

IONISATION ENERGIES

First ionisation energy

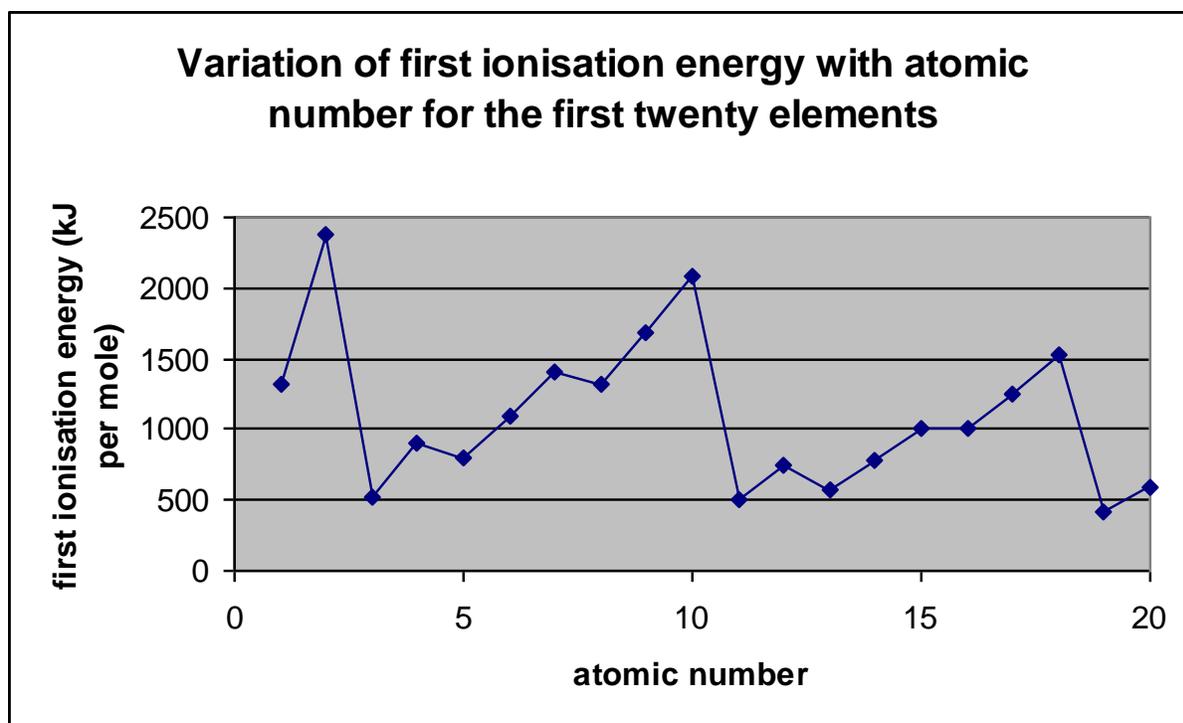
The first ionisation energy of an element is the energy required to remove one electron from each of a mole of free gaseous atoms of that element to form 1 mole of gaseous mono-positive ions

It can also be described as the energy change per mole for the process:



The amount of energy required to remove an electron from an atom depends on the number of protons in the nucleus of the atom and on the electronic configuration of that atom.

The first ionisation energies of the first 20 elements in the periodic table is shown below:



There are various trends in this graph which can be explained by reference to the proton number and electronic configuration of the various elements. A number of factors must be considered:

1. Nuclear Charge

- Energy is required to remove electrons from atoms in order to overcome their attraction to the nucleus. The greater the number of protons, the greater the attraction of the electrons to the nucleus and the harder it is to remove the electrons. The number of protons in the nucleus is known as the **nuclear charge**.

2. Shielding/ Screening Effect

- The effect of this nuclear charge, however, is cancelled out to some extent by the other electrons in the atom. Each inner shell and inner sub-shell electron effectively cancels out one unit of charge from the nucleus. This is known as **shielding**.

The outermost electrons in the atom thus only feel the residual positive charge after all inner shell and inner sub-shell electrons have cancelled out much of the nuclear charge. This residual positive charge is known as the **effective nuclear charge**.

3. Atomic Size

- Small atoms have their electrons closer to the nucleus and these electrons are more strongly held by the positive nucleus. Large amount of energy will thus be required to remove those electrons and the 1st ionisation energy will be high.

4. The electronic configuration

- Electrons repel each other, particularly when they are in the same orbital. The degree of **repulsion** between the outermost electrons affects the ease with which electrons can be moved.

When considering trends in ionisation energies, it is thus necessary to consider 4 factors:

- nuclear charge
- shielding
- effective nuclear charge
- electron repulsion

Trends across period 2

Compare now the first ionisation energies of He ($1s^2$) and Li ($1s^22s^1$). Li has an extra proton in the nucleus (3) but two inner-shell electrons. These inner-shell electrons cancel out the charge of two of the protons, reducing the effective nuclear charge on the 2s electron to +1. This is lower than the effective nuclear charge on the He 1s electrons, +2, and so the electrons are less strongly held and easier to remove.

The first ionisation energy of Li is thus lower than that of He.

Compare the first ionisation energies of Li ($1s^22s^1$) and Be ($1s^22s^2$). Be has one more proton in the nucleus than Li, and no extra inner-shell electrons, so the effective nuclear charge on Be is higher and the Be electrons are more strongly attracted to the nucleus.

The first ionisation energy of Be is thus higher than that of Li.

In general, the first ionisation energy increases across a period because the nuclear charge increases but the shielding remains the same.

Compare the first ionisation energies of Be ($1s^22s^2$) and B ($1s^22s^22p^1$). B has one more proton in the nucleus than Be but there are also 2 extra inner sub-shell electrons. These cancel out the charge of two more of the protons, leaving an effective nuclear charge of only +1. This is less than Be (+2) so the electrons are less strongly attracted to the nucleus and thus less difficult to remove.

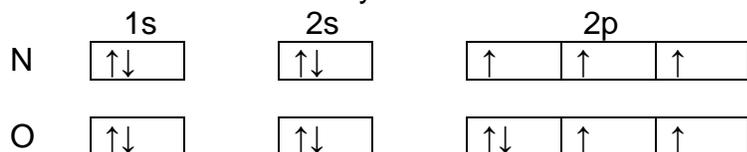
The first ionisation energy of B is thus lower than that of Be.

Ionisation energies decrease from group II to group III because in group III the electrons are removed from a p-orbital, so it is shielded by the s-electrons in the outer shell. Thus the effective nuclear charge decreases.

From B ($1s^22s^22p^1$) to N ($1s^22s^22p^3$) the proton number increases, but the number of electrons shielding the nuclear charge remains the same at 4. Thus the effective nuclear charge increases from B to N and the electrons become progressively harder to remove.

The first ionisation energy thus increases from B to N.

So far the concepts of effective nuclear charge and shielding have been used to explain the trend in first ionisation energies for the first 7 elements. They cannot, however, explain the fall between N and O. The electronic configurations of N and O must be considered more carefully:



Note that in N the electron is removed from an unpaired orbital, but in O it is removed from a paired orbital. In a paired orbital, the two electrons share a confined space and so repel each other. They are therefore less stable and easier to remove. This repulsion effect outweighs the higher effective nuclear charge in O.

The first ionisation energy of O is thus lower than that of N.

First ionisation energies decrease from group V to group VI, since the electron removed from the group VI atom is paired, so there is more repulsion between the electrons and the electron is easier to remove.

The first ionisation energies increase as expected from O to Ne, due to the increase in effective nuclear charge.

The trend in first ionisation energies across period 2 can thus be summarised as follows:

1. There is a general increase across the period as the nuclear charge increases and the shielding remains the same.
2. There is a drop from Be to B because in B a 2p electron is being removed and the extra shielding from the 2s subshell actually causes a fall in the effective nuclear charge.
3. There is also a drop from N to O because the electron in O is being removed from a paired orbital. The repulsion of the electrons in this orbital makes them less stable and easier to remove.

The same trend can also be found in Period 3 (Na - Ar). There is a general increase, but a drop between Mg and Al and also between P and S.