

Atomic Structure

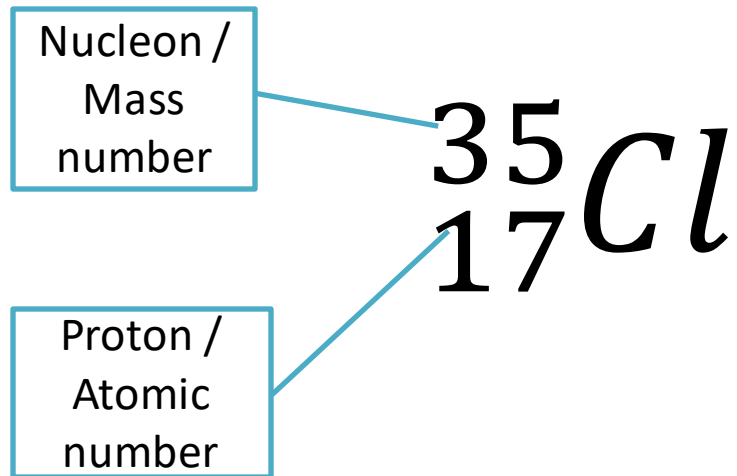
Learning objectives

- recall high school work on fundamental particles
- understand the meaning of mass number, atomic (proton) number
- be able to write and work with full atomic symbols
- understand why isotopes occur and the nature of radioactivity
- understand the significance of the p/n curve of elements
- be able to predict the effects of radioactive decay on proton, neutron and nucleon number
- be able to write simple nuclear equations
- understand the evolution of models of the atom: Dalton, Thomson, Rutherford, Bohr, the 'quantum model'
- be able to calculate relative atomic, molecular and formula mass
- recall a block diagram of the mass spectrometer
- understand the function of the main parts of the mass spectrometer
- be able to interpret a simple mass spectrum to obtain relative atomic mass and relative molecular mass
- understand and be able to work with a shell model of the atom: shell, sub-shell, orbital
- recall the shapes of s, p, d, and f orbital (sets)
- understand the rules for the filling of shells and sub-shells
- recall the Aufbau (Kletchkovsky) principle as a mnemonic for the arrangement of electrons
- be able to draw the electronic configuration for the first 36 elements
- understand ionisation energy
- understand the factors affecting ionisation energy: nuclear charge, distance from the nucleus, shielding
- understand and be able to use the idea of effective nuclear charge to explain trends in ionisation energy

Fundamental particles

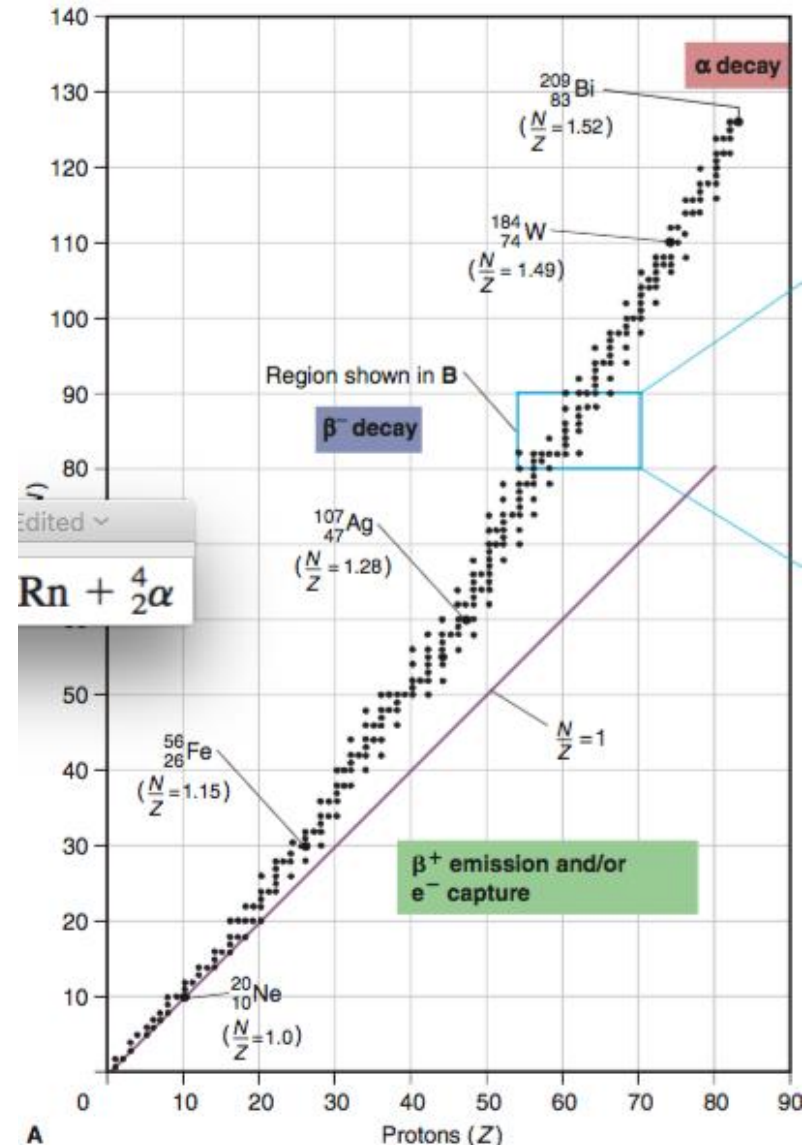
Particle	Symbol	Mass (relative)	Charge
Proton	p	1	+1
Neutron	n	1	no charge
Electron	e	ca. 1/2000 (negligible)	-1

Atom, symbol



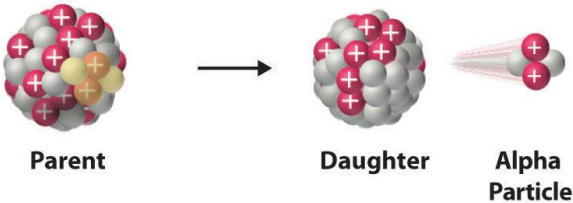
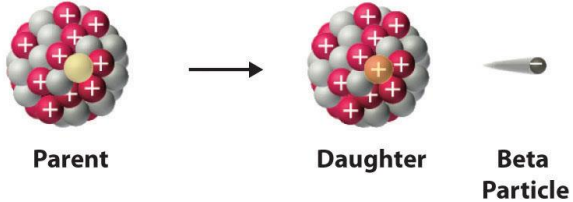
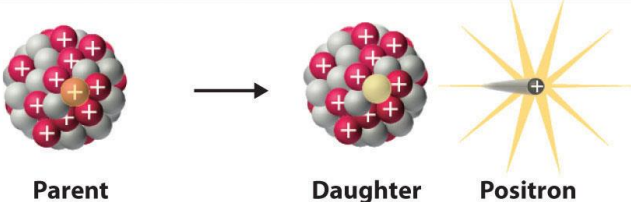
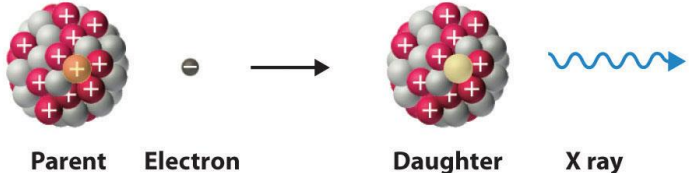
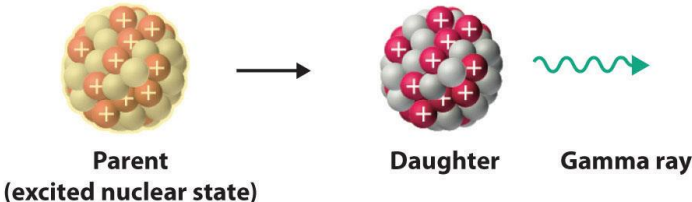
Isotopes

- Atoms of the same element with different mass number
- Radioactive and non-radioactive
- p/n-ratio
- Region of stability
- Nuclear decay



Nuclear decay

Type	Description	Change?	Example
Alpha	Nucleus releases a He atom. He atom is known as an alpha particle	A Helium atom is released. Remaining nucleus weighs 4 less and has 2 less protons	${}_{92}^{238}\text{U} \rightarrow {}_{90}^{234}\text{Th} + {}_2^4\text{He}$
Beta	Nucleus releases an electron and converts a neutron to a proton	Remaining atom has: •Same mass •One more proton, one less neutron	${}_{53}^{231}\text{I} \rightarrow {}_{54}^{231}\text{Xe} + {}_{-1}^0\text{e}$
Gamma	Nucleus goes from high energy state to a low energy state.	Nucleus remains same, but a gamma ray is released	${}_{92}^{238}\text{U} \rightarrow {}_{92}^{238}\text{U} + \gamma$
Positron	Nucleus releases a positively charged electron and converts a proton to a neutron	Remaining atom has: •Same mass •One more neutron, one less proton	${}_{6}^{11}\text{C} \rightarrow {}_{5}^{11}\text{B} + {}_{+1}^0\text{e}$
Electron Capture	An electron from the electron cloud converts a proton into a neutron	Remaining atom has: •Same mass •One more neutron, one less proton	${}_{80}^{201}\text{Hg} + {}_{-1}^0\text{e} \rightarrow {}_{79}^{201}\text{Au}$

Decay Type	Radiation Emitted	Generic Equation	Model
Alpha decay	${}^4_2\alpha$	${}_Z^AX \longrightarrow {}_{Z-2}^{A-4}X' + {}^4_2\alpha$	 <p>Parent Daughter Alpha Particle</p>
Beta decay	${}^0_{-1}\beta$	${}_Z^AX \longrightarrow {}_{Z+1}^AX' + {}^0_{-1}\beta$	 <p>Parent Daughter Beta Particle</p>
Positron emission	${}^0_{+1}\beta$	${}_Z^AX \longrightarrow {}_{Z-1}^AX' + {}^0_{+1}\beta$	 <p>Parent Daughter Positron</p>
Electron capture	X rays	${}_Z^AX + {}^0_{-1}e \longrightarrow {}_{Z-1}^AX' + \text{X ray}$	 <p>Parent Electron Daughter X ray</p>
Gamma emission	${}^0_0\gamma$	${}_Z^AX^* \xrightarrow{\text{Relaxation}} {}_Z^AX' + {}^0_0\gamma$	 <p>Parent (excited nuclear state) Daughter Gamma ray</p>

Video

- <https://www.youtube.com/watch?v=fES21E0qebw&list=PLybg94GvOJ9EbbO2RXPWTUNIIEOC7hSfm&index=41>

Atomic, molecular, formula mass

Relative atomic mass A_r :

- the ratio of the average mass of one atom of an element to one twelfth of the mass of an atom of carbon-12.
 - For example, $^{12}\text{C} = 12$, $^1\text{H} = 1$
- But the mass of carbon is 12,01. Why?

Atomic models

- Democritos: Atomos
- Dalton: Indivisible atom
- Thomson: Electrons, “plum-pudding model”
- Rutherford: Positively charged nucleus
- Bohr: Positively charged nucleus surrounded by electrons that travel in circular orbits around the nucleus
- The quantum model: complex shapes of orbitals, volumes of space in which there is likely to be an electron

Calculating A_r

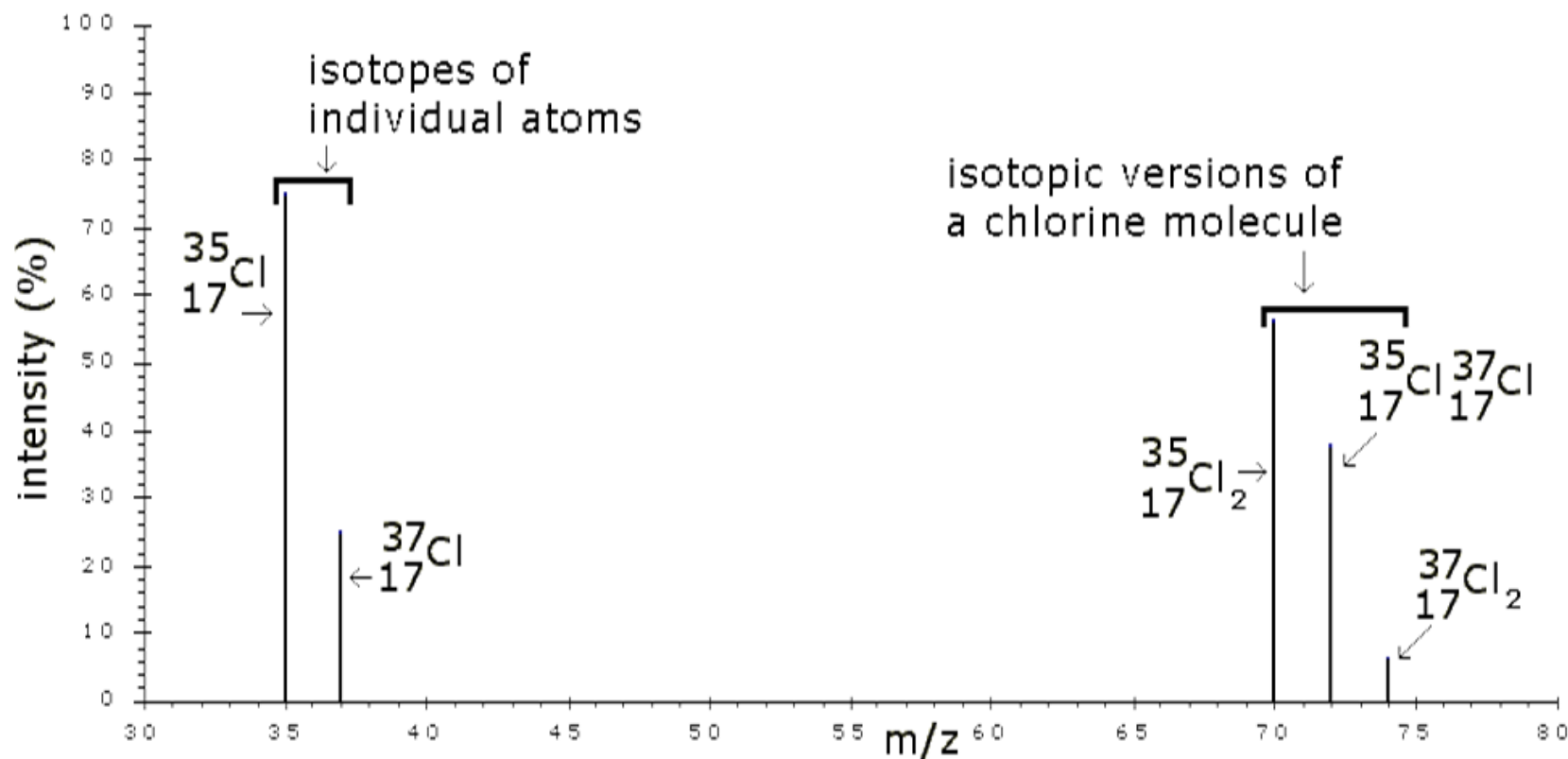
- Many elements have different isotopes, which have different masses.
 - Example chlorine: ^{35}Cl and ^{37}Cl
- Different isotopes have different **abundancies**
 - Example chlorine: ^{35}Cl (75%) and ^{37}Cl (25%)
- Calculate the A_r for chlorine

Mass spectrometry (MS)

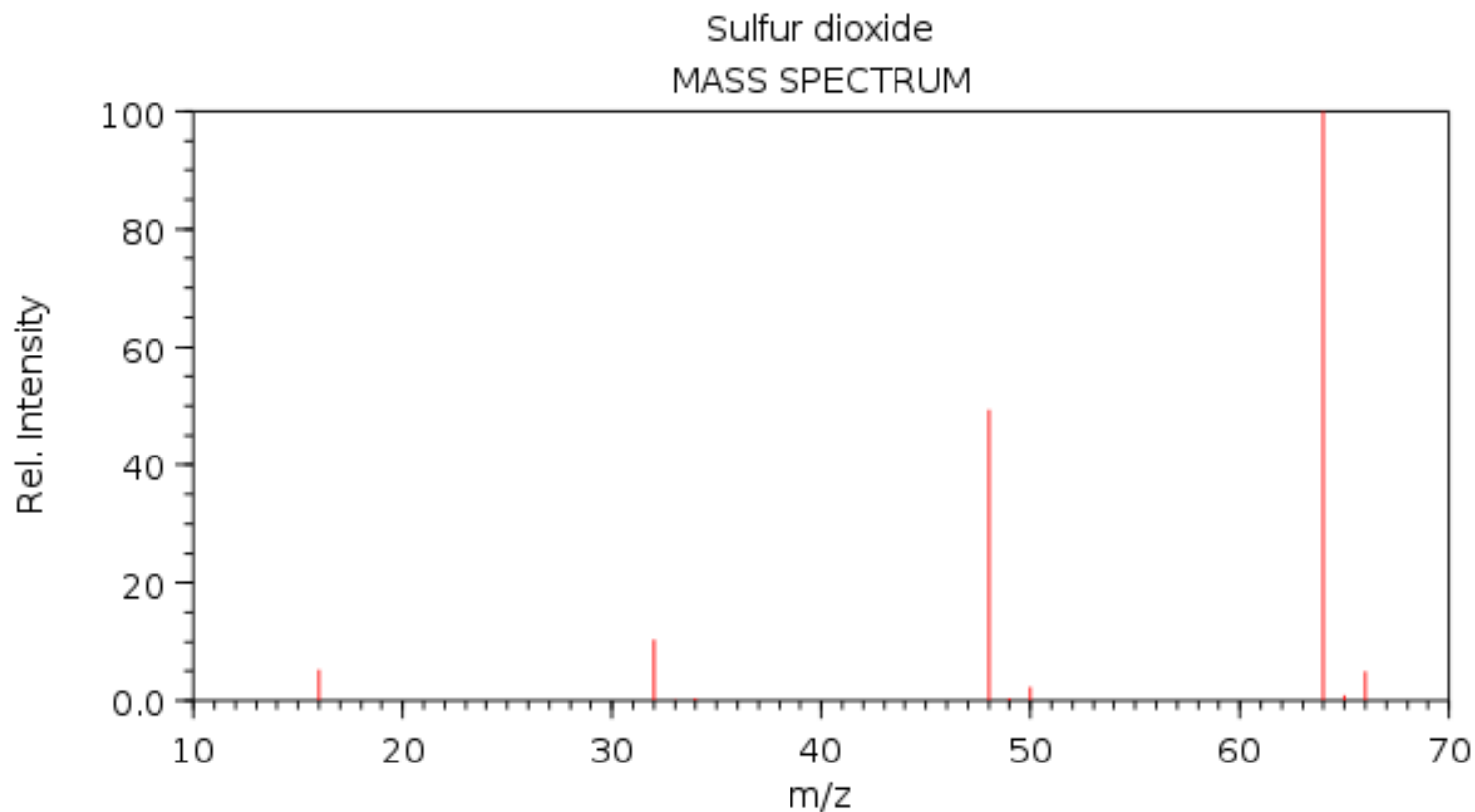
- A method to obtain the abundancies of isotopes.
- A mass spectrometer produces a mass spectrum giving peaks with different mass-to-charge –ratio (m/z).
 - Isotopes, molecules

$$\text{Chlorine: } A_r = \frac{35 \cdot 75\% + 37 \cdot 25\%}{100\%} = 35,50$$

Mass spectrum for chlorine

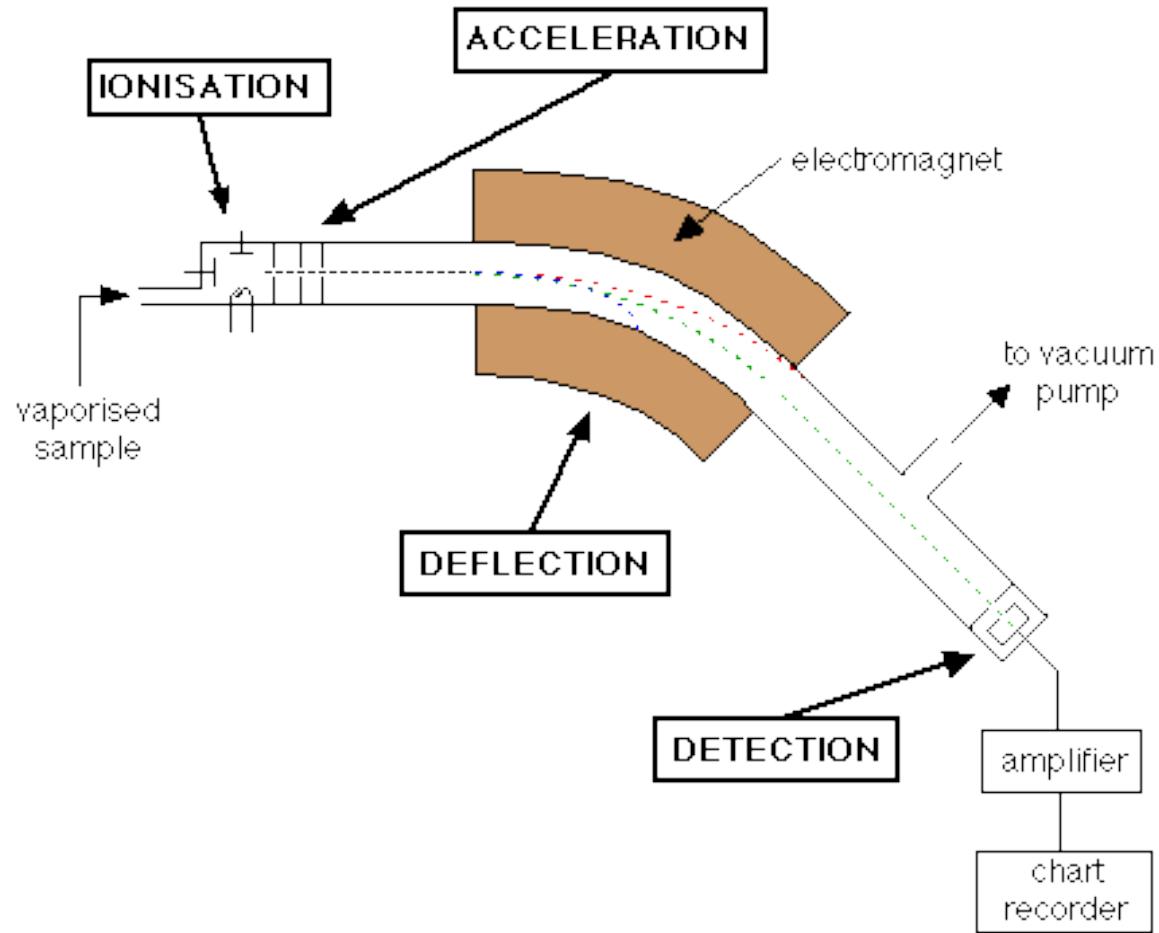


Mass spectrum of SO₂



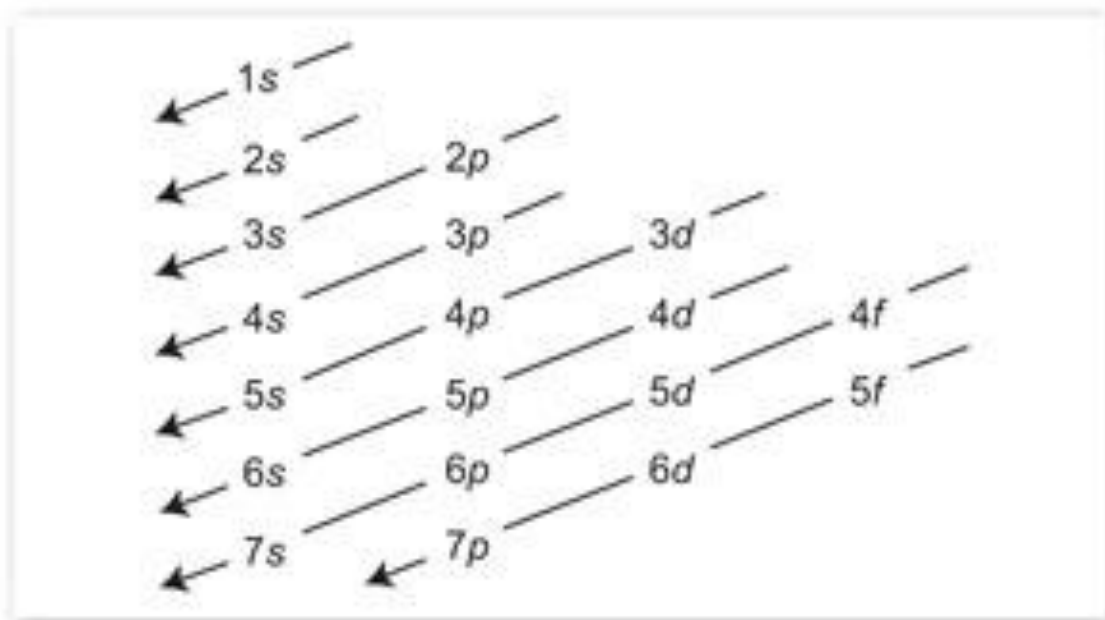
NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Mass spectrometer



Filling the orbitals

- The Aufbau principle (Klechkovsky)

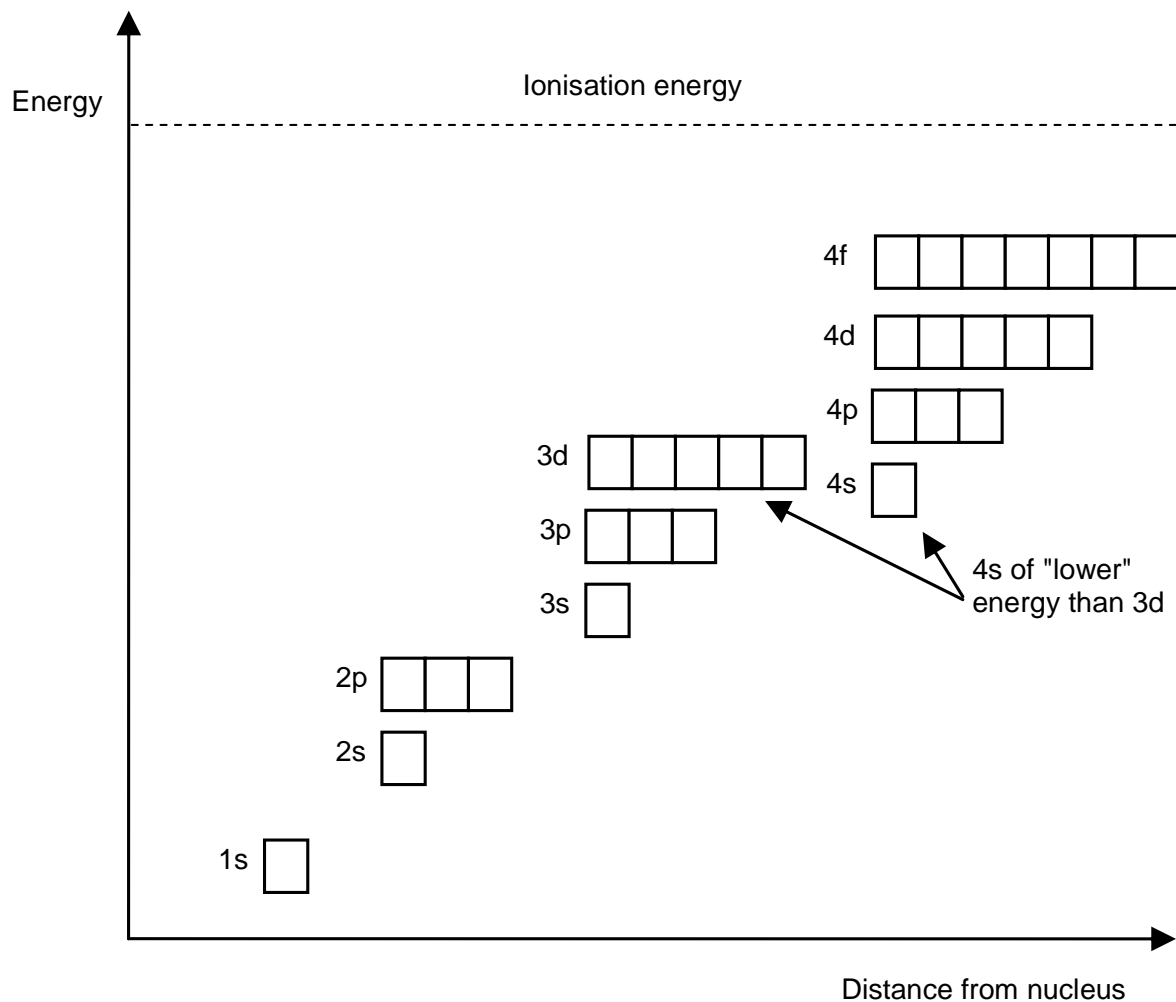


- What about copper and chromium?

Exceptions!

- The experimental electronic configuration of the copper atom is $[\text{Ar}]4s^13d^{10}$. By filling the 3d orbital, copper can be in a lower energy state. Similarly, chromium takes the electronic configuration of $[\text{Ar}]4s^13d^5$ instead of $[\text{Ar}]4s^23d^4$.
- Half-full **s** and half-full **d** is more stable than full **s** and incomplete **d**

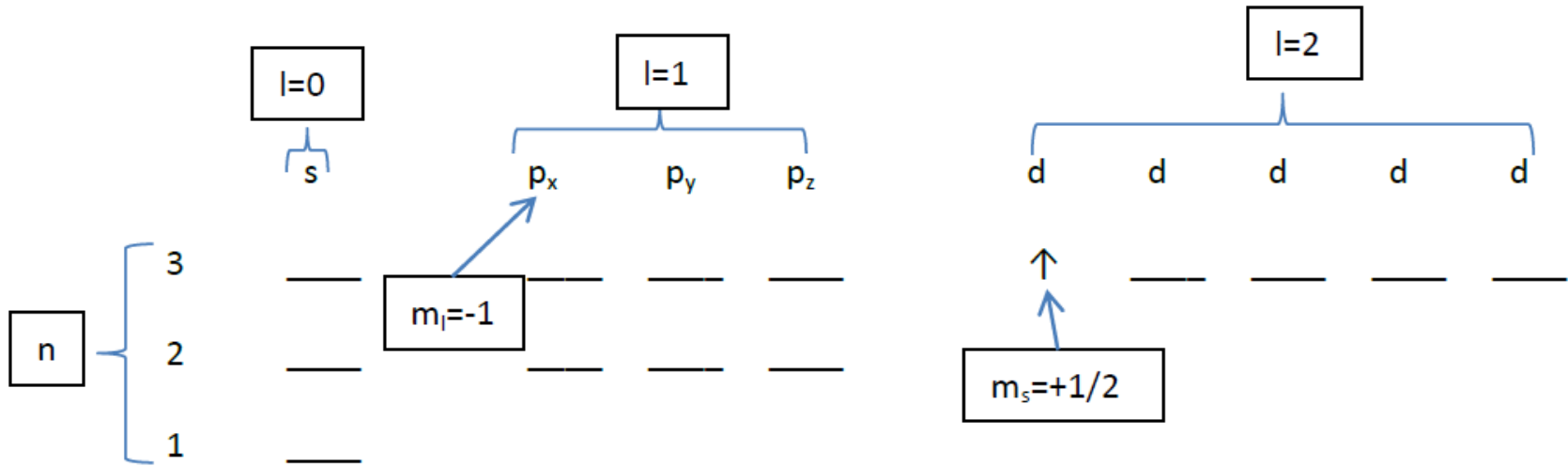
Electrons in the atom



Shell (quantum) model of the atom

- Shell: Energy level (1, 2, 3,...)
- Subshell: Set of orbitals (s, p, d, f)
- Orbital: Space for two electrons (s, p_x , p_y , p_z ,...)
 - Shapes!
- Spin: up or down ($+1/2$, $-1/2$)

Example



$$n = 1, 2, 3, \dots, n$$

$$l = n-1$$

$$m_l = -l, \dots, +l$$

$$m_s = +1/2, -1/2$$

Quantum numbers

Set of numbers, each electron has individual set of quantum numbers.

- Principal quantum number $n = 1, 2, 3, \dots, n$
- Angular quantum number $l = 0, 1, 2, \dots, n-1$
- Magnetic quantum number $m_l = -l, \dots, +l$
- Spin quantum number $m_s = +1/2, -1/2$

**Name, Symbol
(Property)**

Allowed Values

Quantum Numbers

Principal, *n*
(size, energy)

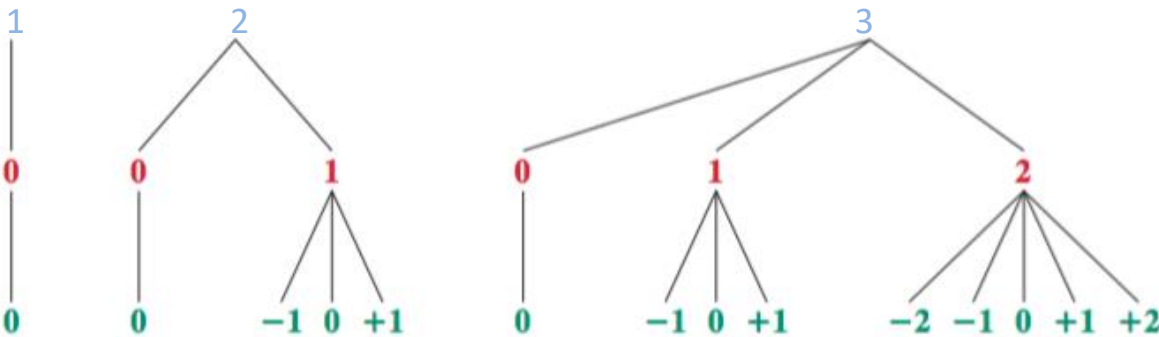
Positive integer
(1, 2, 3, ...)

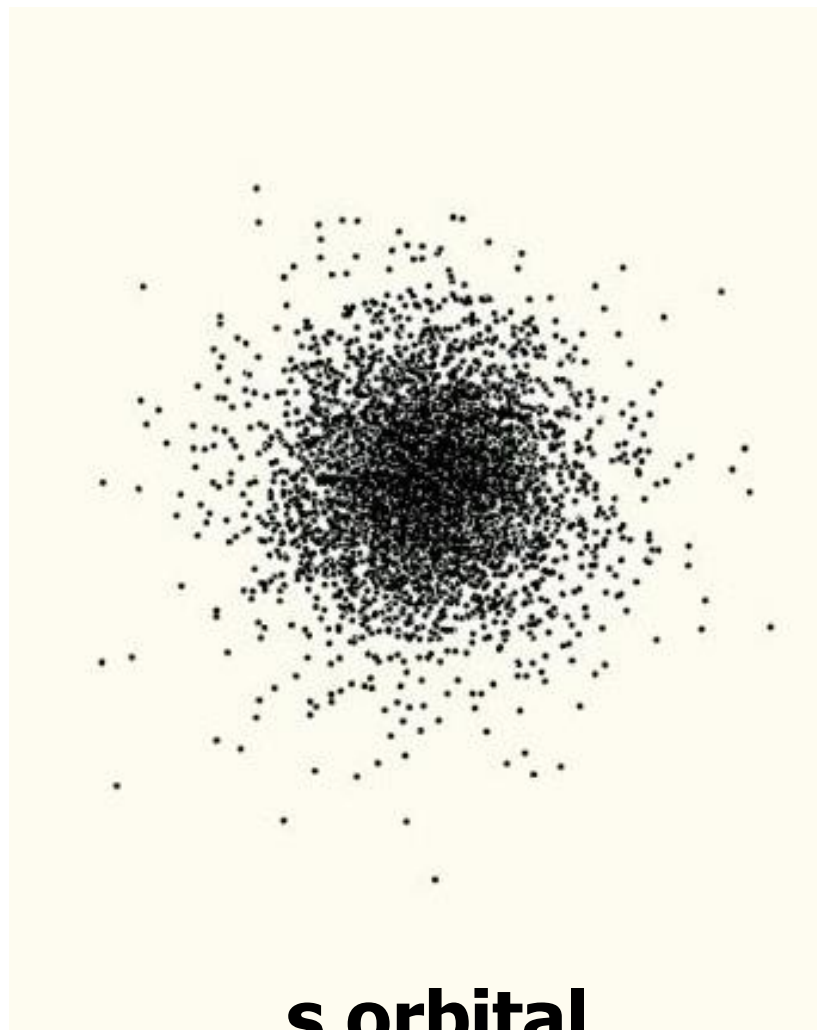
Angular
momentum, *l*
(shape)

0 to *n* - 1

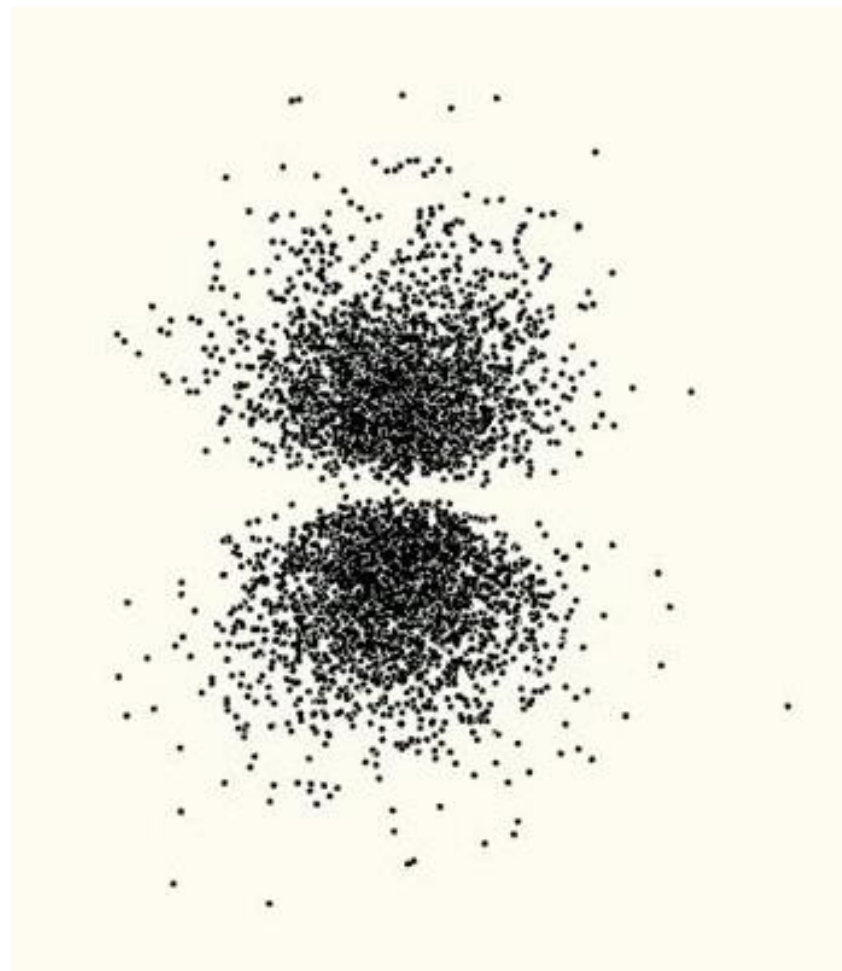
Magnetic, *m_l*
(orientation)

-*l*, ..., 0, ..., +*l*

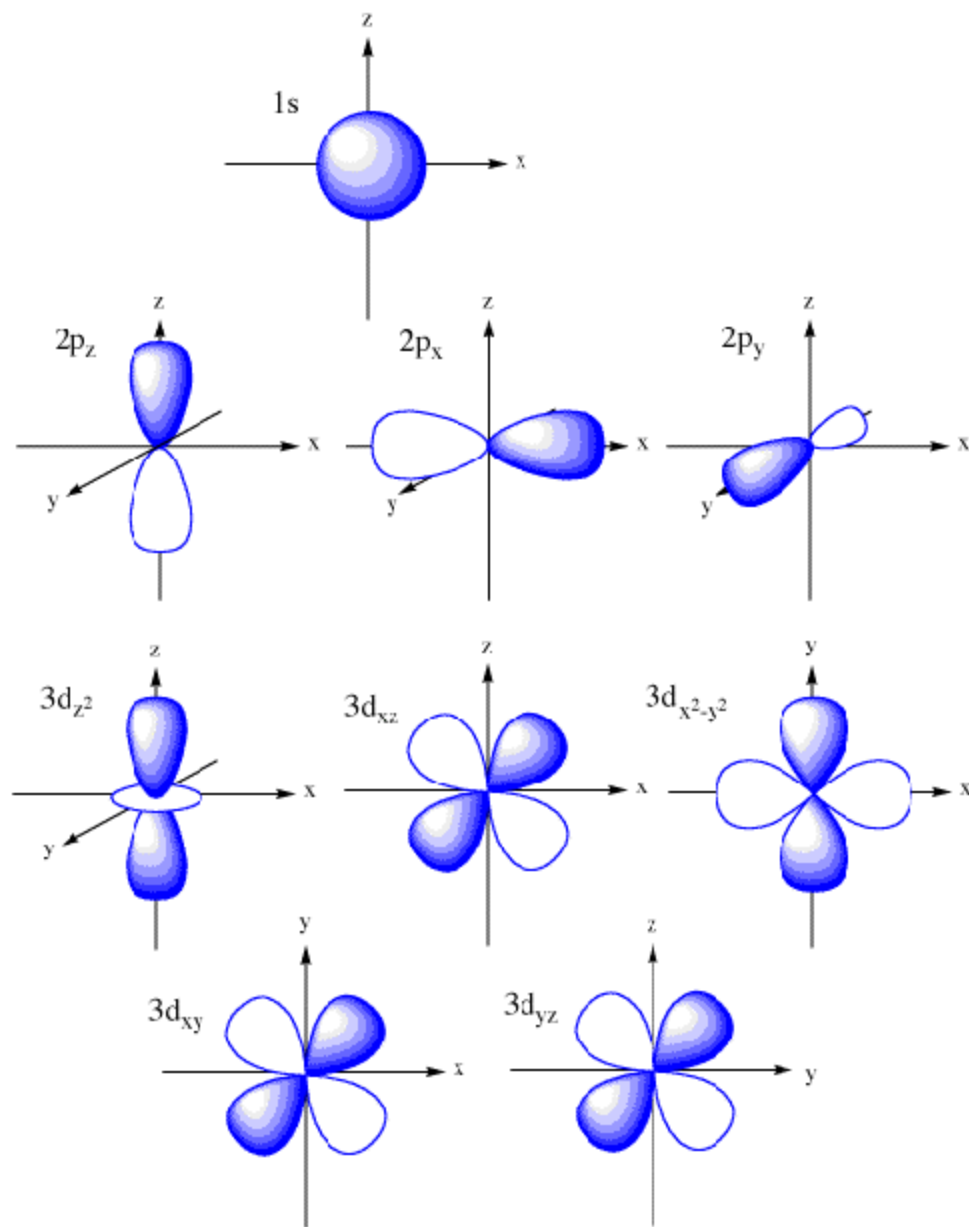




s orbital

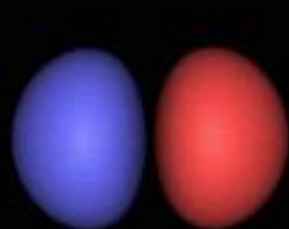


p orbital

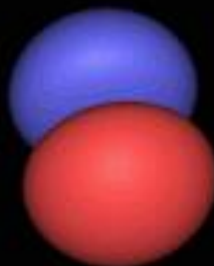




s



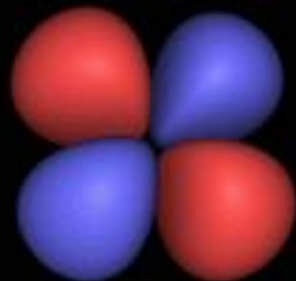
p_x



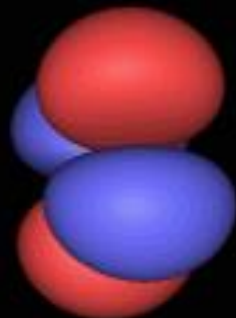
p_y



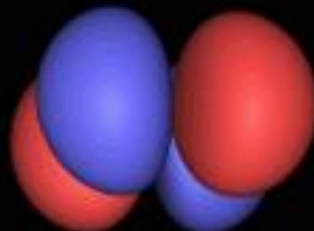
p_z



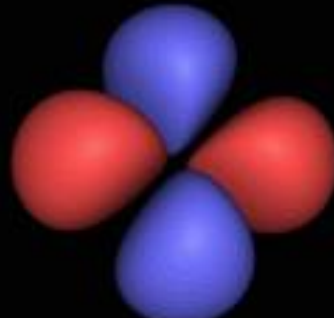
d_{xy}



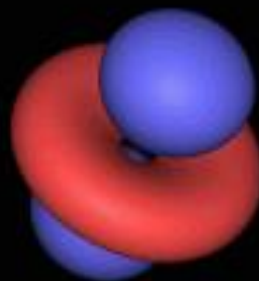
d_{xz}



d_{yz}



$d_{x^2-y^2}$



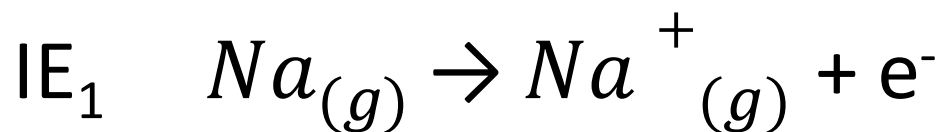
d_{z^2}

The Orbitron

<http://winter.group.shef.ac.uk/orbitron/AOs/1s/index.html>

Ionisation

- The **first ionisation energy** is the energy required to remove the most loosely held electron from one mole of *gaseous atoms* to produce 1 mole of *gaseous ions* each with a charge of **1+**.



Factors affecting ionisation energy

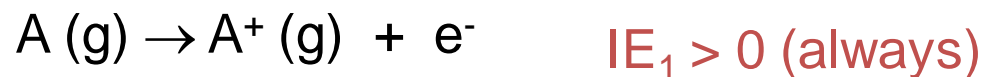
- Nuclear charge (Z)
 - Increase across the period
- Distance from the nucleus
 - Increase down the group
- Shielding
 - Inner electrons cover the nucleus so the outer electrons don't experience the full attraction of the positive nucleus

Ionization Energy

Key factor in an element's reactivity

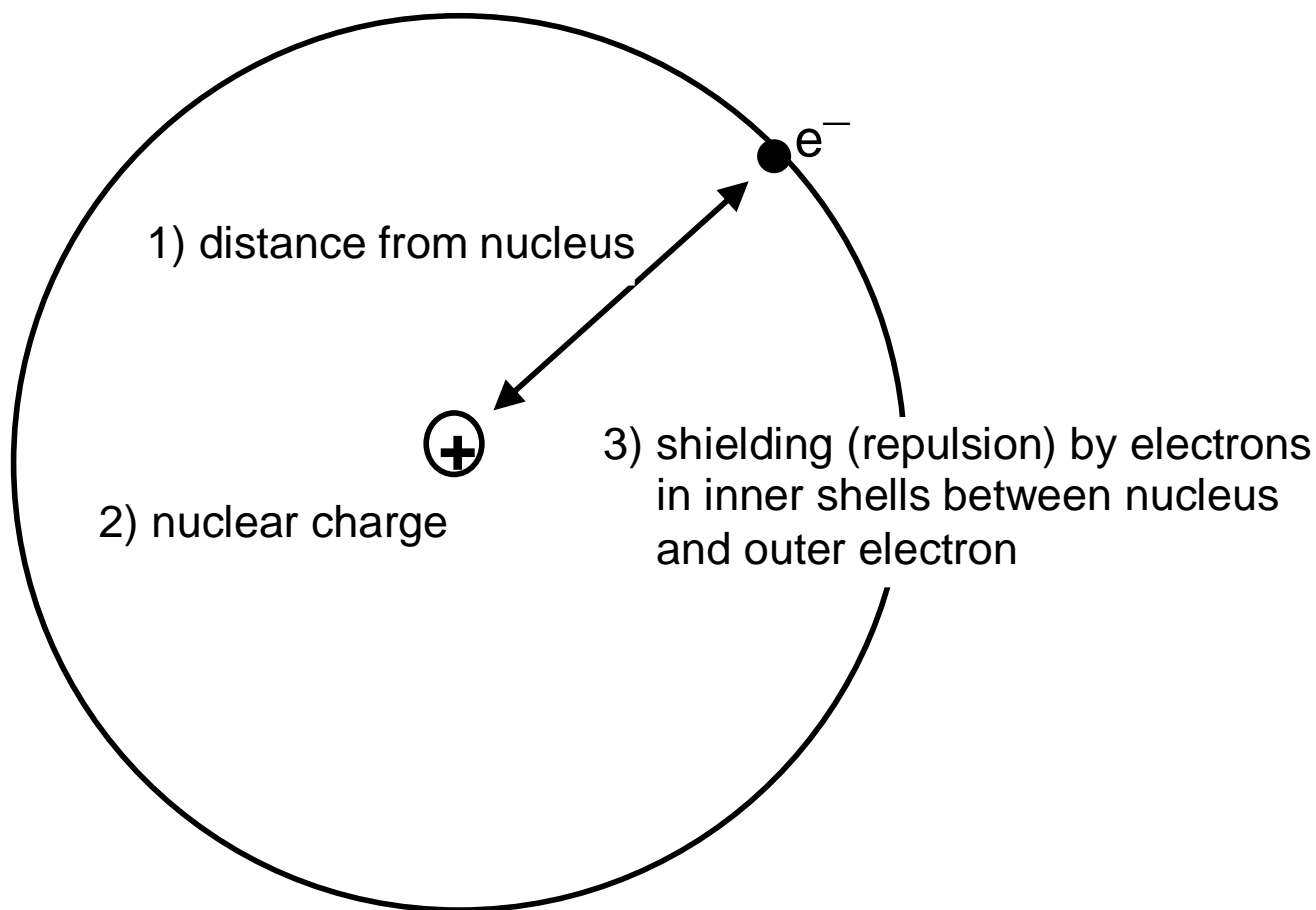
First ionization energy: Energy required to remove the least attracted electron from a neutral atom in the gas phase.

Second ionization energy: Energy required to remove the second least attracted electron, and so forth.



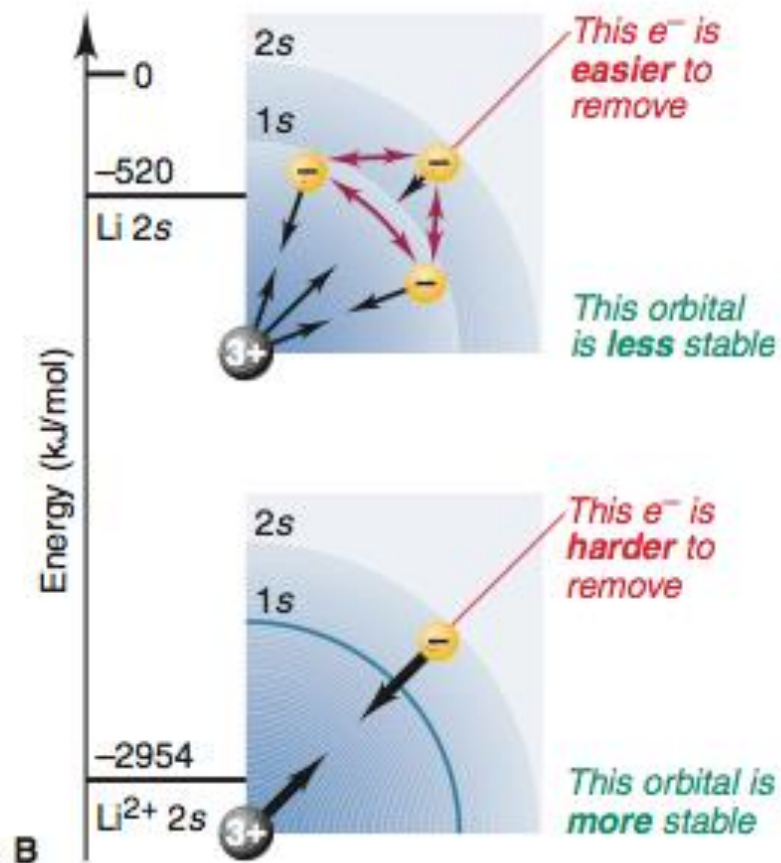
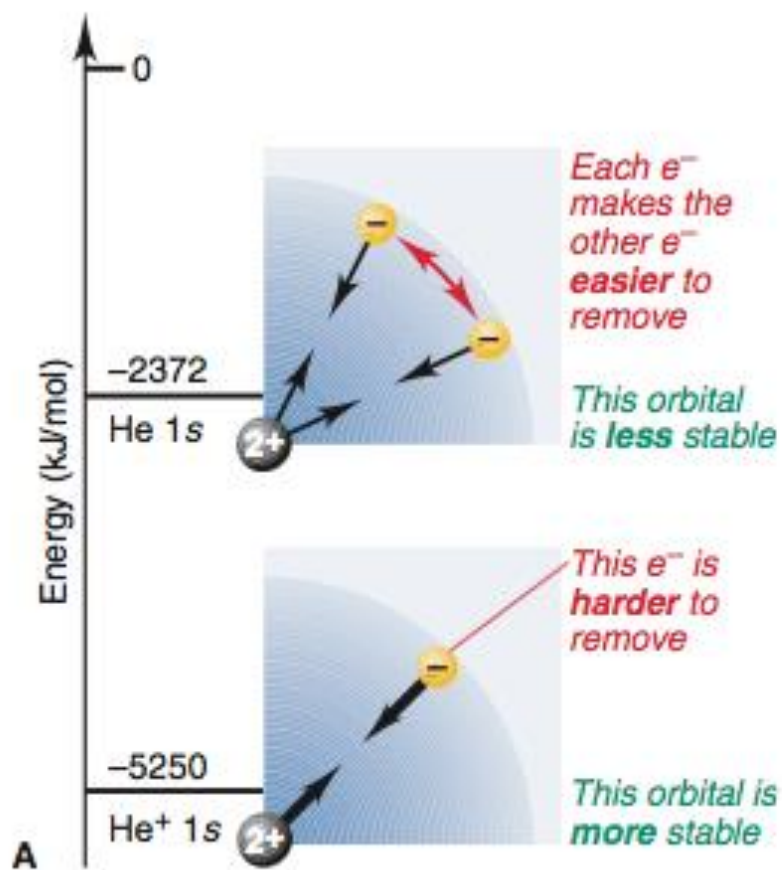
The greater the IE the harder it is to remove the electron

Ionisation Energy



Effective nuclear charge Z_{eff}

- The effective nuclear charge is the net positive charge experienced by an electron.
- The term "effective" is used because the shielding effect of negatively charged electrons prevents higher orbital electrons from experiencing the full nuclear charge of the nucleus due to the repelling effect of inner-layer electrons.



Periodic Trends in First Ionization Energies

In a group:

IE generally decreases down the group

Because the atomic radius increases it is easier to remove the least attracted electron in the atom.

In a period:

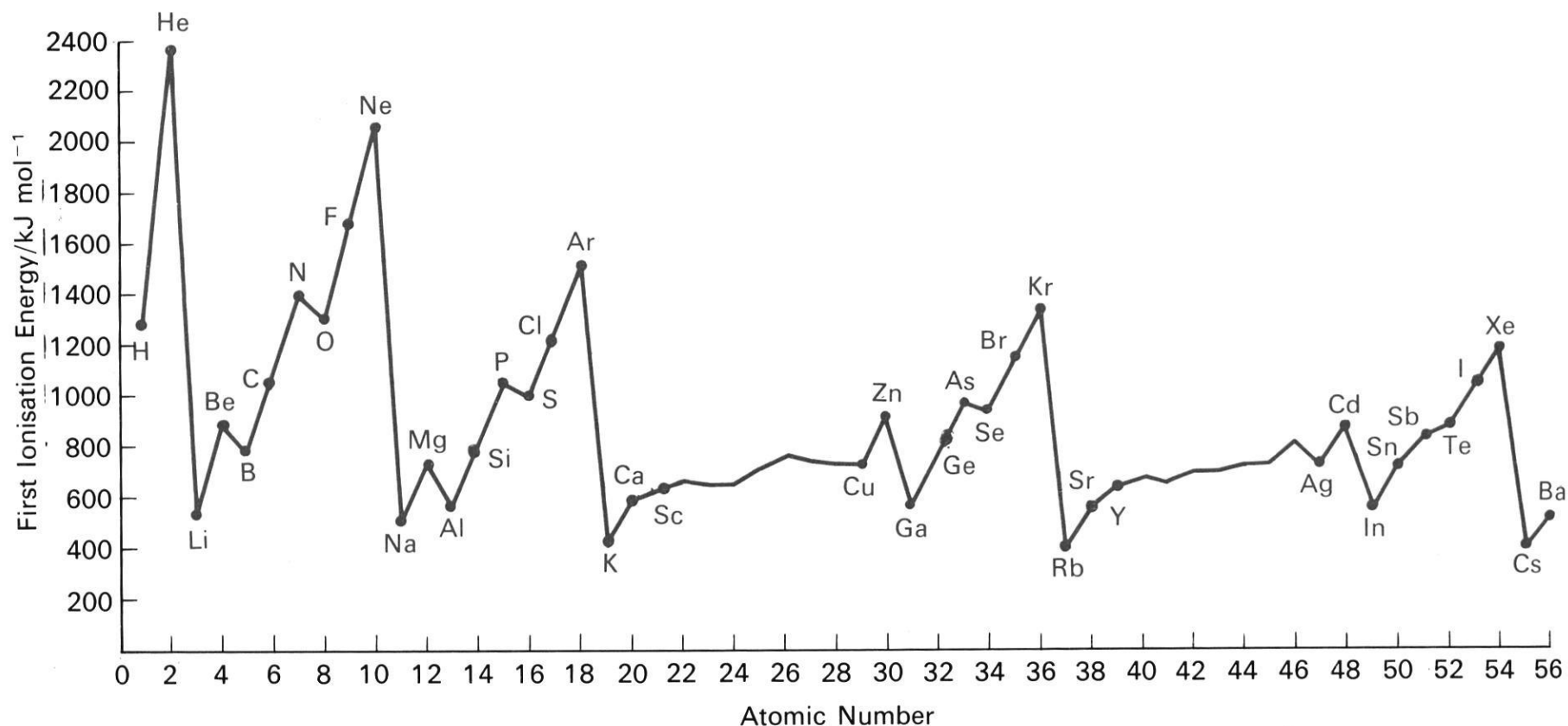
IE generally increases across the period

The alkali metals show the lowest ionization energy and the noble gases the highest

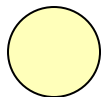
Because the atomic radius decreases (since Z increases) it is harder to remove the least attracted electron in the atom.

In general: Smaller atoms have higher IEs

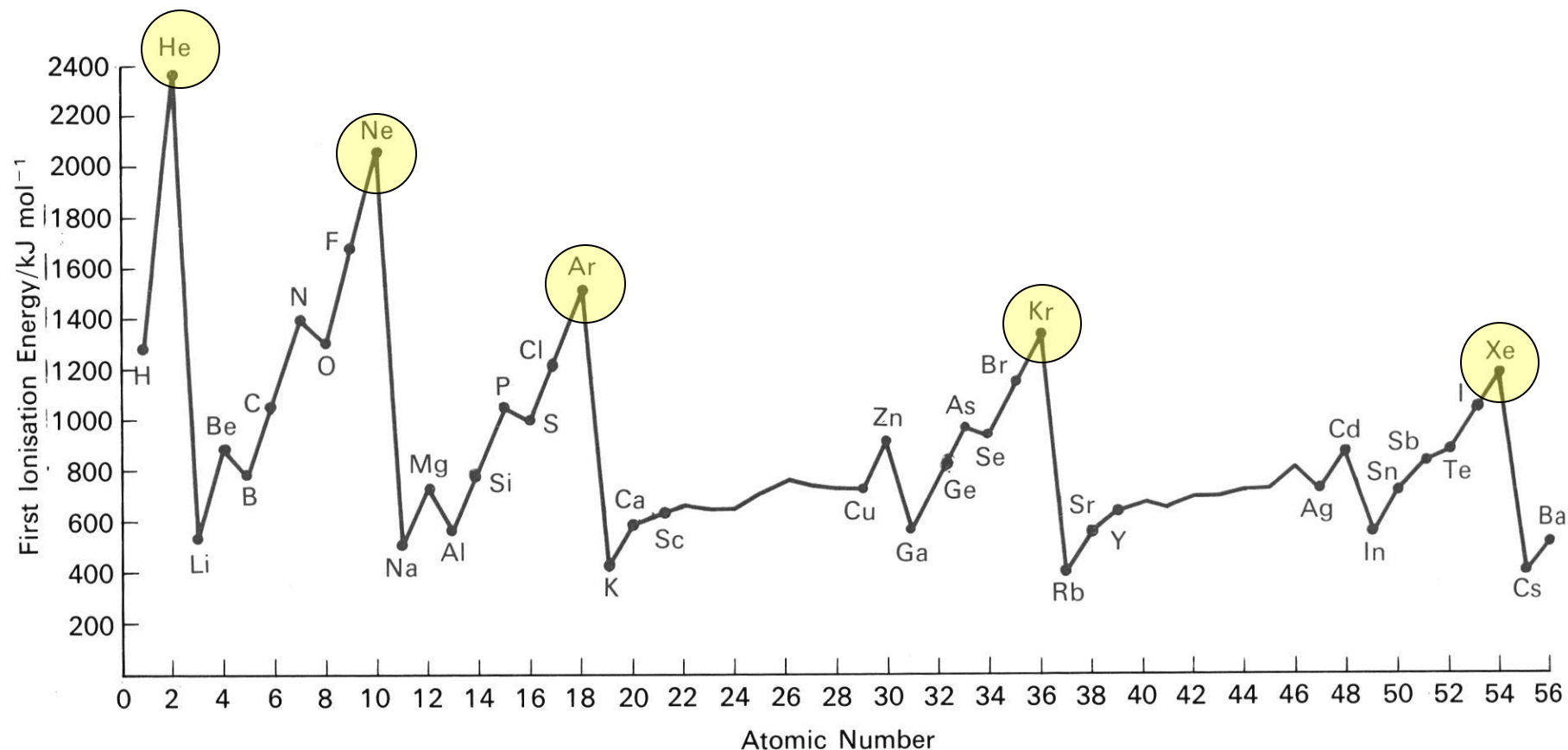
1st ionisation energy



down a group
(group 0)



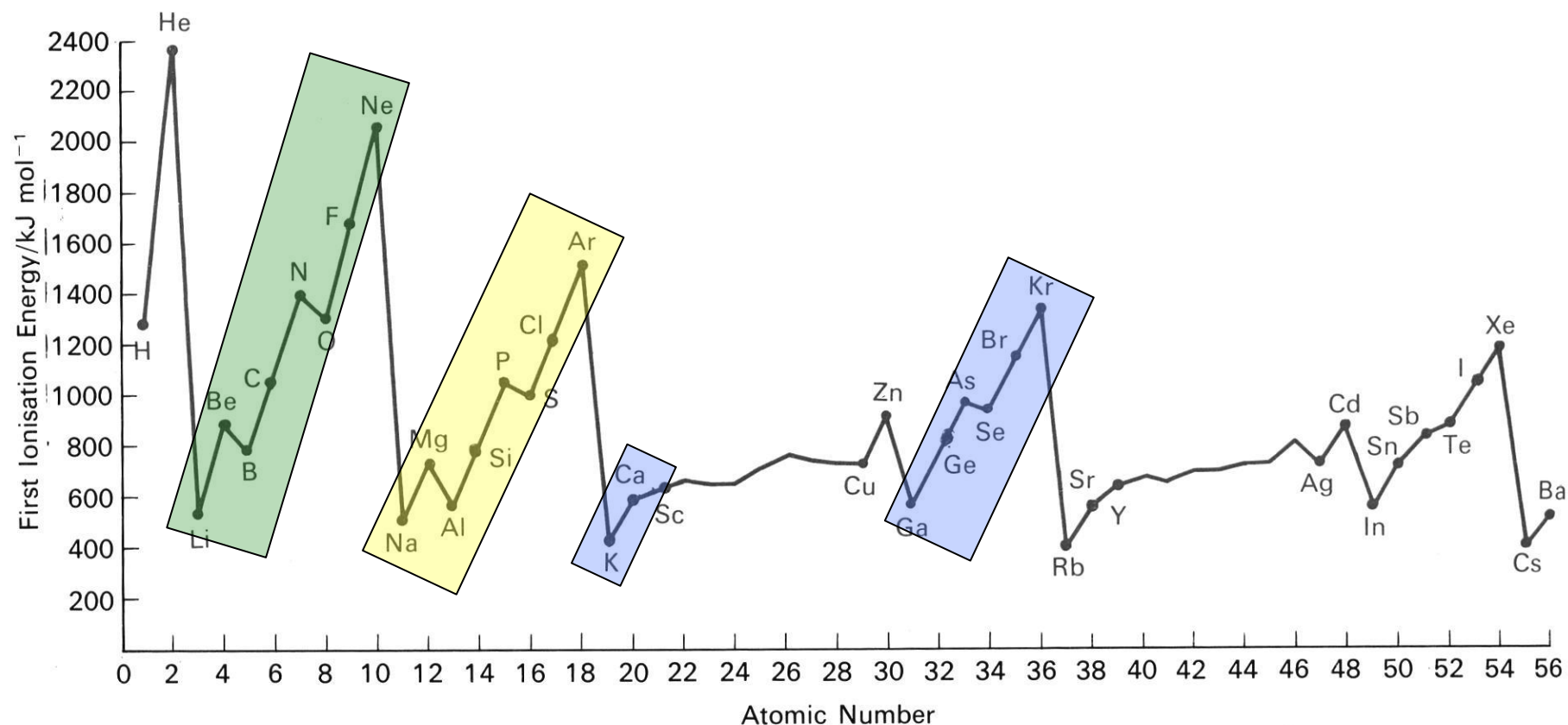
1st ionisation energy



Across a period

1st ionisation energy

period 2
period 3
period 4



Periodic Trends in First Ionization Energies

Exceptions: 1) **Be** \rightarrow B and **N** \rightarrow O in period 2
2) **Mg** \rightarrow Al and **P** \rightarrow S in period 3, etc.

WHY?

- 1) The $2s^2$ (or $3s^2$) configuration is more stable than the $2s^2 2p^1$ (or $3s^2 3p^1$). Therefore it is easier to remove the one p electron than an s electron from a completed s subshell.
- 2) The p^3 configuration is more stable than the p^4 (Rule of maximum unpairing, Hund's rule). Therefore it is easier to remove a p electron from a p^4 configuration than a p^3 configuration.

Successive ionisation energies (K)

