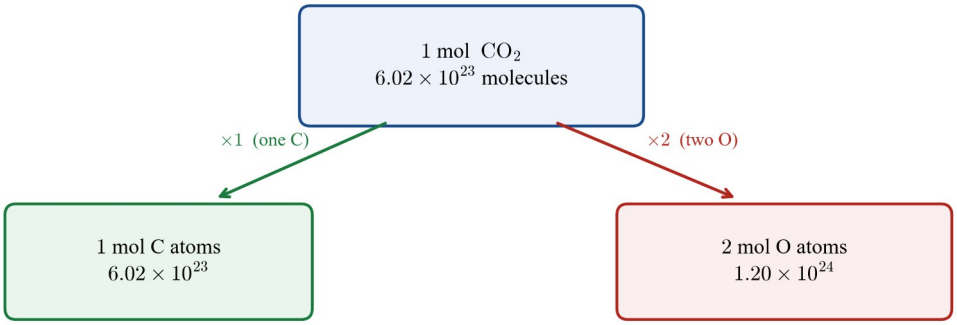


M = molar mass (g mol^{-1}), built by adding the relative atomic masses; $N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$

Reading the map from left to right: **divide by** M to go from mass to amount, then **multiply by** N_A to go from amount to number of particles. Reading it from right to left reverses each step: **divide by** N_A, then **multiply by** M. The middle box — the amount in moles — is the hub through which every conversion passes; there is no direct shortcut from mass to number of particles that skips it.

Counting atoms inside a chemical unit. The number N found from $N = n \times N_A$ counts the **chemical units** of the substance — molecules of a molecular substance, or formula units of an ionic substance. To count the **individual atoms** (or ions) inside those units, multiply by the number of that atom in the formula — its subscript. One molecule of carbon dioxide, CO_2, contains one carbon atom and two oxygen atoms, so one mole of CO_2 contains one mole of carbon atoms and **two** moles of oxygen atoms:

Counting atoms inside a chemical unit: multiply by each element's subscript



In general, the number of atoms of a particular element $= (\text{its subscript}) \times n \times N_A$. The same idea gives the *total* number of atoms in a sample: multiply the number of chemical units by the total number of atoms in one of them (for glucose, $6 + 12 + 6 = 24$).

Working with significant figures and units. Molar masses here are quoted to one decimal place, and N_A to three significant figures, so final answers are given to **three significant figures**. Do **not** round part-way through: carry the full calculator value from one step to the next and round only at the end, or a rounding error builds up over the steps. (For this reason the worked solutions print intermediate values with one extra digit — a *guard digit* — so that every line can be checked exactly as written.) Every answer must carry its **unit**: an amount in mol, a mass in g, while a plain *number* of particles or atoms has no unit (it is a pure count). A bare number with no unit — where a unit is expected — is treated as incomplete. Throughout, keep to the mole map: identify what you are given, decide which arrows lead to what you want, and apply $n = m / M$ and $N = n \times N_A$ in turn. (In this subtopic every sample is a **pure substance of known mass**. The mole is also the key to *reactions*: simple combustion calculations that relate reactant and product masses appear later in Unit 1, and fuller reaction stoichiometry is developed in Unit 2.)

Worked examples

Worked Example 1 — A pure sample of copper metal has a mass of 12.7 g. Calculate the amount, in mol, of copper atoms in the sample. ($A_r(\text{Cu}) = 63.5$)

Working	Comment
$M(\text{Cu}) = 63.5\ \text{g mol}^{-1}$	For an element the molar mass equals its relative atomic mass in g mol^{-1}.
Given $m = 12.7\ \text{g}$; want n	Mass → amount, so use the "÷ M" arrow of the mole map.
$n = \dfrac{m}{M} = \dfrac{12.7}{63.5}$	Apply $n = m / M$; grams divided by g mol^{-1} leaves mol.
$n = 0.200\ \text{mol}$	Quoted to three significant figures, with the unit mol.
∴ the sample contains **0.200 mol** of copper atoms	

Worked Example 2 — A pure sample of water, H_2O, has a mass of 9.00 g. Calculate (a) the amount, in mol, of water molecules, (b) the number of water molecules, and (c) the number of hydrogen atoms in the sample. (A_r: H 1.0, O 16.0)

Working	Comment
$M(\text{H}_2\text{O}) = 2 \times 1.0 + 16.0 = 18.0\ \text{g mol}^{-1}$	Add the relative atomic masses, each times its subscript.
(a) $n = \dfrac{m}{M} = \dfrac{9.00}{18.0} = 0.500\ \text{mol}$	Mass → amount ("÷ M").
(b) $N = n \times N_A = 0.500 \times 6.02 \times 10^{23}$	Amount → number of particles ("× N_A").

Working	Comment
$N = 3.01 \times 10^{23}$ molecules	A pure count — no unit.
(c) each H_2O has 2 H atoms, so $N(H) = 2 \times 3.01 \times 10^{23}$	Multiply by the subscript of hydrogen (2).
$N(H) = 6.02 \times 10^{23}$ hydrogen atoms	
∴ **0.500 mol**, 3.01×10^{23} **molecules**, 6.02×10^{23} **H atoms**	

Worked Example 3 — A pure sample of carbon dioxide, CO_2, contains 1.505×10^{23} molecules. Calculate the mass of the sample. (A_r: C 12.0, O 16.0)

Working from the right of the mole map, first convert the number of molecules to an amount in moles, then the amount to a mass.

$$n = \frac{N}{N_A} = \frac{1.505 \times 10^{23}}{6.02 \times 10^{23}} = 0.250\,\text{mol}$$

The molar mass of carbon dioxide is $M(CO_2) = 12.0 + 2 \times 16.0 = 44.0\,\text{g mol}^{-1}$, so

$$m = n \times M = 0.250 \times 44.0 = 11.0\,\text{g}.$$

∴ the sample has a mass of **11.0 g**.

Worked Example 4 — Calculate the number of oxygen atoms in a 4.00 g pure sample of glucose, $C_6H_{12}O_6$. ($M = 180.0\,\text{g mol}^{-1}$)

The path on the mole map is mass → amount → number of molecules → number of oxygen atoms. First the amount:

$$n = \frac{m}{M} = \frac{4.00}{180.0} = 0.02222\,\text{mol}$$

(an intermediate value, so a guard digit is kept). The number of glucose molecules is

$$N = n \times N_A = 0.02222 \times 6.02 \times 10^{23} = 1.338 \times 10^{22}\,\text{molecules}.$$

Each glucose molecule contains 6 oxygen atoms, so the number of oxygen atoms is

$$N(O) = 6 \times 1.338 \times 10^{22} = 8.03 \times 10^{22}.$$

∴ the sample contains 8.03×10^{22} **oxygen atoms**.

Practice questions

Question 1 — A pure sample of magnesium has a mass of 6.08 g. ($A_r(Mg) = 24.3$)

a. State the molar mass of magnesium, with its unit.
b. Calculate the amount, in mol, of magnesium atoms in the sample.
c. Calculate the number of magnesium atoms in the sample.

Question 2 — A cylinder holds 8.80 g of pure carbon dioxide, CO_2. (A_r: C 12.0, O 16.0)

a. Show that the molar mass of CO_2 is $44.0\,\text{g mol}^{-1}$.
b. Calculate the amount, in mol, of carbon dioxide molecules.
c. Calculate the number of carbon dioxide molecules.

Question 3 — A pure sample of ammonia, NH_3, contains 3.01×10^{23} molecules. ($M = 17.0\,\text{g mol}^{-1}$)

a. Calculate the amount, in mol, of ammonia in the sample.
b. Calculate the mass of the sample.
c. Calculate the number of hydrogen atoms in the sample.

Question 4 — Consider a 5.85 g pure sample of sodium chloride, NaCl. ($M = 58.5\,\mathrm{g\ mol^{-1}}$)

a. Calculate the amount, in mol, of NaCl formula units.
b. Calculate the number of NaCl formula units.
c. State the number of sodium ions and the number of chloride ions present.

Question 5 — A pure sample of glucose, $\mathrm{C_6H_{12}O_6}$, has a mass of 27.0 g. (A_r: C 12.0, H 1.0, O 16.0)

a. Show that the molar mass of glucose is $180.0\,\mathrm{g\ mol^{-1}}$.
b. Calculate the amount, in mol, of glucose molecules.
c. Calculate the total number of atoms of all kinds in the sample.

Question 6 — A pure sample of iron contains 3.01×10^{22} atoms. ($A_\mathrm{r}(\mathrm{Fe}) = 55.8$)

a. Calculate the amount, in mol, of iron atoms.
b. Calculate the mass of the sample.
c. Explain, referring to the idea of "counting by weighing", why chemists measure amounts in moles rather than counting atoms one by one.

Question 7 — Calculate the amount, in mol, of aluminium atoms in a 13.5 g pure sample of aluminium. ($A_\mathrm{r}(\mathrm{Al}) = 27.0$)

Question 8 — A flask contains 3.60 g of pure methane, $\mathrm{CH_4}$. Calculate the number of methane molecules present. ($M = 16.0\,\mathrm{g\ mol^{-1}}$)

Question 9 — A pure sample of oxygen gas, $\mathrm{O_2}$, contains 9.03×10^{23} molecules. Calculate the mass of the sample. ($M = 32.0\,\mathrm{g\ mol^{-1}}$)

Question 10 — A pure sample of ethanol, $\mathrm{C_2H_6O}$, has a mass of 2.30 g. Calculate the number of hydrogen atoms in the sample. ($M = 46.0\,\mathrm{g\ mol^{-1}}$)

Question 11 — A 25.0 g pure sample of calcium carbonate, $\mathrm{CaCO_3}$, is weighed out. Calculate the number of oxygen atoms in the sample. ($M = 100.1\,\mathrm{g\ mol^{-1}}$)

Question 12 — Calculate the number of nitrogen *atoms* in an 8.40 g pure sample of nitrogen gas, $\mathrm{N_2}$. ($M = 28.0\,\mathrm{g\ mol^{-1}}$)

Question 13 — A pure sample of zinc contains 4.515×10^{23} atoms. Calculate its mass. ($A_\mathrm{r}(\mathrm{Zn}) = 65.4$)

Question 14 — A student weighs out 2.00 g of hydrogen gas, $\mathrm{H_2}$ ($M = 2.0\,\mathrm{g\ mol^{-1}}$), and 2.00 g of oxygen gas, $\mathrm{O_2}$ ($M = 32.0\,\mathrm{g\ mol^{-1}}$). Determine, showing calculations, which sample contains the greater number of molecules, and explain why equal masses of the two gases do not contain equal numbers of molecules.

Question 15 — A chemist needs a pure sample of urea, $\mathrm{CO(NH_2)_2}$ ($M = 60.0\,\mathrm{g\ mol^{-1}}$), that contains 0.250 mol of urea. Calculate the mass that must be weighed out, and state the number of nitrogen atoms the sample will contain.

Question 16 — A pure sample of water is found to contain 1.204×10^{24} hydrogen atoms. Calculate the amount, in mol, of water molecules in the sample and hence the mass of the sample. ($M(\mathrm{H_2O}) = 18.0\,\mathrm{g\ mol^{-1}}$)

Question 17 — A 10.0 g sample of carbon ($A_\mathrm{r} = 12.0$) and a 10.0 g sample of magnesium ($A_\mathrm{r} = 24.3$) are compared. Determine, with calculations, which sample contains more atoms, and explain the result in terms of the mass of an individual atom.

Question 18 — A 0.500 g pure sample of sucrose, $C_{12}H_{22}O_{11}$ ($M = 342.0\,\text{g mol}^{-1}$), is analysed. Calculate (i) the amount, in mol, of sucrose, and (ii) the number of carbon atoms in the sample, giving each answer to three significant figures.

Question 19 — State the value and the unit of Avogadro's constant, and explain why the molar mass of a compound expressed in g mol^{-1} has the same numerical value as its relative molecular mass.

Question 20 — A 2.20 g pure sample of carbon dioxide, CO_2 ($M = 44.0\,\text{g mol}^{-1}$), is collected from a respiration experiment. Calculate (i) the amount, in mol, of CO_2, (ii) the number of CO_2 molecules, and (iii) the total number of atoms of all kinds in the sample.

Answers

1 a $24.3\,\text{g mol}^{-1}$; b $0.250\,\text{mol}$; c 1.51×10^{23} atoms. **2** a $12.0+2\times16.0=44.0\,\text{g mol}^{-1}$; b $0.200\,\text{mol}$; c 1.20×10^{23} molecules. **3** a $0.500\,\text{mol}$; b $8.50\,\text{g}$; c 9.03×10^{23} H atoms. **4** a $0.100\,\text{mol}$; b 6.02×10^{22} formula units; c 6.02×10^{22} Na^+ ions and 6.02×10^{22} Cl^- ions. **5** a $6\times12.0+12\times1.0+6\times16.0=180.0\,\text{g mol}^{-1}$; b $0.150\,\text{mol}$; c 2.17×10^{24} atoms. **6** a $0.0500\,\text{mol}$; b $2.79\,\text{g}$; c model answer — weighing a known molar mass counts particles indirectly. **7** $0.500\,\text{mol}$. **8** 1.35×10^{23} molecules. **9** $48.0\,\text{g}$. **10** 1.81×10^{23} H atoms. **11** 4.51×10^{23} O atoms. **12** 3.61×10^{23} N atoms. **13** $49.1\,\text{g}$. **14** H_2: $1.00\,\text{mol}$; O_2: $0.0625\,\text{mol}$ — the hydrogen sample has the greater number of molecules (16 times as many). **15** $15.0\,\text{g}$; 3.01×10^{23} N atoms. **16** $1.00\,\text{mol}$; $18.0\,\text{g}$. **17** carbon: $0.833\,\text{mol}$; magnesium: $0.412\,\text{mol}$ — the carbon sample contains more atoms. **18** (i) $1.46\times10^{-3}\,\text{mol}$; (ii) 1.06×10^{22} C atoms. **19** $6.02\times10^{23}\,\text{mol}^{-1}$; model answer (the size of the mole was set on the carbon-12 scale). **20** (i) $0.0500\,\text{mol}$; (ii) 3.01×10^{22} molecules; (iii) 9.03×10^{22} atoms.

Fully-worked solutions

Question 1 a. For an element the molar mass equals the relative atomic mass in grams per mole: $M(\text{Mg})=24.3\,\text{g mol}^{-1}$. b. $n=\dfrac{m}{M}=\dfrac{6.08}{24.3}=0.250\,\text{mol}$ (unrounded, $0.2502\,\text{mol}$).

c. $N=n\times N_A=0.2502\times6.02\times10^{23}=1.51\times10^{23}$ magnesium atoms.

Question 2 a. Carbon dioxide has one carbon atom and two oxygen atoms: $M(\text{CO}_2)=12.0+2\times16.0=44.0\,\text{g mol}^{-1}$. b. $n=\dfrac{m}{M}=\dfrac{8.80}{44.0}=0.200\,\text{mol}$.

c. $N=n\times N_A=0.200\times6.02\times10^{23}=1.20\times10^{23}$ molecules.

Question 3 a. $n=\dfrac{N}{N_A}=\dfrac{3.01\times10^{23}}{6.02\times10^{23}}=0.500\,\text{mol}$. b. $m=n\times M=0.500\times17.0=8.50\,\text{g}$. c. Each NH_3 molecule contains 3 hydrogen atoms, so $N(\text{H})=3\times3.01\times10^{23}=9.03\times10^{23}$ hydrogen atoms.

Question 4 a. $n=\dfrac{m}{M}=\dfrac{5.85}{58.5}=0.100\,\text{mol}$. b. $N=n\times N_A=0.100\times6.02\times10^{23}=6.02\times10^{22}$ formula units. c. Each NaCl formula unit contains one Na^+ ion and one Cl^- ion, so there are 6.02×10^{22} sodium ions and 6.02×10^{22} chloride ions.

Question 5 a. $M(\text{C}_6\text{H}_{12}\text{O}_6)=6\times12.0+12\times1.0+6\times16.0=72.0+12.0+96.0=180.0\,\text{g mol}^{-1}$. b. $n=\dfrac{m}{M}=\dfrac{27.0}{180.0}=0.150\,\text{mol}$. c. The number of glucose molecules is $N=0.150\times6.02\times10^{23}=9.03\times10^{22}$. Each molecule contains $6+12+6=24$ atoms, so the total number of atoms is $24\times9.03\times10^{22}=2.17\times10^{24}$.

Question 6 a. $n=\dfrac{N}{N_A}=\dfrac{3.01\times10^{22}}{6.02\times10^{23}}=0.0500\,\text{mol}$. b. $m=n\times M=0.0500\times55.8=2.79\,\text{g}$. c. Individual atoms cannot be counted directly — a weighable sample contains of the order of 10^{23} of them. Instead, because one mole of any substance has a fixed mass (its molar mass) and contains a fixed number of particles (N_A), *weighing* the sample and dividing by the molar mass gives the amount in moles, and multiplying by N_A then gives the number of particles. In effect the balance "counts" the particles indirectly: measuring mass is a practical stand-in for counting.

Question 7 $n=\dfrac{m}{M}=\dfrac{13.5}{27.0}=0.500\,\text{mol}$ of aluminium atoms.

Question 8 $n=\dfrac{m}{M}=\dfrac{3.60}{16.0}=0.225\,\text{mol}$; $N=n\times N_A=0.225\times6.02\times10^{23}=1.35\times10^{23}$ methane molecules.

Question 9 $n = \dfrac{N}{N_A} = \dfrac{9.03 \times 10^{23}}{6.02 \times 10^{23}} = 1.50\,\text{mol}$; $m = n \times M = 1.50 \times 32.0 = 48.0\,\text{g}$.

Question 10 $n = \dfrac{m}{M} = \dfrac{2.30}{46.0} = 0.0500\,\text{mol}$; the number of ethanol molecules is $N = 0.0500 \times 6.02 \times 10^{23} = 3.01 \times 10^{22}$. Each ethanol molecule, $\text{C}_2\text{H}_6\text{O}$, contains 6 hydrogen atoms, so $N(\text{H}) = 6 \times 3.01 \times 10^{22} = 1.81 \times 10^{23}$ hydrogen atoms.

Question 11 $n = \dfrac{m}{M} = \dfrac{25.0}{100.1} = 0.250\,\text{mol}$ (unrounded, $0.2498\,\text{mol}$); the number of CaCO_3 formula units is $0.2498 \times 6.02 \times 10^{23} = 1.504 \times 10^{23}$. Each formula unit contains 3 oxygen atoms, so $N(\text{O}) = 3 \times 1.504 \times 10^{23} = 4.51 \times 10^{23}$ oxygen atoms.

Question 12 $n = \dfrac{m}{M} = \dfrac{8.40}{28.0} = 0.300\,\text{mol}$; the number of N_2 molecules is $0.300 \times 6.02 \times 10^{23} = 1.806 \times 10^{23}$. Each molecule contains 2 nitrogen atoms, so $N(\text{N}) = 2 \times 1.806 \times 10^{23} = 3.61 \times 10^{23}$ nitrogen atoms.

Question 13 $n = \dfrac{N}{N_A} = \dfrac{4.515 \times 10^{23}}{6.02 \times 10^{23}} = 0.750\,\text{mol}$; $m = n \times M = 0.750 \times 65.4 = 49.1\,\text{g}$.

Question 14 For hydrogen: $n(\text{H}_2) = \dfrac{2.00}{2.0} = 1.00\,\text{mol}$. For oxygen: $n(\text{O}_2) = \dfrac{2.00}{32.0} = 0.0625\,\text{mol}$. Since the number of molecules is $n \times N_A$, and hydrogen has the greater amount in moles, the **hydrogen sample contains far more molecules** — $1.00 / 0.0625 = 16$ times as many. Equal masses do not contain equal numbers of molecules because an oxygen molecule is 16 times as heavy as a hydrogen molecule ($M = 32.0$ versus $2.0\,\text{g mol}^{-1}$); the same 2.00 g therefore holds 16 times fewer of the heavier oxygen molecules. The number of molecules in a fixed mass depends on the molar mass, not on the mass alone.

Question 15 $m = n \times M = 0.250 \times 60.0 = 15.0\,\text{g}$ of urea must be weighed out. Each urea molecule, $\text{CO(NH}_2)_2$, contains 2 nitrogen atoms, so the number of nitrogen atoms is $N(\text{N}) = 2 \times n \times N_A = 2 \times 0.250 \times 6.02 \times 10^{23} = 3.01 \times 10^{23}$ nitrogen atoms.

Question 16 Each water molecule contains 2 hydrogen atoms, so the number of water molecules is half the number of hydrogen atoms: $N(\text{H}_2\text{O}) = \dfrac{1.204 \times 10^{24}}{2} = 6.02 \times 10^{23}$. Then $n = \dfrac{N}{N_A} = \dfrac{6.02 \times 10^{23}}{6.02 \times 10^{23}} = 1.00\,\text{mol}$, and $m = n \times M = 1.00 \times 18.0 = 18.0\,\text{g}$.

Question 17 Carbon: $n = \dfrac{10.0}{12.0} = 0.833\,\text{mol}$. Magnesium: $n = \dfrac{10.0}{24.3} = 0.412\,\text{mol}$. Since the number of atoms is $n \times N_A$, the **carbon sample contains more atoms**. For the same mass, the element with the smaller molar mass (the lighter atom) provides more atoms: each carbon atom has about half the mass of a magnesium atom, so 10.0 g of carbon packs in about twice as many atoms as 10.0 g of magnesium.

Question 18 (i) $n = \dfrac{m}{M} = \dfrac{0.500}{342.0} = 1.46 \times 10^{-3}\,\text{mol}$ (unrounded, $1.462 \times 10^{-3}\,\text{mol}$). (ii) The number of sucrose molecules is $N = n \times N_A = 1.462 \times 10^{-3} \times 6.02 \times 10^{23} = 8.801 \times 10^{20}$. Each molecule, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, contains 12 carbon atoms, so $N(\text{C}) = 12 \times 8.801 \times 10^{20} = 1.06 \times 10^{22}$ carbon atoms.

Question 19 Avogadro's constant is $N_A = 6.02 \times 10^{23}\,\text{mol}^{-1}$ — the number of particles in one mole of any substance, with the unit "per mole". The molar mass of a compound is the mass of one mole (6.02×10^{23} molecules or formula units). Because the *size* of the mole was set on the carbon-12 scale — one mole being, historically, the number of atoms in exactly 12 g of carbon-12 — the mass of one mole of particles in grams comes out numerically equal to the relative mass of one particle on that same scale. So a compound whose relative molecular mass is, say, 44.0 has a

molar mass of exactly $44.0\,\text{g mol}^{-1}$: the two share a numerical value but carry different meanings (a ratio with no unit versus a mass per mole).

Question 20 (i) $n = \frac{m}{M} = \frac{2.20}{44.0} = 0.0500\,\text{mol}$. (ii) $N = n \times N_A = 0.0500 \times 6.02 \times 10^{23} = 3.01 \times 10^{22}$ molecules. (iii) Each CO_2 molecule contains 3 atoms (one C and two O), so the total number of atoms is $3 \times 3.01 \times 10^{22} = 9.03 \times 10^{22}$.

Chapter 6 Quantifying atoms and compounds — 6C Percentage composition and empirical formula

Theory

The mole (subtopic 6B) lets a chemist count atoms and molecules by weighing them. This subtopic uses that idea in two directions. First, given the **formula** of a compound, we work out its **molar mass** and the **percentage of each element by mass**. Then we reverse the process: given the percentage composition measured in the laboratory, we work back to the **empirical formula**, and — with one extra piece of data, the molar mass — to the **molecular formula**. The study design sets percentage composition by mass for **covalent (molecular) compounds**, so the substances used throughout this subtopic are molecules such as glucose, urea, an oxide of nitrogen or a hydrocarbon; the empirical formula itself, as the method below notes, is defined for *any* compound, ionic ones included.

Molar mass of a compound. The **molar mass** M of a compound is the mass of one mole of its molecules, in g mol^{-1}. It is found by adding the relative atomic masses (A_r) of every atom shown in the formula:

$$M = \sum(\text{number of each atom}) \times A_r$$

For example, carbon dioxide, CO_2, has one carbon ($A_r = 12.0$) and two oxygen atoms ($A_r = 16.0$), so $M = 12.0 + 2(16.0) = 44.0\ \text{g mol}^{-1}$. Throughout this subtopic relative atomic masses are taken from the Data Book to one decimal place (H 1.0, C 12.0, N 14.0, O 16.0, S 32.1). Because M is built from the whole formula, the molar mass of a compound is a whole-number multiple of the molar mass of its **simplest formula unit**: equal to it when the formula is already in its simplest whole-number ratio (as CO_2 is), and larger when it is not. This is the point we return to below.

Percentage composition by mass. The **percentage composition** of a compound states what fraction of its total mass is contributed by each element. For an element whose atom appears x times in the formula,

$$\%\ \text{by mass of the element} = \frac{x \times A_r}{M} \times 100$$

The numerator, $x \times A_r$, is the mass of that element in one mole of the compound; dividing by the molar mass M and multiplying by 100 turns it into a percentage. The percentages of all the elements in a compound must add to 100 (allowing for rounding). Percentage composition depends only on the formula, so it is a fixed property of the compound: every pure sample of glucose, of any size and from any source, has exactly the same percentage composition by mass.

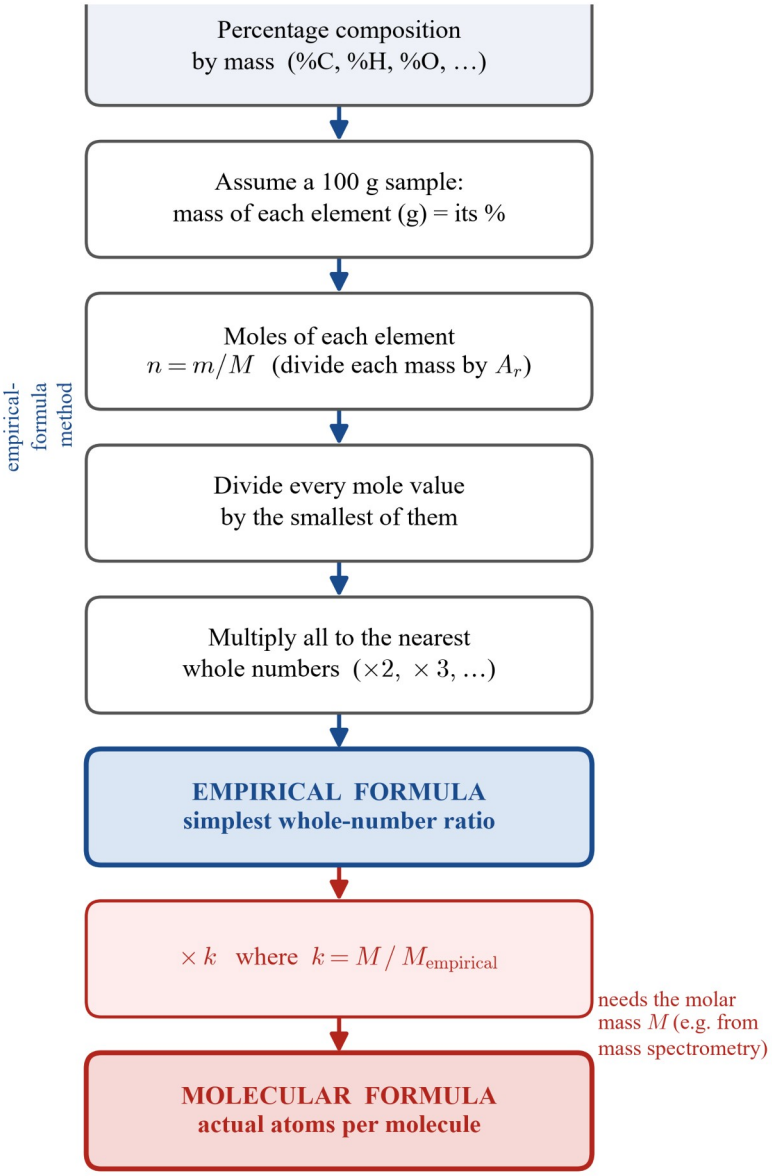
Percentage composition also lets us find the **mass of one element in a sample**. If a compound is $28.0\,\%$ nitrogen by mass, then a $50.0\,\text{g}$ sample contains $\frac{28.0}{100} \times 50.0 = 14.0\,\text{g}$ of nitrogen.

Empirical and molecular formulas. A molecular compound can be described by two formulas.

- The **molecular formula** gives the *actual* number of atoms of each element in one molecule — for glucose, $\text{C}_6\text{H}_{12}\text{O}_6$.
- The **empirical formula** gives the *simplest whole-number ratio* of the atoms — for glucose, CH_2O.

The molecular formula is always a whole-number multiple of the empirical formula: glucose's molecular formula is $6\times$ its empirical formula. Percentage composition by mass fixes only the **ratio** of the atoms, so it can give the empirical formula directly, but *not* the molecular formula on its own — the molar mass is needed to complete the second step.

Finding the empirical formula from percentage composition. The method is always the same, and is set out in the flow diagram below.



1. **Assume a 100 g sample.** Then the percentage of each element is numerically equal to its mass in grams (a 40.0 % element supplies 40.0 g). This step is what makes percentages easy to work with.
2. **Convert each mass to moles** using $n = \frac{m}{M}$ — that is, divide each element's mass by its relative atomic mass. The mole values are now in the same ratio as the *atoms* in the compound.
3. **Divide every mole value by the smallest** of them. This scales the smallest down to 1 and expresses the others relative to it.
4. **Multiply to the nearest whole numbers if necessary.** If the ratios are already close to whole numbers, read off the empirical formula. If one of them instead ends in a simple fraction — in .5 (a half), or in .33/.67 (a third or two-thirds) — multiply *all* of the ratios by 2 (for a half) or by 3 (for thirds) to clear it. For instance a ratio of 1 : 1.5 becomes 2 : 3 after multiplying by 2.

Small departures from whole numbers (for example 2.02 or 2.97) come from rounding in the data and should simply be rounded to the nearest whole number; a value such as 2.50 or 2.67 is *not* rounding error and must be cleared by multiplying.

Compounds that have no molecules. Steps 1–4 use nothing but mass data, so they work for **any** compound, not only a molecular one. An ionic compound has no molecules, so it has no molecular formula at all: the simplest whole-number ratio reached in step 4 *is* its formula, which is why magnesium oxide is written MgO and iron(III) oxide Fe_2O_3. For an ionic compound or a hydrated salt the work therefore stops at the empirical formula; only a molecular compound goes on to the step below.

Finding the molecular formula. Once the empirical formula is known, the molecular formula follows from the molar mass M of the compound (which must be given, or measured — for example by mass spectrometry). Find the molar mass of the empirical unit, $M_{\text{empirical}}$, then

$$k = \frac{M}{M_{\text{empirical}}}, \quad \text{molecular formula} = (\text{empirical formula}) \times k$$

where k is a whole number. For glucose the empirical unit $\mathrm{CH_2O}$ has $M_{\text{empirical}} = 30.0\ \text{g mol}^{-1}$; the measured molar mass is $180\ \text{g mol}^{-1}$, so $k = \dfrac{180}{30.0} = 6$ and the molecular formula is $(\mathrm{CH_2O})_6 = \mathrm{C_6H_{12}O_6}$. If $k = 1$, the molecular formula and the empirical formula are the same.

Worked examples

Worked Example 1 — Urea, an important nitrogen fertiliser, has the molecular formula $\mathrm{CH_4N_2O}$. Calculate its molar mass and its percentage composition by mass. (A_r: H 1.0, C 12.0, N 14.0, O 16.0.)

Working	Comment
$M = 12.0 + 4(1.0) + 2(14.0) + 16.0$	Add A_r for every atom in the formula: 1 C, 4 H, 2 N, 1 O.
$M = 60.0\ \text{g mol}^{-1}$	Molar mass of urea.
$\%\,\mathrm{C} = \dfrac{1 \times 12.0}{60.0} \times 100 = 20.0\,\%$	Mass of C in one mole, over the molar mass.
$\%\,\mathrm{H} = \dfrac{4 \times 1.0}{60.0} \times 100 = 6.7\,\%$	Four hydrogen atoms contribute $4.0\ \text{g}$.
$\%\,\mathrm{N} = \dfrac{2 \times 14.0}{60.0} \times 100 = 46.7\,\%$	Two nitrogen atoms contribute $28.0\ \text{g}$.
$\%\,\mathrm{O} = \dfrac{1 \times 16.0}{60.0} \times 100 = 26.7\,\%$	One oxygen atom contributes $16.0\ \text{g}$.
Check: $20.0 + 6.7 + 46.7 + 26.7 = 100.1 \approx 100$	The four percentages sum to 100 (within rounding).

Worked Example 2 — A covalent compound is found by analysis to contain, by mass, $62.1\,\%$ carbon, $10.3\,\%$ hydrogen and $27.6\,\%$ oxygen. Determine its empirical formula. (A_r: H 1.0, C 12.0, O 16.0.)

Working	Comment
In $100\ \text{g}$: $\mathrm{C} = 62.1\ \text{g}$, $\mathrm{H} = 10.3\ \text{g}$, $\mathrm{O} = 27.6\ \text{g}$	Assume 100 g, so each percentage becomes a mass in grams.
$n(\mathrm{C}) = \dfrac{62.1}{12.0} = 5.175\ \text{mol}$	$n = m / M$: divide each mass by the element's A_r.
$n(\mathrm{H}) = \dfrac{10.3}{1.0} = 10.30\ \text{mol}$	
$n(\mathrm{O}) = \dfrac{27.6}{16.0} = 1.725\ \text{mol}$	Oxygen has the smallest number of moles.
Divide by the smallest (1.725): $\mathrm{C}\,\dfrac{5.175}{1.725} = 3.00$, $\mathrm{H}\,\dfrac{10.30}{1.725} = 5.97$, $\mathrm{O}\,\dfrac{1.725}{1.725} = 1.00$	Scales the smallest to 1.
Ratio $\mathrm{C:H:O} = 3:6:1$	Already whole numbers ($5.97 \approx 6$, rounding).
$\therefore$ empirical formula $= \mathrm{C_3H_6O}$	Simplest whole-number ratio of atoms.

Worked Example 3 — An oxide of nitrogen contains $25.9\,\%$ nitrogen and $74.1\,\%$ oxygen by mass. Determine its empirical formula. (A_r: N 14.0, O 16.0.)

Assume a $100\,\text{g}$ sample, so it contains $25.9\,\text{g}$ of nitrogen and $74.1\,\text{g}$ of oxygen. Converting each to moles,

$$n(\text{N}) = \frac{25.9}{14.0} = 1.850\,\text{mol}, n(\text{O}) = \frac{74.1}{16.0} = 4.631\,\text{mol}.$$

Dividing both by the smaller value (1.850):

$$\text{N}:\text{O} = \frac{1.850}{1.850} : \frac{4.631}{1.850} = 1.00 : 2.50.$$

The ratio $1:2.50$ is not a whole-number ratio, and 2.50 is a genuine half — not rounding error — so multiply *both* numbers by 2:

$$\text{N}:\text{O} = 2:5.$$

$\therefore$ the empirical formula of the oxide is N_2O_5.

Worked Example 4 — Ethylene glycol, the main ingredient of engine coolant, contains $38.7\,\%$ carbon, $9.7\,\%$ hydrogen and $51.6\,\%$ oxygen by mass, and has a molar mass of $62.0\,\text{g mol}^{-1}$. Determine its empirical formula and its molecular formula. (A_r: H 1.0, C 12.0, O 16.0.)

In a $100\,\text{g}$ sample there are $38.7\,\text{g}$ C, $9.7\,\text{g}$ H and $51.6\,\text{g}$ O. Converting to moles,

$$n(\text{C}) = \frac{38.7}{12.0} = 3.225, n(\text{H}) = \frac{9.7}{1.0} = 9.70, n(\text{O}) = \frac{51.6}{16.0} = 3.225.$$

Dividing by the smallest (3.225):

$$\text{C}:\text{H}:\text{O} = 1.00 : 3.01 : 1.00 = 1:3:1,$$

so the **empirical formula is** CH_3O. Its empirical formula mass is $M_{\text{empirical}} = 12.0 + 3(1.0) + 16.0 = 31.0\,\text{g mol}^{-1}$. Comparing with the measured molar mass,

$$k = \frac{M}{M_{\text{empirical}}} = \frac{62.0}{31.0} = 2,$$

so the molecular formula contains twice the empirical unit: $(\text{CH}_3\text{O})_2$.

$\therefore$ the empirical formula is CH_3O and the molecular formula is $\text{C}_2\text{H}_6\text{O}_2$.

Practice questions

Question 1 — Calculate the molar mass of each of the following covalent compounds. (A_r: H 1.0, C 12.0, O 16.0.)

a. methane, CH_4
b. carbon dioxide, CO_2
c. glucose, $\text{C}_6\text{H}_{12}\text{O}_6$

Question 2 — Methanol, CH_4O, is a covalent liquid used as a fuel and solvent. (A_r: H 1.0, C 12.0, O 16.0.)

a. Calculate the molar mass of methanol.
b. Calculate the percentage by mass of carbon, of hydrogen and of oxygen in methanol.
c. Using your answer to part b, calculate the mass of carbon in a $64.0\,\text{g}$ sample of methanol.

Question 3 — A hydrocarbon contains $85.7\,\%$ carbon and $14.3\,\%$ hydrogen by mass. (A_r: H 1.0, C 12.0.)

a. Assuming a $100\,\text{g}$ sample, state the mass of carbon and of hydrogen present.
b. Calculate the number of moles of carbon atoms and of hydrogen atoms in the sample.
c. Divide by the smaller value to find the empirical formula of the hydrocarbon.

Question 4 — An oxide of nitrogen contains $36.8\,\%$ nitrogen and $63.2\,\%$ oxygen by mass. (A_r: N 14.0, O 16.0.)

a. Calculate the number of moles of nitrogen atoms and of oxygen atoms in a $100\,\text{g}$ sample.
b. Divide by the smaller value and write down the ratio obtained.
c. Explain why the ratio must be multiplied by 2, and state the empirical formula.

Question 5 — A compound has the empirical formula CH_2O and a molar mass of $60.0\,\text{g mol}^{-1}$. (A_r: H 1.0, C 12.0, O 16.0.)

a. Calculate the molar mass of the empirical unit CH_2O.
b. Calculate the whole number $k = M / M_{\text{empirical}}$.
c. State the molecular formula of the compound.

Question 6 — A covalent compound contains $92.3\,\%$ carbon and $7.7\,\%$ hydrogen by mass and has a molar mass of $78.0\,\text{g mol}^{-1}$. (A_r: H 1.0, C 12.0.)

a. Determine the empirical formula of the compound.
b. Calculate the molar mass of the empirical unit.
c. Determine the molecular formula.

Question 7 — Ethanoic acid (acetic acid), the acid in vinegar, has the molecular formula CH_3COOH (that is, $\text{C}_2\text{H}_4\text{O}_2$). Calculate its molar mass. (A_r: H 1.0, C 12.0, O 16.0.)

Question 8 — Calculate the percentage composition by mass of carbon dioxide, CO_2. (A_r: C 12.0, O 16.0.)

Question 9 — Glucose has the molecular formula $\text{C}_6\text{H}_{12}\text{O}_6$. ($A_r$: H 1.0, C 12.0, O 16.0.)

a. Calculate the percentage by mass of each element in glucose.
b. Hence calculate the mass of carbon in a $25.0\,\text{g}$ sample of glucose.

Question 10 — An oxide of sulfur is a covalent compound containing $40.1\,\%$ sulfur and $59.9\,\%$ oxygen by mass. Determine its empirical formula. (A_r: O 16.0, S 32.1.)

Question 11 — A gaseous hydrocarbon contains $81.8\,\%$ carbon and $18.2\,\%$ hydrogen by mass. Determine its empirical formula, showing clearly how you obtain whole numbers. (A_r: H 1.0, C 12.0.)

Question 12 — A covalent acid contains $26.7\,\%$ carbon, $2.2\,\%$ hydrogen and $71.1\,\%$ oxygen by mass, and has a molar mass of $90.0\,\text{g mol}^{-1}$. Determine its empirical formula and its molecular formula. (A_r: H 1.0, C 12.0, O 16.0.)

Question 13 — A compound has the empirical formula CH_2 and a molar mass of $56.0\,\text{g mol}^{-1}$. Determine its molecular formula. (A_r: H 1.0, C 12.0.)

Question 14 — An ester contains $54.5\,\%$ carbon, $9.1\,\%$ hydrogen and $36.4\,\%$ oxygen by mass, and has a molar mass of $88.0\,\text{g mol}^{-1}$. Determine its empirical formula and its molecular formula. (A_r: H 1.0, C 12.0, O 16.0.)

Question 15 — An amine contains $38.7\,\%$ carbon, $16.1\,\%$ hydrogen and $45.2\,\%$ nitrogen by mass, and has a molar mass of $31.0\,\text{g mol}^{-1}$. Determine its empirical formula and its molecular formula. (A_r: H 1.0, C 12.0, N 14.0.)

Question 16 — Explain the difference between the empirical formula and the molecular formula of a covalent compound. In your answer, use CH_2O and $\text{C}_6\text{H}_{12}\text{O}_6$ as an example, and explain why the percentage composition by mass alone is not enough to determine the molecular formula.

Question 17 — In the method for finding an empirical formula from percentage composition, explain the purpose of each of the following steps: (i) assuming a $100\,\text{g}$ sample; (ii) dividing each mass by the relative atomic mass; (iii) dividing all the mole values by the smallest; and (iv) multiplying the resulting ratio by 2 or 3 in some problems.

Question 18 — A gaseous hydrocarbon used as a fuel is analysed and found to contain $82.8\,\%$ carbon and $17.2\,\%$ hydrogen by mass. A mass spectrometer shows that its molar mass is $58.0\,\text{g mol}^{-1}$.

a. Determine the empirical formula of the hydrocarbon.
b. Determine its molecular formula.
c. State how the value of the molar mass was needed in your answer.

Question 19 — Dinitrogen tetroxide has the molecular formula N_2O_4. (A_r: N 14.0, O 16.0.)

a. Calculate its percentage composition by mass.
b. Determine its empirical formula.
c. State the relationship between the molecular formula and the empirical formula.

Question 20 — Methanal, CH_2O, ethanoic acid, $\text{C}_2\text{H}_4\text{O}_2$, and glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, are three different covalent compounds. (A_r: H 1.0, C 12.0, O 16.0.)

a. Show that all three have the same empirical formula.
b. Show that all three have the same percentage composition by mass.
c. Explain what this demonstrates about using percentage composition to identify a compound.

Answers

1 a $16.0\,\text{g mol}^{-1}$; b $44.0\,\text{g mol}^{-1}$; c $180.0\,\text{g mol}^{-1}$. **2** a $32.0\,\text{g mol}^{-1}$; b C 37.5 %, H 12.5 %, O 50.0 %; c 24.0 g. **3** a C 85.7 g, H 14.3 g; b $n(\text{C}) = 7.14$, $n(\text{H}) = 14.3$; c CH_2. **4** a $n(\text{N}) = 2.63$, $n(\text{O}) = 3.95$; b 1 : 1.50; c × 2 clears the half → N_2O_3. **5** a $30.0\,\text{g mol}^{-1}$; b $k = 2$; c $\text{C}_2\text{H}_4\text{O}_2$. **6** a CH; b $13.0\,\text{g mol}^{-1}$; c C_6H_6. **7** $60.0\,\text{g mol}^{-1}$. **8** C 27.3 %, O 72.7 %. **9** a C 40.0 %, H 6.7 %, O 53.3 %; b 10.0 g. **10** SO_3. **11** C_3H_8 (ratio 1 : 2.67, × 3). **12** empirical CHO_2; molecular $\text{C}_2\text{H}_2\text{O}_4$. **13** C_4H_8. **14** empirical $\text{C}_2\text{H}_4\text{O}$; molecular $\text{C}_4\text{H}_8\text{O}_2$. **15** empirical CH_5N; molecular CH_5N (same; $k = 1$). **16** empirical = simplest ratio (CH_2O), molecular = actual atoms ($\text{C}_6\text{H}_{12}\text{O}_6 = 6 \times$ empirical); % composition gives only the ratio, so the molar mass is needed to find k. **17** (i) makes each % equal a mass in grams; (ii) converts mass → moles = atom ratio; (iii) scales the smallest to 1; (iv) clears a half or thirds to whole numbers. **18** a C_2H_5; b C_4H_{10}; c the molar mass gave $k = 2$, fixing the multiple of the empirical unit. **19** a N 30.4 %, O 69.6 %; b NO_2; c molecular = 2 × empirical. **20** a all reduce to CH_2O; b all are C 40.0 %, H 6.7 %, O 53.3 %; c % composition alone cannot distinguish compounds that share an empirical formula.

Fully-worked solutions

Question 1 a. $M(\text{CH}_4) = 12.0 + 4(1.0) = 16.0\,\text{g mol}^{-1}$. b. $M(\text{CO}_2) = 12.0 + 2(16.0) = 44.0\,\text{g mol}^{-1}$. c. $M(\text{C}_6\text{H}_{12}\text{O}_6) = 6(12.0) + 12(1.0) + 6(16.0) = 72.0 + 12.0 + 96.0 = 180.0\,\text{g mol}^{-1}$.

Question 2 a. $M(\text{CH}_4\text{O}) = 12.0 + 4(1.0) + 16.0 = 32.0\,\text{g mol}^{-1}$. b. $\%\,\text{C} = \dfrac{12.0}{32.0} \times 100 = 37.5\,\%$; $\%\,\text{H} = \dfrac{4(1.0)}{32.0} \times 100 = 12.5\,\%$; $\%\,\text{O} = \dfrac{16.0}{32.0} \times 100 = 50.0\,\%$. (Check: $37.5 + 12.5 + 50.0 = 100.0$.) c. Mass of carbon $= \dfrac{37.5}{100} \times 64.0 = 24.0\,\text{g}$.

Question 3 a. In 100 g: carbon = 85.7 g and hydrogen = 14.3 g. b. $n(\text{C}) = \dfrac{85.7}{12.0} = 7.14\,\text{mol}$; $n(\text{H}) = \dfrac{14.3}{1.0} = 14.3\,\text{mol}$. c. Divide by the smaller value (7.14): $\text{C} : \text{H} = \dfrac{7.14}{7.14} : \dfrac{14.3}{7.14} = 1.00 : 2.00$. ∴ the empirical formula is CH_2.

Question 4 a. In 100 g: $n(\text{N}) = \dfrac{36.8}{14.0} = 2.63\,\text{mol}$; $n(\text{O}) = \dfrac{63.2}{16.0} = 3.95\,\text{mol}$. b. Divide by the smaller value (2.63): $\text{N} : \text{O} = 1.00 : \dfrac{3.95}{2.63} = 1.00 : 1.50$. c. The value 1.50 is a genuine half, not rounding error, so it cannot simply be rounded. Multiplying both numbers by 2 clears it: $\text{N} : \text{O} = 2 : 3$. ∴ the empirical formula is N_2O_3.

Question 5 a. $M_{\text{empirical}}(\text{CH}_2\text{O}) = 12.0 + 2(1.0) + 16.0 = 30.0\,\text{g mol}^{-1}$. b. $k = \dfrac{M}{M_{\text{empirical}}} = \dfrac{60.0}{30.0} = 2$. c. Molecular formula $= (\text{CH}_2\text{O})_2 = \text{C}_2\text{H}_4\text{O}_2$.

Question 6 a. In 100 g: $n(\text{C}) = \dfrac{92.3}{12.0} = 7.69\,\text{mol}$, $n(\text{H}) = \dfrac{7.7}{1.0} = 7.70\,\text{mol}$. Divide by the smaller (7.69): $\text{C} : \text{H} = 1.00 : 1.00$, so the empirical formula is CH. b. $M_{\text{empirical}}(\text{CH}) = 12.0 + 1.0 = 13.0\,\text{g mol}^{-1}$. c. $k = \dfrac{78.0}{13.0} = 6$, so the molecular formula is $(\text{CH})_6 = \text{C}_6\text{H}_6$ (benzene).

Question 7 $M(\text{C}_2\text{H}_4\text{O}_2) = 2(12.0) + 4(1.0) + 2(16.0) = 24.0 + 4.0 + 32.0 = 60.0\,\text{g mol}^{-1}$.

Question 8 $M(\text{CO}_2) = 44.0\,\text{g mol}^{-1}$. $\%\,\text{C} = \dfrac{12.0}{44.0} \times 100 = 27.3\,\%$; $\%\,\text{O} = \dfrac{2(16.0)}{44.0} \times 100 = 72.7\,\%$. (Check: $27.3 + 72.7 = 100.0$.)

Question 9 a. $M(\mathrm{C_6H_{12}O_6}) = 180.0\ \mathrm{g\ mol^{-1}}$. $\%\,\mathrm{C} = \dfrac{6(12.0)}{180.0} \times 100 = 40.0\,\%$; $\%\,\mathrm{H} = \dfrac{12(1.0)}{180.0} \times 100 = 6.7\,\%$; $\%\,\mathrm{O} = \dfrac{6(16.0)}{180.0} \times 100 = 53.3\,\%$. b. Mass of carbon $= \dfrac{40.0}{100} \times 25.0 = 10.0\ \mathrm{g}$.

Question 10 In 100 g: $n(\mathrm{S}) = \dfrac{40.1}{32.1} = 1.249\ \mathrm{mol}$, $n(\mathrm{O}) = \dfrac{59.9}{16.0} = 3.744\ \mathrm{mol}$. Divide by the smaller (1.249): $\mathrm{S:O} = 1.00:3.00$. $\therefore$ the empirical formula is $\mathrm{SO_3}$.

Question 11 In 100 g: $n(\mathrm{C}) = \dfrac{81.8}{12.0} = 6.82\ \mathrm{mol}$, $n(\mathrm{H}) = \dfrac{18.2}{1.0} = 18.2\ \mathrm{mol}$. Divide by the smaller (6.82): $\mathrm{C:H} = 1.00:2.67$. The value 2.67 is close to $2\,2/3$, so multiply both numbers by 3: $\mathrm{C:H} = 3:8.01 \approx 3:8$. $\therefore$ the empirical formula is $\mathrm{C_3H_8}$.

Question 12 In 100 g: $n(\mathrm{C}) = \dfrac{26.7}{12.0} = 2.225$, $n(\mathrm{H}) = \dfrac{2.2}{1.0} = 2.20$, $n(\mathrm{O}) = \dfrac{71.1}{16.0} = 4.444\ \mathrm{mol}$. Divide by the smallest (2.20): $\mathrm{C:H:O} = 1.01:1.00:2.02 \approx 1:1:2$, so the empirical formula is $\mathrm{CHO_2}$. Its empirical mass is $M_{\text{empirical}} = 12.0 + 1.0 + 2(16.0) = 45.0\ \mathrm{g\ mol^{-1}}$, so $k = \dfrac{90.0}{45.0} = 2$. $\therefore$ the molecular formula is $(\mathrm{CHO_2})_2 = \mathrm{C_2H_2O_4}$ (oxalic acid).

Question 13 $M_{\text{empirical}}(\mathrm{CH_2}) = 12.0 + 2(1.0) = 14.0\ \mathrm{g\ mol^{-1}}$. $k = \dfrac{56.0}{14.0} = 4$. $\therefore$ the molecular formula is $(\mathrm{CH_2})_4 = \mathrm{C_4H_8}$.

Question 14 In 100 g: $n(\mathrm{C}) = \dfrac{54.5}{12.0} = 4.54$, $n(\mathrm{H}) = \dfrac{9.1}{1.0} = 9.10$, $n(\mathrm{O}) = \dfrac{36.4}{16.0} = 2.275\ \mathrm{mol}$. Divide by the smallest (2.275): $\mathrm{C:H:O} = 2.00:4.00:1.00$, so the empirical formula is $\mathrm{C_2H_4O}$. Its empirical mass is $M_{\text{empirical}} = 2(12.0) + 4(1.0) + 16.0 = 44.0\ \mathrm{g\ mol^{-1}}$, so $k = \dfrac{88.0}{44.0} = 2$. $\therefore$ the molecular formula is $(\mathrm{C_2H_4O})_2 = \mathrm{C_4H_8O_2}$.

Question 15 In 100 g: $n(\mathrm{C}) = \dfrac{38.7}{12.0} = 3.225$, $n(\mathrm{H}) = \dfrac{16.1}{1.0} = 16.1$, $n(\mathrm{N}) = \dfrac{45.2}{14.0} = 3.229\ \mathrm{mol}$. Divide by the smallest (3.225): $\mathrm{C:H:N} = 1.00:4.99:1.00 \approx 1:5:1$, so the empirical formula is $\mathrm{CH_5N}$. Its empirical mass is $M_{\text{empirical}} = 12.0 + 5(1.0) + 14.0 = 31.0\ \mathrm{g\ mol^{-1}}$, so $k = \dfrac{31.0}{31.0} = 1$. $\therefore$ the molecular formula is the same as the empirical formula, $\mathrm{CH_5N}$ (methanamine).

Question 16 The **empirical formula** gives the simplest whole-number ratio of the atoms in a compound, while the **molecular formula** gives the actual number of atoms of each element in one molecule. The molecular formula is always a whole-number multiple of the empirical formula. For example, glucose has the empirical formula $\mathrm{CH_2O}$ but the molecular formula $\mathrm{C_6H_{12}O_6}$, which is six times the empirical unit. Percentage composition by mass is fixed by the *ratio* of the atoms, so it can give only the empirical formula — it cannot tell $\mathrm{CH_2O}$, $\mathrm{C_2H_4O_2}$ and $\mathrm{C_6H_{12}O_6}$ apart, because all three have the same ratio. To find which multiple (k) is present, we also need the molar mass of the compound; only then can the molecular formula be determined.

Question 17 (i) Assuming a 100 g sample makes each element's percentage numerically equal to its mass in grams, so the percentages can be used directly as masses. (ii) Dividing each mass by the relative atomic mass converts a mass into an amount in moles ($n = m / M$); because equal numbers of moles contain equal numbers of atoms, the mole values are in the same ratio as the atoms in the compound. (iii) Dividing every mole value by the smallest scales that element down to 1 and expresses the others relative to it, which produces the simplest ratio. (iv) If a ratio comes out as a simple fraction such as $1:1.5$ or $1:2.67$, multiplying all the numbers by 2 or 3 clears the fraction and gives the whole-number ratio required for an empirical formula.

Question 18 a. In $100\,\text{g}$: $n(\text{C}) = \dfrac{82.8}{12.0} = 6.90$, $n(\text{H}) = \dfrac{17.2}{1.0} = 17.2\,\text{mol}$. Divide by the smaller (6.90): $\text{C}:\text{H} = 1.00:2.49 \approx 1:2.5$. Multiplying by 2 gives $\text{C}:\text{H} = 2:5$, so the empirical formula is C_2H_5. b. $M_{\text{empirical}}(\text{C}_2\text{H}_5) = 2(12.0) + 5(1.0) = 29.0\,\text{g mol}^{-1}$. $k = \dfrac{58.0}{29.0} = 2$, so the molecular formula is $(\text{C}_2\text{H}_5)_2 = \text{C}_4\text{H}_{10}$ (butane). c. The percentage composition gave only the empirical formula, C_2H_5. The molar mass ($58.0\,\text{g mol}^{-1}$) was needed to find $k = 2$, which fixes how many empirical units make up one molecule and therefore gives the molecular formula.

Question 19 a. $M(\text{N}_2\text{O}_4) = 2(14.0) + 4(16.0) = 28.0 + 64.0 = 92.0\,\text{g mol}^{-1}$. $\%\,\text{N} = \dfrac{28.0}{92.0} \times 100 = 30.4\,\%$; $\%\,\text{O} = \dfrac{64.0}{92.0} \times 100 = 69.6\,\%$. b. The ratio of atoms in N_2O_4 is $\text{N}:\text{O} = 2:4 = 1:2$, so the empirical formula is NO_2. c. The molecular formula is twice the empirical formula: $\text{N}_2\text{O}_4 = (\text{NO}_2)_2$, i.e. $k = 2$.

Question 20 a. Reducing each molecular formula to its simplest ratio: CH_2O is already simplest; $\text{C}_2\text{H}_4\text{O}_2$ divides by 2 to give CH_2O; $\text{C}_6\text{H}_{12}\text{O}_6$ divides by 6 to give CH_2O. All three share the empirical formula CH_2O. b. Each has the atom ratio $\text{C}:\text{H}:\text{O} = 1:2:1$, so each has $\%\,\text{C} = \dfrac{12.0}{30.0} \times 100 = 40.0\,\%$, $\%\,\text{H} = \dfrac{2(1.0)}{30.0} \times 100 = 6.7\,\%$ and $\%\,\text{O} = \dfrac{16.0}{30.0} \times 100 = 53.3\,\%$ (using the empirical unit, or equivalently the full formula — the ratio, and hence the percentages, are identical). c. Because these three different compounds have identical percentage compositions, percentage composition by mass **cannot by itself identify a compound**: it fixes only the empirical formula. The molar mass is also required to determine the molecular formula and so distinguish the compounds.