

CHEMISTRY



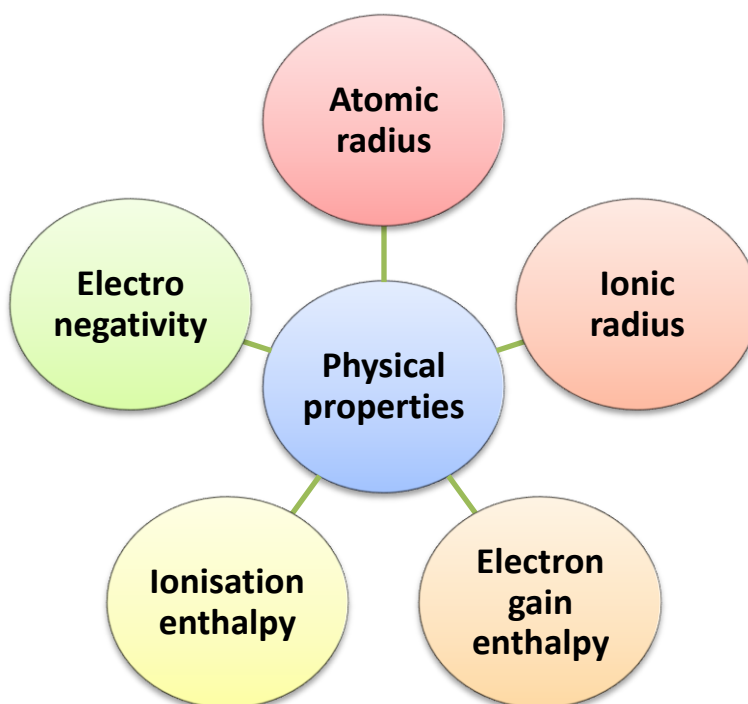
Periodic Trends in Properties of Elements

Introduction

- Several properties of elements vary in a regular manner in going across a period or down a group. Such properties are called **periodic properties**.
- The periodic recurrence of elements with similar properties after regular intervals is called **periodicity**.
- The distribution of electrons in the valence shell of an atom is important and responsible for physical and chemical properties of elements.

Example: Halogens present in Group 17 possess $ns^2 np^5$ configuration in their valence shell and show similar properties.

Trends in Physical Properties



Atomic Radius

- The size of an atom, i.e. the atomic size, is a very important property of an atom.
- If an atom is a sphere, then the atomic size is given by the radius of the sphere.
- The distance from the centre of the nucleus to the outermost shell (valence shell) of electrons is known as its **atomic radius**.
- The atomic radius refers to both covalent and metallic radii depending on whether the element is a non-metal or a metal.
- The atomic radius can be measured by X-ray or other spectroscopic methods.

Non-Metallic Elements

- The size of the non-metallic element can be measured by the distance between two atoms when they are bound together by a single covalent bond of a molecule.
- The measured value helps calculate the **covalent radius** of the element.

Example: Bond distance in the chlorine molecule (Cl_2) is 198 pm and half of this distance (99 pm) is taken as the atomic radius of chlorine.

- The internuclear distance in a diatomic molecule of an element is known as its **covalent bond length**.

$$r_{\text{covalent}} = \frac{1}{2} [\text{bond length}]$$

One-half the covalent bond length is the **covalent radius**.

$$r_{\text{covalent}} = \frac{1}{2} [\text{Internuclear distance between two bonded atoms}]$$

Metallic Elements

- **Metallic radius** is taken as half the internuclear distance separating the metal cores in the metallic crystal.

Example: The distance between two adjacent copper atoms in solid copper is 256 pm. Hence, the metallic radius of copper is assigned a value of 128 pm.

In atoms of elements which are not chemically bound to each other, the only attractive forces are **van der Waal's forces**.

The shortest distance to which the atoms can approach before their electron clouds start repelling each other is called **van der Waal's radii**.

Factors Affecting Atomic Size/Atomic Radius

Number of shells	Nuclear charge	Screening effect or shielding effect
•Atomic size increases with an increase in the number of electronic shells. •Atomic number is proportional to the number of electronic shells.	•Atomic radius decreases with an increase in the nuclear charge. If the nuclear charge is more, then the nucleus attracts the electrons towards it and the atomic size decreases. •Atomic radius is inversely proportional to the nuclear charge.	•In an atom with many electrons, the electrons in the inner shells tend to prevent the attractive influence of the nucleus from reaching the outermost electron. •They act as a screen or shield between the nuclear attraction and the outermost valence electrons.

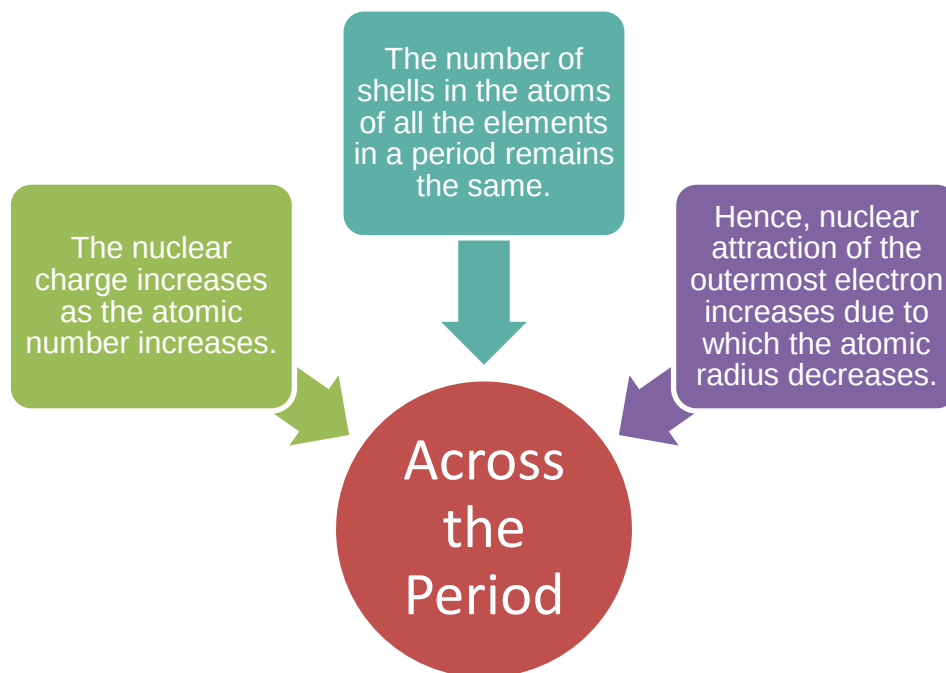
Screening or shielding effect: The effect of inner electrons on the outermost electrons is known as the **screening** or **shielding effect**.

For a given quantum shell, the shielding ability of inner electrons decreases in the order of $s > p > d > f$.

With the increase in the screening or shielding effect, the atomic radius increases.

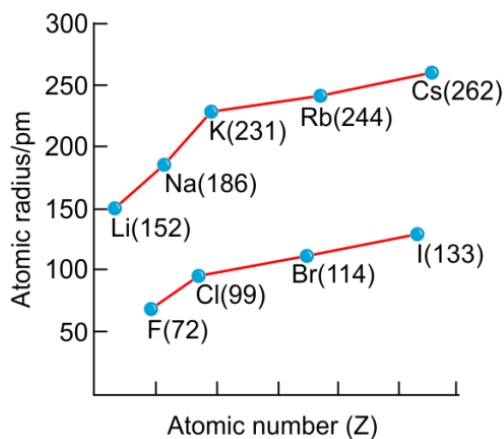
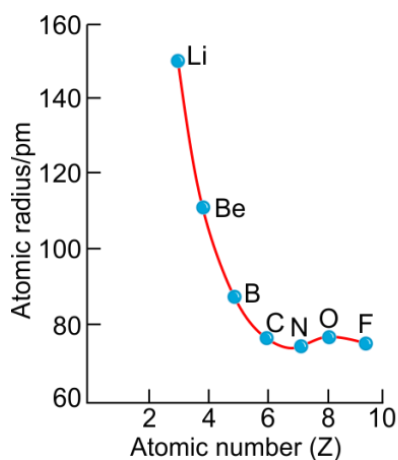
The atomic radius is directly proportional to the shielding effect.

Periodic Trends in Atomic Radius (Atomic Size)



In Periods

- The atomic size is largest for alkali metals, decreases gradually and it becomes smallest for halogen elements.
- At the end of every period, inert gases have larger van der Waal's radii because of a completed outer shell with all the electrons paired which causes greater repulsion.



- Nuclear attraction on the outermost electrons increases and the atomic radius decreases.
- The atomic size generally decreases across a period because the outer electrons are in the same valence shell and the effective nuclear charge increases as the atomic number increases, thus resulting in the increased attraction of electrons to the nucleus.

Atom (Period II)	Li	Be	B	C	N	O	F
Atomic radius	152	111	88	77	74	66	64
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Atomic radius	186	160	143	117	110	104	99

In Groups

- Within a family or vertical column of the periodic table, the atomic radius increases regularly with atomic number.
- For alkali metals and halogens, as we move down the group, the principal quantum number (n) increases and the valence electrons are farther from the nucleus.
- This is because the inner energy levels are filled with electrons, which serve to shield the outer electrons from the pull of the nucleus.
- Hence, the size of the atom increases as reflected in the atomic radii.

Atom (Group I)	Atomic radius	Atom (Group 17)	Atomic radius
Li	152	F	64
Na	186	Cl	99
K	231	Br	114
Rb	244	I	133
Cs	262	At	140

Ionic Radius

- **Ionic radius** is the distance of the valence shell of electrons from the centre of the nucleus in an ion.
- The removal of an electron from an atom forms a **cation**.
- The gain of an electron by an atom leads to an **anion**.

- The ionic radii can be estimated by measuring the distances between cations and anions in ionic crystals.
- The ionic radii of elements exhibit the same trend as the atomic radii.
- A cation is smaller than its parent atom because it has fewer electrons, while its nuclear charge remains the same.
- The size of an anion will be larger than that of the parent atom because of the addition of one or more electrons.

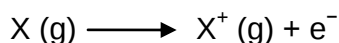
Example: The ionic radius of fluoride ion (F^-) is 136 pm, whereas the atomic radius of fluorine is only 64 pm. The atomic radius of sodium is 186 pm as compared to the ionic radius of 95 pm for Na^+ .

Trends in Ionic Radius

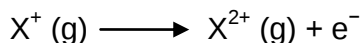
- **Period:** The ionic radius decreases with an increase in atomic number.
- **Group:** The ionic radius increases down the group with an increase in atomic number.

Ionisation Enthalpy or Ionisation Potential (IE)

- A quantitative measure (ΔH) of the tendency of an element to lose an electron is given by its ionisation enthalpy.
- **Ionisation enthalpy** is the minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom (X) of the element to form a positive gaseous ion in its ground state.
- The energy required to remove the first electron is the first ionisation enthalpy and that for the second electron is the second ionisation enthalpy and so forth.
- The first ionisation enthalpy ($\Delta_1 H$) for an element X is the enthalpy change for the reaction depicted in the following equation:



- The ionisation enthalpy is expressed in units of kJ mol^{-1} .
- The second ionisation enthalpy ($\Delta_2 H$) is the energy required to remove the second most loosely bound electron.
- It is the energy required to carry out the following reaction:



- Energy is required to remove electrons from an atom, and hence, ionisation enthalpies are always positive.

- It is more difficult to remove an electron from the positive charged ion than from a neutral atom. Thus, the second ionisation enthalpy is higher than the first ionisation enthalpy, the third ionisation enthalpy is higher than the second and so on.

$$IE_3 > IE_2 > IE_1$$

Factors Affecting the Magnitude of Ionisation Enthalpy

i) Size (radius) of atom

- Larger the atom, lesser is the attraction between the nucleus and the outermost electron, and hence, it is easier to remove electrons from it.
- Therefore, with an increase in atomic size, ionisation enthalpy decreases.

ii) Nuclear charge

- Greater the charge on the nucleus of an atom, greater will be the attraction between the nucleus and the outermost electron.
- It becomes more difficult to remove electrons from an atom and hence greater would be the value of ionisation enthalpy.

iii) Shielding or screening effect of inner electrons

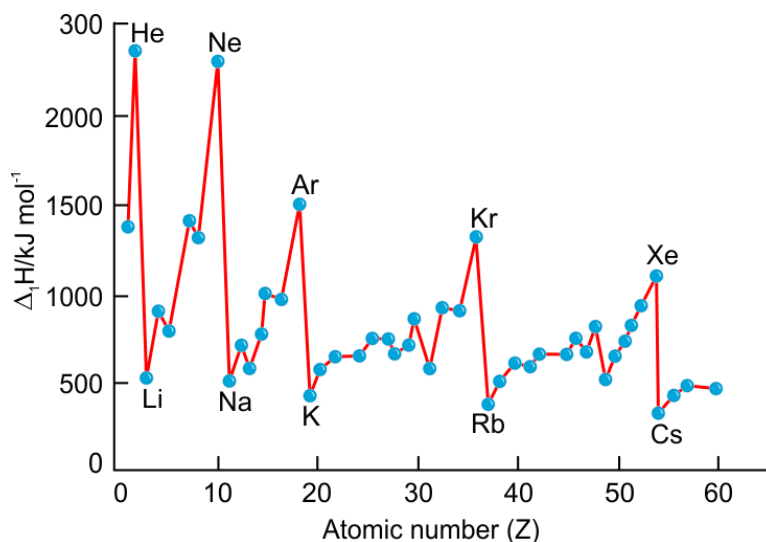
- With the increase in the screening effect of the inner electrons, the nuclear attraction for the outermost electron decreases.
- The effective nuclear charge decreases, and hence, the ionisation enthalpy decreases.
- Because of the shielding effect of inner electrons for a given quantum shell decreases in the order of $s > p > d > f$, the ionisation enthalpy also decreases in the same order.
- Hence, for the same principal shell, the ionisation enthalpy will be more for the removal of the s electron and it will be less to remove the f electron.
- When orbitals in the inner shells are completely filled, shielding is effective.

iv) Nature of electronic configuration

- Ionisation enthalpy values are high for stable configuration such as half-filled and completely filled orbitals because of their extra stability.

Periodic Trends in Ionisation Enthalpy

- The ionisation enthalpy increases from left to right and decreases from top to bottom in the periodic table with a few exceptions.



- From the given plot, it is clear that the maxima occur at the noble gases and the minima at the alkali metals.
- Noble gases with the most stable electronic configuration resist ionisation, and hence, their ionisation enthalpies are high.
- Alkali metals have only one electron outside the preceding noble gas configuration; hence, the electron can be easily lost and ionisation enthalpies of alkali elements are thus very low.

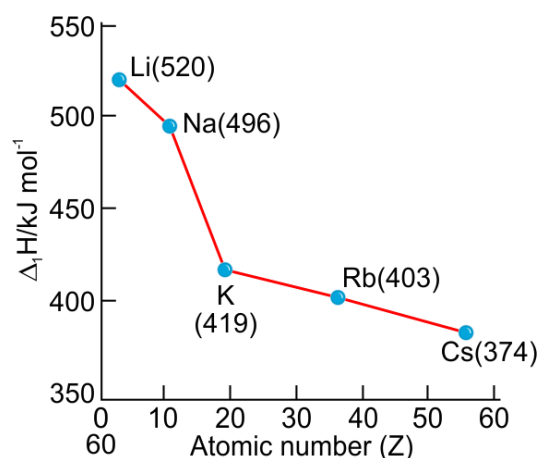
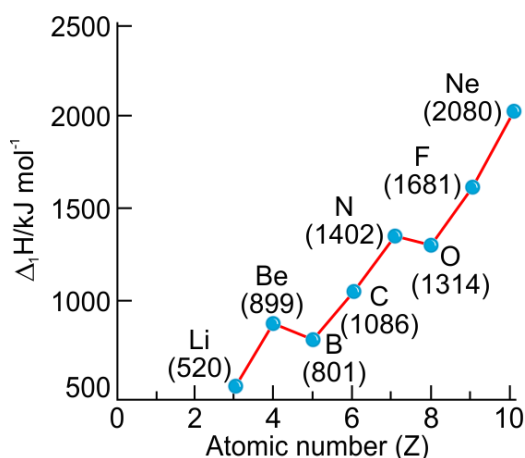
In Groups

- As we move down the groups, the atomic radius of the elements increases with the increase in the number of shells.
- This leads to more shielding effect of inner electrons on the outermost electrons.
- Hence, the force of attraction between the nucleus and the outermost electron decreases, i.e. the effective nuclear charge decreases steadily, thereby decreasing ionisation enthalpy.

Elements	Li	Na	K	Rb	Cs
1 st I.E. in kJ mol ⁻¹	520	496	419	403	374

In Periods

- As we move across a period from one element to the other, electrons are being successively added to the same principal shell.
- The added electrons shield each other from the nucleus even though the nuclear charge (atomic number) increases.
- As a result, there is an increase in the effective nuclear charge which causes a decrease in the atomic radii and hence an increase in ionisation enthalpy along a period.



Elements	Li	Be	B	C	N	O	F	Ne
1 st I.E. in kJ mol^{-1}	520	899	801	1086	1402	1324	1681	2080

Exceptions:

i) Boron and Beryllium

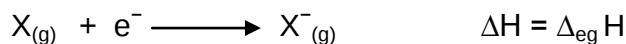
- The first ionisation enthalpy of the boron atom is less than that of the beryllium atom.
- Electronic configuration of B is $1s^2 2s^2 2p^1$ and that of Be is $1s^2 2s^2$.
- Boron has a single electron in the 2p orbital and beryllium has a pair of electrons in the 2s orbital.
- Less energy is required to remove a p-electron than an s-electron from the same principal quantum shell.
- Hence, the first ionisation enthalpy of B is less than Be.

ii) Oxygen and Nitrogen

- The first ionisation enthalpy of oxygen is less than that of the nitrogen atom.
- Electronic configuration of N is $1s^2 2s^2 2p^3$ and that of O is $1s^2 2s^2 2p^4$.
- Nitrogen has half-filled 2p orbitals which are very stable.
- Hence, it requires more energy to remove an electron from such a stable configuration.
- Therefore, the first ionisation enthalpy of oxygen is less than that of oxygen.

Electron Gain Enthalpy

- Electron gain enthalpy of an element is the energy released when a neutral isolated gaseous atom accepts an extra electron to form the gaseous negative ion. It is represented as $\Delta_{\text{eg}} H$.



- For many elements, energy is released when an electron is added to the atom and the electron gain enthalpy is negative.

Example: Halogens (group 17 elements) have very high negative electron gain enthalpy. They can attain a stable noble gas electronic configuration by accepting an electron.

- Noble gases have large positive electron gain enthalpies.
- Depending on the elements, the process of adding an electron to an atom may be either endothermic or exothermic.

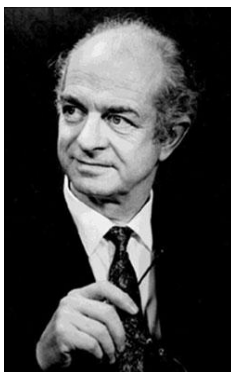
Trends in Periods and Groups

- The electron gain enthalpies become more negative with an increase in the atomic number as a rule.
- The effective nuclear charge increases from left to right across the period.
- Smaller the size of the atom, lesser will be the distance between the added electron and the nucleus. Thus, the attraction between them will be stronger and hence electron gain enthalpy will be more negative.
- Electron gain enthalpy becomes less negative as we go down a group.
- Larger the size of an atom, larger will be the distance between the added electron and the nucleus. Thus, the attraction between them will be weaker and hence electron gain enthalpy will be less negative.
- Consider the electron gain enthalpies of P and S, Cl and F. Electron gain enthalpy becomes more negative across a period as we move from left to right (P to S). Within a group (F and Cl), the electron gain enthalpy becomes less negative down the group. However, adding an electron to the 2p orbital (F) leads to greater repulsion than adding an electron to the larger 3p orbital (Cl). Hence, chlorine is the element with most negative electron gain enthalpy and phosphorus is the one with least negative electron gain enthalpy.

Values (in kJ mol^{-1})	P	-71.7
	S	-200
	F	-328
	Cl	-349

Electronegativity

- The qualitative measure of the tendency of an atom in a chemical compound to attract a shared pair or electrons to itself is called **electronegativity**.
- It gives an idea about the metallic and non-metallic properties of elements.
- It also helps explain and predict many properties concerning energy and the distribution of charge in bonds.
- Such properties are bond dissociation energy, bond polarity and ionic character of covalent bonds.
- A number of scales to determine the electronegativity of elements such as the **Pauling scale**, **Mulliken–Jaffe scale** and **Allred–Rochow scale** have been developed.
- In 1922, an American scientist, **Linus Pauling**, assigned arbitrarily a value of 4.0 to fluorine as it has greater ability to attract electrons.



Factors Affecting Electronegativity

Atomic radius (size): Electronegativity decreases with an increase in atomic radius.

Nuclear charge: Electronegativity is directly proportional to nuclear charge; with an increase in nuclear charge, electronegativity increases.

Screening effect: With an increase in the screening or shielding effect, electronegativity decreases.

Trends in Electronegativity

In a Period

- Electronegativity increases from left to right (e.g. lithium to fluorine).
- As the atomic number increases from left to right, the atomic radius decreases and the nuclear charge increases from left to right.
- Hence, the tendency to attract a shared pair of electrons increases from left to right in a period.

In a Group

- Electronegativity decreases down the group, i.e. from fluorine to astatine.
- With an increase in the atomic number, the atomic radius increases. Thus, the tendency to attract a shared pair of electrons decreases, and hence, electronegativity decreases down the group.
- Non-metallic elements have a tendency to gain electrons. Hence, electronegativity is directly related to the non-metallic properties of elements.
- It can be extended so that the electron is inversely proportional to the metallic properties of elements. Thus, the increase in electronegativity across a period is accompanied by an increase in non-metallic properties or a decrease in metallic properties of elements. Similarly, the decrease in electronegativity down a group is accompanied by a decrease in non-metallic properties or increase in metallic properties of elements.

