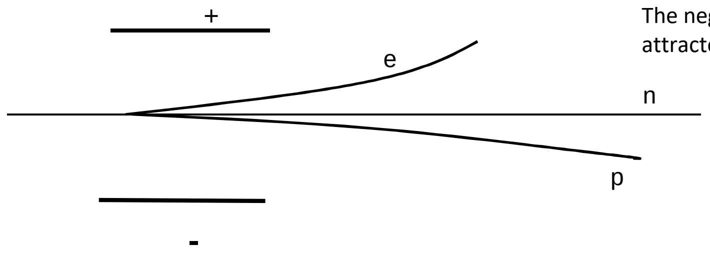
Atomic Structure

Details of the three Sub-atomic (fundamental) Particles

Particle	Position	Relative Mass	Relative Charge
Proton	Nucleus	1	+1
Neutron	Nucleus	1	0
Electron	Orbitals	1/1840	-1

Behaviour of beams of protons, neutrons and electrons in electric fields



The negatively charged electron is attracted towards the positive plate.

The neutron has no charge and is unaffected by a charged field

The positively charged proton is attracted towards the negative plate. It is deflected less than an electron as it has a larger mass

An atom of Lithium (Li) can be represented as follows:

Nucleon(mass) Number → **7**

Proton (atomic) Number → **3** **Li** ← Atomic Symbol

The **proton** (**atomic number**) ,Z, is the number of protons in the nucleus.
The **Nucleon** (**mass number)** ,A, is the total number of protons and neutrons in the atom.

Number of neutrons = A - Z

Isotopes

Isotopes are atoms with the same number of protons, but different numbers of neutrons.

Isotopes have similar chemical properties because they have the same electronic structure. They may have slightly varying physical properties because they have different masses.

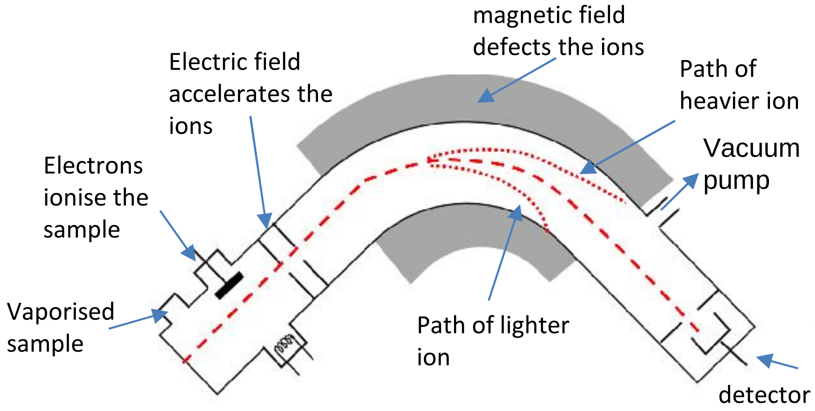
DEFINITION: **Relative isotopic mass** is the **mass** of one atom of an isotope compared to one twelfth of the mass of one atom of carbon-12

DEFINITION: **Relative atomic mass** is the **average mass** of one atom compared to one twelfth of the mass of one atom of carbon-12

DEFINITION: **Relative molecular mass** is the **average mass** of a molecule compared to one twelfth of the mass of one atom of carbon-12

There are two sorts of mass spectrometer. The following is the more old fashioned type. The time of flight spectrometer on the next page is the more modern type.

THE MASS SPECTROMETER – electron bombardment



The mass spectrometer can be used to determine all the isotopes present in a sample of an element and to therefore identify elements.

It needs to be under a vacuum otherwise air particles would ionise and register on the detector

The following are the essential 4 steps in a mass spectrometer.

Learn all these steps carefully!

1.Ionisation

•A Vaporised sample is injected at low pressure
•An electron gun fires high energy electrons at the sample
•This Knocks out an (outer) electron
•Forming positive ions with different charges E.g. Ti → $Ti^+ + e^-$

If the sample is not vaporized then vaporizing it would be the first step.

2. Acceleration

•A negative electric field accelerates the positive ions and makes them into a beam

3. Deflection

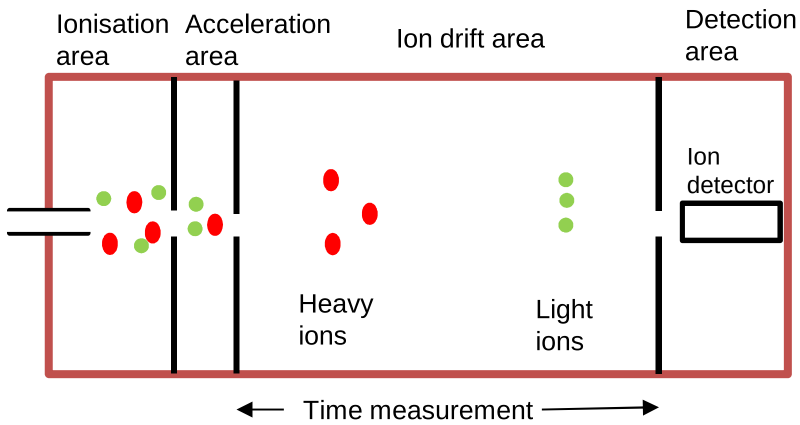
•The beam of positive ions is deflected by a strong magnetic field.
•The degree of deflection depends on the mass-to-charge ratio, m/z.
•The smaller this ratio the larger the deflection.
•By varying the magnetic field ratio, ions of different m/z ratios pass through the centre.

The heavier an ion the less it is deflected

4. Detection

•The ions reach the detector and generate a small current, which is fed to a computer for analysis. The current is produced by electrons transferring from the detector to the positive ions. The size of the current is proportional to the abundance of the species

The Time of Flight Mass Spectrometer



The mass spectrometer can be used to determine all the isotopes present in a sample of an element and to therefore identify elements.

It needs to be under a vacuum otherwise air particles would ionise and register on the detector

The following are the essential 4 steps in a mass spectrometer.

1. Ionisation

The sample can be ionised in a number of ways. Two of these techniques are electron impact and electrospray ionisation

Electron impact

•A Vaporised sample is injected at low pressure
•An electron gun fires high energy electrons at the sample
•This Knocks out an outer electron
•Forming positive ions with different charges E.g. Ti (g)→ Ti^+ (g)+ e^-

Electron impact is used for elements and substances with low formula mass. Electron impact can cause larger organic molecules to fragment

Electro Spray Ionisation

- The sample is dissolved in a volatile, polar solvent
- injected through a fine hypodermic needle giving a fine mist or aerosol
- the tip of needle has high voltage
- at the tip of the needle the sample molecule, M, gains a proton, H^+, from the solvent forming MH^+
- M(g) + H^+ → MH^+(g)
- The solvent evaporates away while the MH^+ ions move towards a negative plate

Electro Spray Ionisation is used preferably for larger organic molecules. The softer conditions of this technique mean fragmentation does not occur

2. Acceleration

•Positive ions are accelerated by an electric field
•To a constant kinetic energy

$KE = \frac{1}{2} m v^2$

KE = kinetic energy of particle (J)
m = mass of the particle (kg)
v = velocity of the particle (ms^{-1})

Given that all the particles have the same kinetic energy, the velocity of each particle depends on its mass. Lighter particles have a faster velocity, and heavier particles have a slower velocity.

You don't need to learn these equations but may be asked to use them in a calculation

Rearranged gives $v = \sqrt{\frac{2KE}{m}}$

3. Flight Tube

•The positive ions with smaller m/z values will have the same kinetic energy as those with larger m/z and will move faster.
•The heavier particles take longer to move through the drift area.
•The ions are distinguished by different flight times

$t = d/v$

t = time of flight (s)
d = length of flight tube (m)
v = velocity of the particle ($m\ s^{-1}$)

Combining the two equations gives you

$$t = d\sqrt{\frac{m}{2KE}}$$

4. Detection

•The ions reach the detector and generate a small current, which is fed to a computer for analysis. The current is produced by electrons transferring from the detector to the positive ions. The size of the current is proportional to the abundance of the species

For each isotope the mass spectrometer can measure a **m/z (mass/charge ratio)** and an **abundance**

Sometimes two electrons may be removed from a particle forming a 2+ ion. $^{24}Mg^{2+}$ with a 2+ charge would have a m/z of 12

Example A sample of Nickel was analysed and one of the isotopes found was ^{59}Ni. The ions were accelerated to have 1.000 x 10^{-16} J of kinetic energy and travelled through a flight tube that was 0.8000 m long.
How long would one ion of $^{59}Ni^+$ take to travel along the flight tube?
The Avogadro constant L = 6.022 × 10^{23} mol^{-1}

$$\text{Mass of one ion of } ^{59}Ni^+ = \frac{\text{mass of one mole of } ^{59}Ni^+}{\text{The Avogadro constant}}$$

= 59/ 6.022 × 10^{23}
= 9.797X10^{-23} g
= 9.797X10^{-26} kg

$$t = d\sqrt{\frac{m}{2KE}}$$

t= 0.8000 √(9.797X10^{-26}/(2x 1.000 x 10^{-16}))
t=1.771X10^{-5} s

Uses of Mass spectrometers

- Mass spectrometers have been included in planetary space probes so that elements on other planets can be identified. Elements on other planets can have a different composition of isotopes.
- Drug testing in sport to identify chemicals in the blood and to identify breakdown products from drugs in body
- quality control in pharmaceutical industry and to identify molecules from sample with potential biological activity
- radioactive dating to determine age of fossils or human remains

Radioactive Carbon Dating

All living things have small amounts of the radioactive Carbon-14 isotope. When a living thing dies no more 14C is produced and its starts to decay. The object becomes less radioactive over time.

Measure the abundance of **14C** in the material to be tested. By use of the half-life of **14C** work out how old the object is by working out how much it has decayed.

Calculating Relative Atomic Mass

The relative atomic mass quoted on the periodic table is a weighted average of all the isotopes

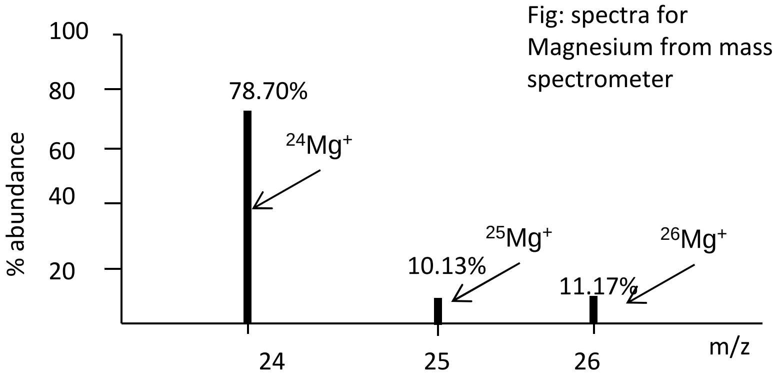


Fig: spectra for Magnesium from mass spectrometer

If asked to give the species for a peak in a mass spectrum then give charge and mass number e.g. $^{24}Mg^+$

$$\text{R.A.M} = \frac{\Sigma\ (\text{isotopic mass x \% abundance})}{100}$$

Use these equations to work out the R.A.M

For above example of Mg
R.A.M = [(78.7 x 24) + (10.13 x 25) + (11.17 x 26)] /100 = 24.3

$$\text{R.A.M} = \frac{\Sigma\ (\text{isotopic mass x relative abundance})}{\text{total relative abundance}}$$

If relative abundance is used instead of percentage abundance use this equation

Example: Calculate the relative atomic mass of Tellurium from the following abundance data:
124-Te relative abundance 2; 126-Te relative abundance 4; 128-Te relative abundance 7;
130-Te relative abundance 6

$$\text{R.A.M} = \frac{[(124\text{x}2) + (126\text{x}4) + (128\text{x}7) + (130\text{x}6)]}{19}$$

$$= 127.8$$

Example: Copper has two isotopes 63-Cu and 65-Cu. The relative atomic mass of copper is 63.5. Calculate the percentage abundances of these two isotopes.

63.55 = y*x*63 + (1-y)*x*65
63.55 = 63y +65 -65y
63.55 = 65 -2y
2y = 1.45
y = 0.725

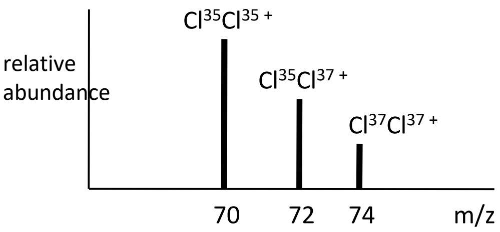
%abundance 63-Cu =72.5% %abundance 65-Cu = 27.5%

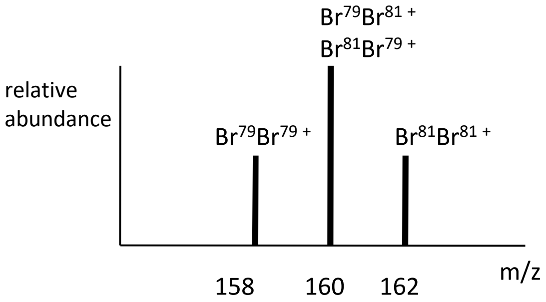
Mass spectra for Cl_2 and Br_2

Cl has two isotopes Cl^{35} (75%) and Cl^{37}(25%)

Br has two isotopes Br^{79} (50%) and Br^{81}(50%)

These lead to the following spectra caused by the diatomic molecules





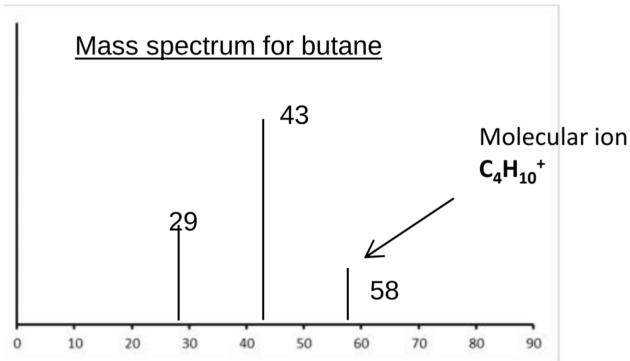
The 160 peak has double the abundance of the other two peaks because there is double the probability of 160 Br^{79}-Br^{81+} as can be Br79-Br81 and Br81-79

Mass spectrometers have been included in planetary space probes so that elements on other planets can be identified. Elements on other planets can have a different composition of isotopes

Measuring the M_r of a molecule

If a molecule is put through a mass spectrometer with an **Electron impact ionisation stage** it will often break up and give a series of peaks caused by the fragments. The peak with the largest m/z, however, will be due to the complete molecule and will be equal to the relative molecular mass , M_r ,of the molecule. This peak is called the parent ion or **molecular ion**

Spectra for C_4H_{10}



If a molecule is put through a mass spectrometer with **Electro Spray Ionisation** then fragmentation will not occur. There will be one peak that will equal the **mass of the MH^+ ion**. It will therefore be necessary to subtract 1 to get the M_r of the molecule. So if a peak at 521.1 is for MH^+, the relative molecular mass of the molecule is 520.1.