Chemistry 1000 Lecture 1: Atoms

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Atoms and subatomic particles

- Atoms are mostly empty space.
  - Protons and neutrons occupy small, dense nucleus.
  - Electrons move around outside of the nucleus.
- The proton and neutron are each more than 1800 times heavier than the electron.
- Charge of proton $= -$(charge of electron) $= e$
- A neutral atom has an equal number of electrons and protons.

Atomic number and mass number

Atomic number: Number of protons in the nucleus

Symbol: Z

Mass number: Total number or protons and neutrons in the nucleus

Symbol: A

Elements and isotopes

Elements are characterized by a common value of Z.

Isotopes have the same Z (same element) but different A.

Notation: ${}^{A}_{Z}\mathrm{E}$, e.g. ${}^{3}_{2}\mathrm{He}$

or

${}^{A}\mathrm{E}$, e.g. ${}^{3}\mathrm{He}$

Isotopomers are molecules that differ only in the isotopes they contain.

Example: ${}^{12}\mathrm{C}{}^{16}\mathrm{O}$ and ${}^{13}\mathrm{C}{}^{16}\mathrm{O}$ are isotopomers.

Isotopic masses

Atomic mass unit: $\frac{1}{12}$ of the mass of a single atom of ^{12}C

Symbol: u

- The mass in u is *approximately* equal to A.

  Example: The mass of an ^{16}O atom is 15.9949 u.

- 1 mol = number of atoms in 12 g of ^{12}C
- $\therefore$ 1 u $\equiv$ 1 g/mol

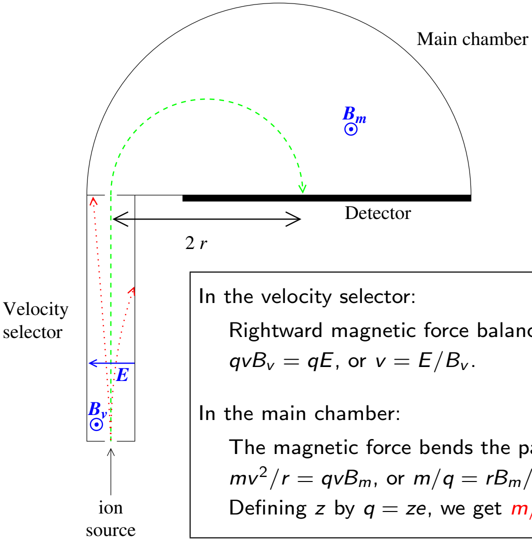
Aside: the new mole

- In November of this year, the Conférence générale des poids et mesures will redefine several SI units in terms of fixed values of the universal constants.
- The mole will be redefined as follows:

  One mole contains exactly $6.022\,140\,76 \times 10^{23}$ *entities.*

- This means that Avogadro's constant will be fixed at the above value, but the link with the mass of ^{12}C will be lost. 1 mol of ^{12}C will no longer weigh exactly 12 g or, to put it another way, it will only approximately be true that 1 u is equivalent to 1 g/mol.
- Practical implications? Few for those of us who aren't trying to measure things to 8 decimal places.

Bainbridge mass spectrometer



In the velocity selector:

Rightward magnetic force balances leftward electric force when $qvB_v = qE$, or $v = E/B_v$.

In the main chamber:

The magnetic force bends the particle's path into a circle.
$mv^2/r = qvB_m$, or $m/q = rB_m/v$.
Defining z by $q = ze$, we get $m/z = reB_m/v$.

Bainbridge mass spectrometer (continued)

$$\frac{m}{z} = \frac{reB_m}{v}$$

- The key measurement is r, the radius of the orbit of the charged particles.
- In theory, if we know B_m and $v = E/B_v$, we can calculate m/z.
- Suppose that we introduce a standard with a known m/z. Then

$$\frac{m_2/z_2}{m_1/z_1} = \frac{r_2}{r_1}.$$

- If we use gentle ionization methods, then $z_1 = z_2 = 1$, so we have, simply,

$$\frac{m_2}{m_1} = \frac{r_2}{r_1}.$$

Bainbridge mass spectrometer (continued)

- In addition to m/z, the intensity of a signal (i.e. the number of ion impacts in the detector at a given r) gives the relative abundance, which gives us the isotopic composition of a sample.

Isotopic composition

- A sample of an element typically contains several isotopes.
- The isotopic composition depends on where the sample came from. Examples:
    - 1.06% of the CO_2 at sea level is $^{13}C^{16}O_2$, but this isotopomer accounts for only 0.98% of the CO_2 at 20 000 m of altitude (highest altitude from which viable bacteria have been recovered in air samples).
    - In natural samples from various sources, the ratio of ^{234}U to ^{238}U can vary from 2.8×10^{-5} to 7.8×10^{-5}.

Application: Where did that caviar come from?

- Caviar originally referred to salted sturgeon roe (eggs), but now often refers to salted roe from other fish species.
- Caviars vary widely in price.
- Is there a reasonably easy way to tell if a roe is being sold as something it isn't?
- Isotopically, you are what you eat!

Application: Where did that caviar come from?
(continued)

- Vendace is a species of whitefish that can live either in salt water or in fresh water. Caviar from salt-water vendace, commercially available only from Kalix, Sweden, is superior.
- The ratio of ^{87}Sr to ^{86}Sr turns out to be significantly different for salt-water vendace caviar ($\sim 0.71049 \pm 0.00029$) than for the fresh-water version ($\sim 0.7207 \pm 0.0021$), probably for two reasons:
  1. differences in this isotope ratio between sea water and fresh water, and
  2. differences in this isotope ratio in the salt used to prepare the caviar.

Source: I. Rodushkin et al., *Anal. Chim. Acta* **583**, 310 (2007).

Atomic mass

- The (average) atomic mass is an average over all isotopes in a sample.
- Since $1\,\mathrm{u} \equiv 1\,\mathrm{g/mol}$, the molar mass is also an average value for a sample.

$$\text{atomic mass of E} = \sum_{\substack{\text{isotopes}\\ \text{of E}}} \begin{pmatrix} \text{fractional} \\ \text{abundance} \end{pmatrix} \begin{pmatrix} \text{isotope} \\ \text{mass} \end{pmatrix}$$

Review: Significant figures

- The last significant figure of a number is the last digit in which you have some degree of confidence.

- Significant figure rules:
  - In addition and substraction, keep the least number of significant decimal places.
  - In multiplication and division, keep the least number of total significant figures.

Example: The atomic mass of copper

- Copper has two naturally occurring isotopes, with the following masses and abundances:

Isotope	Mass/u	Abundance/%
^{63}Cu	62.929 597 7	69.15
^{65}Cu	64.927 789 7	30.85

- The atomic mass is computed as follows:

$$\begin{aligned}\bar{m}_{\mathrm{Cu}} &= 0.6915(62.929\,597\,7\,u) + 0.3085(64.927\,789\,7) \\ &= 43.5\underline{1}58 + 20.0\underline{3}02\,u \\ &= 63.55\,u.\end{aligned}$$

Natural variability and atomic mass

- For some elements, the natural variability in the isotopic abundances is such that the atomic mass calculated from different samples varies significantly (i.e. the variation is in the significant figures). For others, the variability is negligible.
- In terms of how we present atomic masses, there are four cases:
  1. Elements with no long-lived isotopes: No standard atomic mass can be calculated.
  2. Elements with exactly one stable isotope: The atomic mass is the mass of the one isotope (so very precisely known).
  3. Elements with more than one stable isotope for which the sample-to-sample variation is negligible: The atomic mass can meaningfully be given as a single number.
  4. Elements for which the spread of atomic mass values for samples from different sources is larger than the uncertainty: The 2009 IUPAC recommendations recommend giving a range for the atomic mass instead of a single number.

Elements whose atomic masses are now given as a range

Element	**atomic mass/u**
H	[1.007 84,1.008 11]
Li	[6.938,6.997]
B	[10.806,10.821]
C	[12.0096,12.0116]
N	[14.006 43,14.007 28]
O	[15.999 03,15.999 77]
Mg	[24.304,24.307]
Si	[28.084,28.086]
S	[32.059,32.076]
Cl	[35.446,35.457]
Br	[79.901,79.907]
Tl	[204.382,204.385]

So how do you do a calculation with a range?

- Two options:
  1. Take the midpoint of the range.
     Example: The atomic weight of hydrogen is given by the range $[1.007\,84, 1.008\,11]$ u. We could take a "typical" atomic weight to be
     $$\bar{m}_H = \frac{1}{2}(1.007\,84 + 1.008\,11\,u) = 1.007\,98\,u.$$
  2. Use both ends of the range in a calculation and give your answer as a range.
     Example: a 10.052 g sample of H_2 would contain between 4.9856 and 4.9869 mol of H_2. (Try it!)

Atomic and molar masses

Example 1

Iron has four naturally occurring isotopes:

Isotope	Mass/u	Abundance/%
^{54}Fe	53.939 6105	5.845
^{56}Fe	55.934 9375	91.754
^{57}Fe	56.935 3940	2.119
^{58}Fe	57.933 2756	0.282

What is the molar mass of iron?

Answer: 55.845 g/mol

Atomic and molar masses

Example 2

Silver has two stable isotopes, ^{107}Ag (106.905 097 u) and ^{109}Ag (108.904 752 u). The molar mass of a silver sample (determined by chemical means) is 107.89 g/mol. What are the abundances of the two isotopes in this sample?

Hint: The fractional abundances sum to 1.

Answer: 51% ^{107}Ag, 49% ^{109}Ag

Atomic and molar masses

Example 3

The molar mass of carbon is [12.0096,12.0116] g/mol, and the abundance of ^{13}C (13.003 354 835 07 u) is 1.07% in typical sea-level samples. How many grams of carbon (all isotopes) are there in 10.00 g of sucrose ($C_{12}H_{22}O_{11}$)? How much of that carbon, in grams, is ^{13}C?

Answer: 4.211 g of carbon, 0.0488 g of ^{13}C