IONISATION ENERGIES (IE) → always positive / endothermic

- Defined as the amount of energy required to remove 1 mol of electrons from 1 mol of gaseous atoms to form 1 mol of univalent, positively charged ions.

ie. ① $Cl_2(g) \xrightarrow{\text{energy}} 2Cl(g)$

Cl–Cl covalent bond is broken

②

$Cl(g) \longrightarrow Cl^+(g) + e^-$ $\quad \Delta H = +$

ie. $Na(s)$ held together by metallic bonds

break metallic bonds

$Na(g)$ atom

$Na(g) \longrightarrow Na^+(g) + e^-$ $\quad \Delta H =$ 1st Ionisation Energy

Q. Why do we need gaseous atoms?

Ans. Because in the gas phase, the atoms are uninfluenced by intermolecular forces and/or bonds

↳ Therefore, the measured energy that is put in to remove the electron can be called purely "ionisation energy", as exactly this much energy was required to remove an electron and not act upon anything else (ie. breaking molecular bonds)

- The magnitude of the ionisation energy tells us how tightly the electrons are held by the positively charged nucleus.

↳ The larger the ionisation energy, the more tightly the electrons are held and the more difficult it is to remove the electron

TRENDS IN IONISATION ENERGIES

1. Successive Ionisation Energies (for a particular element)

$X(g) \longrightarrow X^{+}(g) + e^{-}$ ΔH = 1st ionisation energy

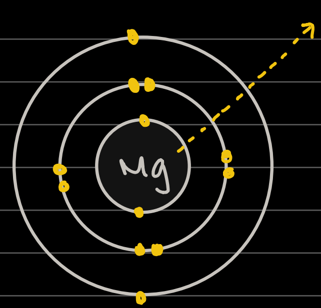
$X^{+}(g) \longrightarrow X^{2+}(g) + e^{-}$ ΔH = 2nd ionisation energy

$X^{2+}(g) \longrightarrow X^{3+}(g) + e^{-}$ ΔH = 3rd ionisation energy

Trend: The successive ionisation energies of any particular element tend to increase.
That is, each subsequent ionisation energy is greater than the one before it.

Justification:
- when an electron is removed from an atom, the repulsion between electrons decreases but the nuclear charge remains the same (because the number of protons in the nucleus is unchanged)
  - ↳ Therefore, the remaining electrons experience a greater effective nuclear charge, so more energy is required to remove the 2nd electron.

SHIELDING



- outer electrons experience a lesser nuclear attraction
  - ↳ because the outermost electrons are shielded by the full force of the positively charged nucleus
- All electrons in the outer shell are shielded / screened from the full nuclear charge by the electrons in the filled, inner shells.

- This shielding has the effect of decreasing the effective nuclear charge experienced by the outermost electrons.

Q. Connection between successive ionisation energies and the shielding effect?

- When removing electrons from an atom or ion, the ionisation energy required to remove an electron from a lower energy level is significantly greater than that required to remove one from a higher energy level.
  - ↳ This is because electrons at lower energy level are closer to the

nucleus and experience a lesser shielding effect and a greater effective nuclear charge than the electrons in higher energy levels.

↳ As they are held more tightly by the nucleus, more energy is required to remove them, thus the increasing trend in successive ionisation energies.

2. Group trend in 1st Ionisation Energy

Trend : 1st ionisation energy decreases as you go down any group.

- As you go down the group, the valence electron is at a greater energy level and is farther from the nucleus, hence, experiences a greater shielding effect from the nuclear attraction

↳ Therefore, the first ionisation energies decrease down a group

Teacher's Notes :

- Ionisation energy decreases down the group
- As the proton number increases , the electrons enter new shells
- They are increasingly further away from the nucleus and more shielded from the positively charged nucleus.
- The electrons experience a lesser nuclear attraction , that is , they are less tightly held.

↳ And therefore, less energy is required to remove an electron

3. Period trends in 1st Ionisation Energy

Trend : 1st ionisation energy increases across a period

- As proton number increases , electrons enter the same shell / energy level and are at the same distance from the nucleus .
- As a result, the shielding effect is almost the same

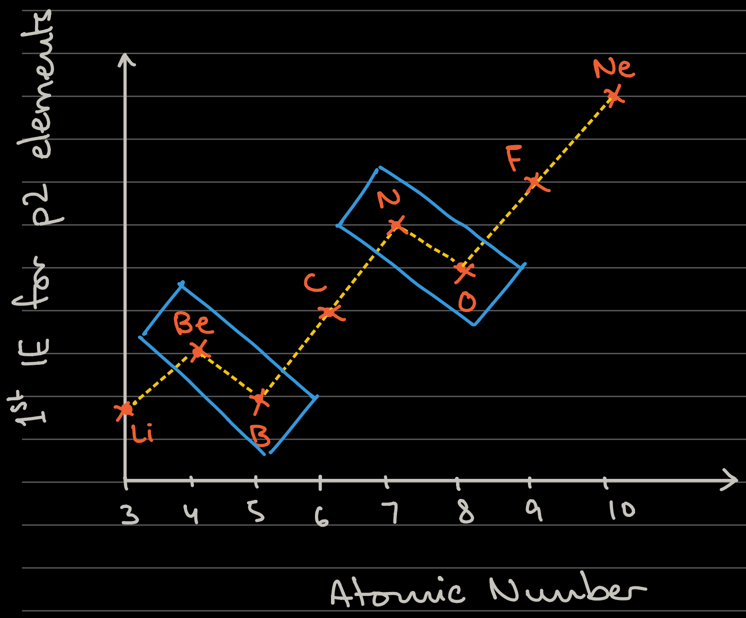
↳ However , the nuclear charge is increasing (due to more protons in the nucleus)

↳ As a result, the greater nuclear charge pulls the electron cloud closer , causing it to shrink, due to which the atomic radius decreases

↓ As all electrons are now closer to the nucleus , more energy is required to remove the outermost electron.

EXCEPTIONS TO THE PERIODIC TRENDS

↳ application of these to p2 and p3 are in our syllabus



Exceptions :

① Be → B
② N → O

Justification for ①

- The outermost electron in Boron is in the 2p orbital, which is on average further away from the nucleus and is more shielded from the positively nucleus than the 2s orbital in Be, which contains it's outermost electrons

    ↳ Therefore, less energy is required to remove an electron from Boron than from Beryllium.

(Also applies to the Mg → Al exception in p3)

Justification for ②

- The 1st ionisation energy of oxygen is less than that of Nitrogen, as the 2p orbital of oxygen contains a set of paired electrons

    ↳ Electron pair repulsion lowers the 1st IE as compared to the p-orbitals in Nitrogen, which are all only singly filled in which case electron pair repulsion is minimized.

(Also applies to the P → S exception in p3)