Chem Factsheet

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# Revision Summary: Electronegativity, Ionisation Energies & Electron Affinities

**Before reading through this Factsheet you should:**
- Have a good understanding of atomic structure;
- Have a good appreciation of how the Periodic Table is arranged.

**After working through this Factsheet you will be able to:**
- Define electronegativity, ionisation energies and electron affinities;
- Explain electronegativity, ionisation energies and electron affinities in terms of electron movement;
- Recall trends in electronegativity, ionisation energies and electron affinities within the Periodic table.

This Factsheet is written as a revision aid, the main objective being to ensure that there are no misconceptions or confusion about electronegativity, ionisation energies and electron affinities.

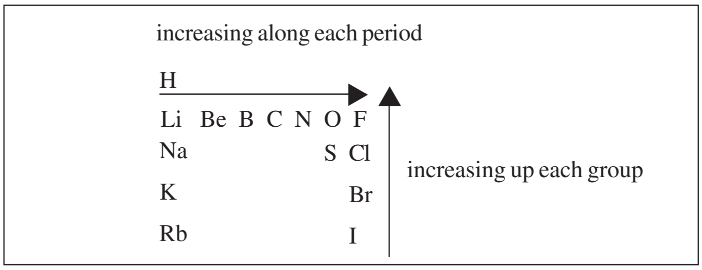
## Electronegativity

*Definition: The electronegativity of an atom is the ability of its nucleus to attract electrons in a bond pair.*

A very electronegative nucleus has the ability to strongly attract bonding electrons, whilst a nucleus which is not very electronegative (is electropositive) does not attract bonding electrons strongly.

Trends in the electronegativity in the Periodic Table are shown clearly in this diagram, and need to be remembered:

**Fig 1. Electronegativity trends**



*Electronegativity increases:*
- *Across each period.*
- *Up each group.*

This makes fluorine the most electronegative atom.

Electronegativity increases across a period because the effective nuclear charge of the atoms increases, hence increasing the electron-attracting power.

Electronegativity decreases down each group because the number of quantum shells of electrons increases, increasing the shielding effect around the nucleus, hence decreasing the electron-attracting power.

A chemist named Pauling assigned electronegativities to elements on an arbitrary scale from 0 to 4. The following is a list of some such values:

**Fig 2. Pauling electronegativities**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Value** | 0.9 | 1.0 | 1.2 | 1.5 | 1.5 | 1.8 | 2.0 | 2.1 |
| **Element** | Na | Li | Mg | Al | Be | Si | B | H |
| **Value** | 2.1 | 2.5 | 2.5 | 3.0 | 3.0 | 3.5 | 4.0 | |
| **Element** | P | C | S | Cl | N | O | F | |

This list simply helps chemists to quantify the power an atom has to attract bond pair electrons.

Electronegativity can be used to classify the bond type between particles:

**Ionic bonds:** Occur between two particles which differ greatly in electronegativity - commonly bonds between metals and non-metals.

The bond pair of electrons are drawn close to the more electronegative particle forming a negative anion, and also a positive cation.

**Covalent bonds**: Occur between two particles which do not differ significantly in electronegativity - commonly bonds between two non-metals. The bond pair electrons are shared between the two neutral atoms.

Pauling estimated the percentage of ionic character of a bond in a binary molecule from the difference in electronegativity of the two atoms in a bond.

**Fig 3. Estimated % ionic character**

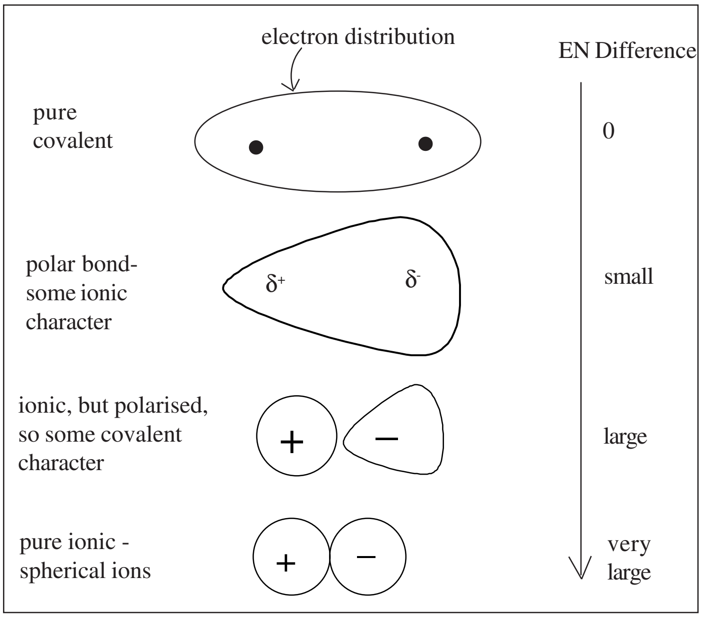
| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Difference in EN | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 | 1.6 |
| % ionic character | 1.0 | 4.0 | 9.0 | 15 | 22 | 30 | 39 | 47 |
| Difference in EN | 1.8 | 2.0 | 2.2 | 2.4 | 2.6 | 2.8 | 3.0 | 3.2 |
| % ionic character | 55 | 63 | 70 | 76 | 82 | 86 | 89 | 92 |

Note that the greater the difference in electronegativity between the two particles, the more ionic the bond between them.
Ionic, covalent and intermediate bonding are discussed in detail in Factsheet 5.

Examples:
- Carbon has an EN of 2.5 and hydrogen has an EN of 2.1. So the C - H bond has a very small percentage ionic character - 4% only.
- Aluminium has an EN of 1.5 and chlorine has an EN of 3.0. So we would expect aluminium chloride to be just over 40% ionic

*NB: You do not have to remember actual electronegativity figures or the percentages in the above table!*

**Fig 4. EN difference and bonding**



### Ionisation Energy

If an atom is supplied with enough energy, it will lose an electron. Additional supplies of energy may cause the loss of a second electron, then a third, and so on.

If a neutral atom loses an electron, it becomes a positive ion (a cation).

***Definition***

***First ionisation energy*** *– the energy required to remove 1 mole of electrons from 1 mole of gaseous atoms.*

$X(g) \rightarrow X^+(g) + e^-$

***Second ionisation energy*** *– the energy required to remove 1 mole of electrons from 1 mole of gaseous 1+ charged cations.*

$X^+(g) \rightarrow X^{2+}(g) + e^-$

### Trends in ionisation energies in the Periodic Table

- *Ionisation energies decrease down a group.*
- *Ionisation energies generally increase across a period.*

Going down a **group**, we are adding more electron shells. So in each successive period, the outer electrons are:

- Further away from the nucleus
- More shielded from the nucleus by the inner electrons

Accordingly, ionisation energies decrease down a group.

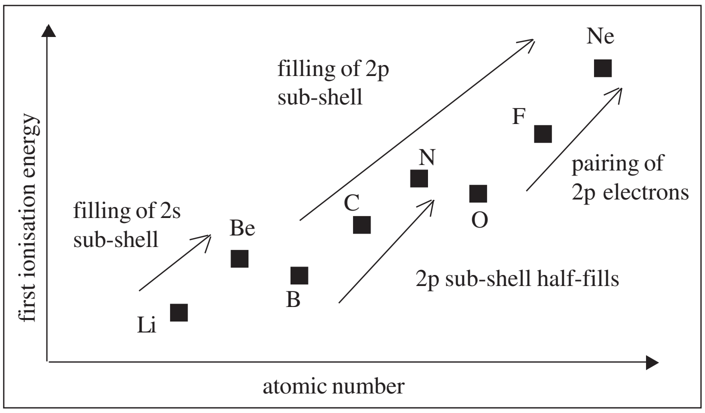
Moving across a **period** the nuclear charge increases, but we are adding electrons in the same shell, so they add little to the shielding. This means that the outer shell electrons are attracted increasingly strongly to the nucleus – thus more energy is required to remove them. So generally we would expect ionisation energy to increase across the period.

***Exam Hint: -*** *Many candidates lose marks by:*

- *when explaining the group trends, not referring to shielding,*
- *when explaining trends across the period, just referring to "increased nuclear charge" without explaining why it is not counterbalanced by increasing numbers of electrons*

Whilst there is a **general** increase in IE across a period, this is not a smooth trend – as shown in fig 5.

**Fig 5. First ionisation energies for the elements of period 2**



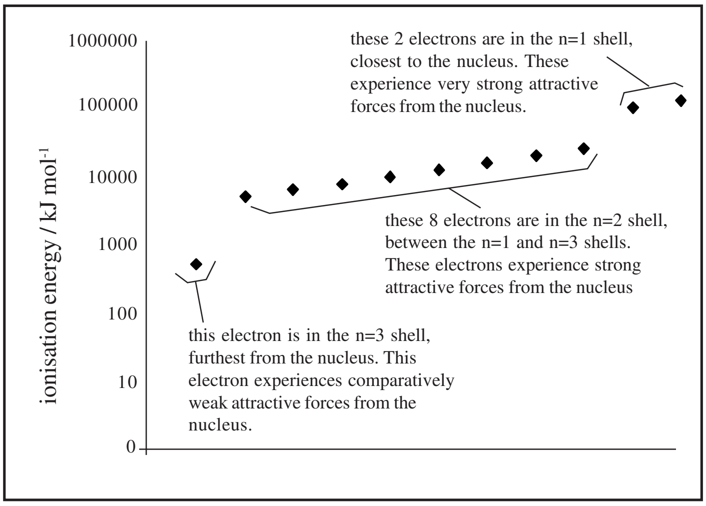
As the graph shows, the first ionisation energy decreases from Be to B and from N to O. A similar phenomenon occurs between groups 2 to 3 and 5 to 6 in the other periods. This can be explained by the existence of sub shells:

- group 2 elements have **full subshell stability**, hence are more difficult to ionise than group 3 elements.
- group 5 elements have **half subshell stability**, hence are more difficult to ionise than group 6 elements.

### Electronic Structure from Ionisation Energies

Examining successive ionisation energies for an element gives us an insight into the electronic structure of that element.

**Fig 6. Successive ionisation energies for sodium**



The pattern shows us that sodium has 11 electrons arranged in three quantum shells, or energy levels. The first electron is relatively easy to remove as:

- It exists further from the nucleus
- The electrons orbiting closer to the nucleus shield the outer electron from the positive centre so attractive forces are comparatively weak.

The next 8 electrons have similar ionisation energies (as they are all a similar distance from the nucleus) but do get successively more difficult to remove as the relative positive charge within the ion is increasing.

The last 2 electrons are very difficult to remove as they exist very close to the unshielded nucleus.

## Electron Affinities

It is possible to **add** electrons to an atom, forming a negative anion. The energy change associated with this is the **electron affinity.**

***Definition***

***First electron affinity** – the energy change when 1 mole of electrons is added to 1 mole of gaseous atoms.*

$O(g) + e^- \rightarrow O^-(g) \qquad \Delta H^{\ominus}_{EA1} = -141\ kJmol^{-1}$

***Second electron affinity** – the energy required to add 1 mole of electrons to 1 mole of gaseous 1- charged anions.*

$O^-(g) + e^- \rightarrow O^{2-}(g) \qquad \Delta H^{\ominus}_{EA2} = +798\ kJmol^{-1}$

The first EA is always **exothermic** (energy is released) because the electron goes into a vacancy in the outer energy level. This is 'bond-making' so energy is released.

However, this creates a 1- charged anion, so to add a second electron **requires** energy to overcome the repulsion (-ve to –ve) between the electron and the anion. Consequently the second EA is always **endothermic** (energy is absorbed).

## Trends in Electron Affinities in the Periodic Table

*Electron Affinity*

- *Increases across a period (to group 7)*
- *Decreases down a group.*

Electron affinity follows the same trends as electronegativity for similar reasons.

As we move across a period there is increased effective nuclear charge, so an additional electron would be more strongly bound to the nucleus and more stable, releasing more energy on the formation of this bond. Note that this is not a uniform increase - full sub-shell stability and half sub-shell stability result in a lower than expected first electron affinity in groups 2 and 5.

As we move down a group, the available site for an additional electron would be further away from the positive nucleus, in a position where there is greater electron shielding from the nucleus. Hence there is a weaker force of attraction between the additional electron and the nucleus, so EA is less.

## Practice Questions

1. Explain the term 'electronegativity'.

2. (a) Use the data below to plot a graph of 'electronegativity difference' (y-axis) against '% ionic character' (x-axis).

| Difference in EN | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 | 1.6 |
|---|---|---|---|---|---|---|---|---|
| % ionic character | 1.0 | 4.0 | 9.0 | 15 | 22 | 30 | 39 | 47 |
| Difference in EN | 1.8 | 2.0 | 2.2 | 2.4 | 2.6 | 2.8 | 3.0 | 3.2 |
| % ionic character | 55 | 63 | 70 | 76 | 82 | 86 | 89 | 92 |

(b) Use the data below to calculate the electronegativity difference between the following bonded elements:

| **Value** | 0.9 | 1.0 | 1.2 | 1.5 | 1.5 | 1.8 | 2.0 | 2.1 |
|---|---|---|---|---|---|---|---|---|
| **Element** | Na | Li | Mg | Al | Be | Si | B | H |
| **Value** | 2.1 | 2.5 | 2.5 | 3.0 | 3.0 | 3.5 | 4.0 | |
| **Element** | P | C | S | Cl | N | O | F | |

| Bond | EN difference | Bond | EN difference |
|---|---|---|---|
| LiF | | HO | |
| NO | | BeCl | |
| CO | | NaF | |
| PO | | SCl | |

(c) Use the graph to estimate the ionic character, and then place in order of increasing ionic character, the above bonds.

3. Define the fourth ionisation energy of an element.

4. Use the idea of ionisation energies to explain why group 2 metals are less reactive than group 1 metals.

5. Define the fourth electron affinity of an element.

6. State whether the fourth electron affinity of an element is likely to be exothermic or endothermic.

## Answers

1. The electronegativity of an atom is the ability of its nucleus to attract electrons in a bond pair.
2. (b) LiF 3.0; HO 1.4; NO 0.5; BeCl 1.5; CO 1.0; NaF 3.1; PO 1.4; SCl 0.5
   (c) Order: NO, SCl, CO, HO, PO, BeCl, LiF, NaCl.
3. Fourth ionisation energy – the energy required to remove 1 mole of electrons from 1 mole of gaseous 3+ charged cations.

   $X^{3+}(g) \rightarrow X^{4+}(g) + e^-$
4. When metals react the donate electrons (reducing agents). Ionisation energy increases across a period (from group 1 to group 2) meaning more energy would be required for group 2 metals to remove electrons than group 1. Also group 2 metals form stable 2+ cations, involving the donation of 2 electrons (hence 2 ionsation energies required) whereas group1 form stable 1+ cations. Hence activation energies are lower for reactions of the group 1 metals.
5. Fourth electron affinity – the energy required to add 1 mole of electrons to 1 mole of gaseous 3- charged anions.

   $O^{3-}(g) + e^- \rightarrow O^{4-}(g)$
6. The fourth electron affinity is likely to be endothermic, as it involves adding a negatively charged electron to a negatively charged 3- anion, and overcoming this repulsion will **require** energy.

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