

Topic 1.2: Mass Spectrometry

Revision Notes · AP Chemistry

UNIT 1 · ATOMIC STRUCTURE AND PROPERTIES

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What a Mass Spectrum Shows

A mass spectrometer sorts the atoms of a sample by mass. The sample is vaporized and ionized, the ions are accelerated, and they are then separated according to their mass-to-charge ratio, written m/z .

A detector records how many ions arrive at each value of m/z . The result is a mass spectrum: a graph with m/z on the horizontal axis and relative abundance on the vertical axis.

For the singly charged ions met in AP Chemistry, m/z is effectively the mass of the isotope in atomic mass units. Each peak on the spectrum is one isotope of the element.

The position of a peak tells you the mass of that isotope. The height of a peak tells you how much of that isotope is present, compared with the others.

Isotopes: Same Element, Different Masses

Isotopes are atoms of the same element with the same number of protons but different numbers of neutrons. They behave almost identically in chemical reactions, but their masses differ.

Most elements do not occur as a single isotope. A natural sample of chlorine, for example, is a mixture of ^{35}Cl and ^{37}Cl atoms, roughly three of the first for every one of the second.

That mixture is why the masses on the periodic table are not whole numbers. The table does not list the mass of any single atom; it lists the average mass of the mixture.

Read a peak's position carefully. The peak for ^{35}Cl sits at the exact isotopic mass, 34.97, not at the mass number 35. The two are close, but calculations use the exact value.

Average Atomic Mass Is a Weighted Average

The average atomic mass of an element is the mass of each isotope weighted by how common that isotope is:

$$\text{average atomic mass} = \Sigma (\text{fractional abundance} \times \text{isotopic mass})$$

The symbol Σ means "add up the contributions of every isotope". The fractional abundance is the percentage abundance divided by 100, so the fractions in any calculation must add up to exactly 1.

A weighted average is pulled toward the heavy contributors. Because ^{35}Cl is about three times as common as ^{37}Cl , the average for chlorine, 35.45, sits much closer to 35 than to 37.

Two checks catch most errors before they cost marks. The average must fall between the lightest and heaviest isotope masses, and it must sit closer to the mass of the most abundant isotope. An answer outside that range is impossible.

Finding an Unknown Abundance

Some questions give the average atomic mass and ask for the abundances. With two isotopes, the fractions must add to 1, so one unknown is enough.

Call the fraction of the first isotope x . The fraction of the second is then $(1 - x)$.

Substitute both into the weighted average formula, solve for x , and convert the fractions back to percentages at the end. Worked Example 3 runs this method in full.

Worked Examples

Example 1: A two-isotope average

Chlorine has two isotopes: ^{35}Cl (mass 34.969, abundance 75.77%) and ^{37}Cl (mass 36.966, abundance 24.23%). Calculate the average atomic mass.

$$\text{average} = (0.7577 \times 34.969) + (0.2423 \times 36.966) = 26.50 + 8.96 = 35.45.$$

The result matches the periodic table value for chlorine, and it sits closer to 34.97, the mass of the more abundant isotope, exactly as it should.

Example 2: Three isotopes

Magnesium has three isotopes: ^{24}Mg (mass 23.985, abundance 78.99%), ^{25}Mg (mass 24.986, abundance 10.00%) and ^{26}Mg (mass 25.983, abundance 11.01%). Calculate the average atomic mass.

$$\text{average} = (0.7899 \times 23.985) + (0.1000 \times 24.986) + (0.1101 \times 25.983) = 18.95 + 2.50 + 2.86 = 24.31.$$

The method does not change with more isotopes. Each isotope adds one term to the sum, and the fractions still add to 1.

Example 3: Solving for an unknown abundance

Copper has two isotopes, ^{63}Cu (mass 62.930) and ^{65}Cu (mass 64.928), and an average atomic mass of 63.546. Find the percentage abundance of each isotope.

Let x be the fraction of ^{63}Cu , so $(1 - x)$ is the fraction of ^{65}Cu :

$$63.546 = (x \times 62.930) + ((1 - x) \times 64.928)$$

Solving gives $x = 0.692$. So copper is 69.2% ^{63}Cu and 30.8% ^{65}Cu .

The average, 63.546, sits closer to 62.930 than to 64.928, which fits ^{63}Cu being the more abundant isotope.

Example 4: Reading abundances off a spectrum

A mass spectrum of neon shows three peaks: at mass 19.992 with relative abundance 90.48%, at 20.994 with 0.27%, and at 21.991 with 9.25%. Calculate the average atomic mass of neon.

$$\text{average} = (0.9048 \times 19.992) + (0.0027 \times 20.994) + (0.0925 \times 21.991) = 18.09 + 0.06 + 2.03 = 20.18.$$

The tiny middle peak barely moves the average. A peak's contribution depends on its mass and its abundance together, never on either one alone.

Traps Specific to This Topic

Percentages must be converted to fractions before they enter the formula. Multiplying by 75.77 instead of 0.7577 gives an "average" near 3,545, and the size of the number is itself the warning sign.

Never take a simple mean of the isotope masses. The simple mean of 34.969 and 36.966 is 35.97, but chlorine's real average is 35.45, because the lighter isotope is three times as common.

No single atom has the average mass. There is no chlorine atom with a mass of 35.45; that number describes the mixture, not any atom in it.

Peak heights are sometimes scaled so the tallest peak reads 100, and those numbers are not percentages. Divide each height by the total of all heights to get true fractions before calculating.

An element is identified by its average atomic mass, not by one peak. Several elements can share a peak position; only the full pattern of peaks and abundances, and the average they produce, points to one element.

Key Relationships to Remember

- Each peak on a mass spectrum is one isotope: position gives its mass, height gives its relative abundance
- average atomic mass = Σ (fractional abundance $\times$ isotopic mass)
- Fractional abundances always add to 1; percentages must be divided by 100 first
- The average lies between the lightest and heaviest isotope masses, closer to the most abundant one
- For two isotopes with an unknown split, use x and $(1 - x)$ and solve the weighted average equation

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