

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Earlier classifications

1) Dobereiner's classification:

Johann Dobereiner classified elements into small groups each containing three elements. These small groups were called *triads*.

E.g. for triads are:

i)	${}^7\text{Li}$	${}^{23}\text{Na}$	${}^{39}\text{K}$
ii)	${}^{40}\text{Ca}$	${}^{88}\text{Sr}$	${}^{137}\text{Ba}$

In triads, the atomic mass of the middle element is approximately the average of the other two elements. This is known as Law of Triads. This classification was applicable to very few elements and so it was rejected.

2) Newlands classification:

Newland arranged elements in the increasing order of their atomic masses. He noted that the properties of every eighth element, starting from a given element, are similar to that of the first element. The relationship is just like the resemblance of first and eighth musical notes. He named this as **law of octaves**.

But his classification was rejected since the law of octaves was applicable to elements upto calcium. Also by the discovery of noble gases, the properties of eighth element become not similar to that of the first element.

3) Mendeleev's classification:

Dimitri Mendeleev classified the elements in the increasing order of their atomic weights. He founded that the properties of elements repeat after a regular interval. Based on this observation, he proposed a **periodic law** which states that "**The properties of elements are the periodic functions of their atomic weights.**" That is, when elements are arranged in the increasing order of their atomic weights, their properties repeat after a regular interval.

Mendeleev arranged elements in horizontal rows (periods) and vertical columns (groups) in such a way that the elements with similar properties occupied in the same group. He mainly depends on the similarities in the empirical formulae and the properties of the compounds formed by the elements. He realized that some of the elements did not fit in with his scheme of classification if the order of increasing atomic weight was strictly followed. So he ignored the order of atomic weights and placed the elements with similar properties together.

When Mendeleev proposed his periodic table, some of the elements were not discovered. He left some vacant places (gaps) for them in the periodic table and predicted some of their properties. For e.g. both Gallium and Germanium were not discovered at that time. He named these elements as Eka-Aluminium and Eka-Silicon respectively and predicted their properties. These elements were discovered later and found that Mendeleev's predictions were correct.

Merits of Mendeleev's periodic table

- 1) It was the first comprehensive classification of elements.
- 2) He corrected the wrong atomic weights of some elements and placed them in correct position in the periodic table.
- 3) He left vacant places for undiscovered elements and predicted some of their properties.
- 4) Elements with similar properties are placed in the same group.

Demerits of Mendeleev's periodic table

- 1) Elements with dissimilar properties are found in same group.
- 2) He could not give an exact position for hydrogen.
- 3) He could not give exact position for Lanthanoids and Actinoids and also for isotopes.
- 4) Mendeleev's periodic table did not strictly obey the increasing order of atomic weights.

Modern Periodic table

Henry Moseley's work on the atomic spectra of elements proved that atomic number is a more fundamental property than atomic mass. Based on this observation, he modified the Mendeleev's periodic law as "*the physical and chemical properties of elements are the periodic functions of their atomic numbers*". This is known as **Modern Periodic law**.

Based on modern periodic law, numerous forms of periodic tables have been proposed. The most commonly used is the long form of periodic table.

In this periodic table, the elements are arranged in the increasing order of their atomic number. It contains **7** horizontal rows called **periods** and **18** vertical columns called **groups**. Elements having similar outer electronic configurations are arranged in same group or family. The groups are numbered from 1 to 18. Due to the similar outer electronic configuration and same valency, the elements present in the same group have similar properties.

There are 7 periods in Modern periodic table. The period number corresponds to the highest principal quantum number of the elements. The *first period* contains 2 elements (H and He). Here the subshell filled is 1s. This period is called *very short period*.

The *second period* contains 8 elements (Li to Ne). Here the subshells filled are 2s and 2p. The *third period* also contains 8 elements (Na to Ar). Here the subshells filled are 3s and 3p. These 2 periods are called *short periods*.

The *fourth period* contains 18 elements (K to Kr). Here the subshells filled are 4s, 3d and 4p. The *fifth period* also contains 18 elements (Rb to Xe). Here the subshells filled are 5s, 4d and 5p. These 2 periods are called *long periods*.

The *sixth period* contains 32 elements (Cs to Rn). Here the subshells filled are 6s, 4f, 5d and 6p. This period is the longest period in the periodic table and is called the *Monster period*. The *seventh period* is an incomplete period. It can also accommodate 32 elements. Here the subshells filled are 7s, 5f, 6d and 7p.

The 14 elements each of sixth and seventh periods are placed in separate rows below the main body of the periodic table. These are together called **inner transition elements**. The 14 elements of sixth period (from cerium to lutetium) are called *Lanthanides or Lanthanones or Lanthanoids or rare earths*. The 14 elements of seventh period (from thorium to lawrencium) are called *Actinides or Actinones or Actinoids*.

The blocks in the Modern periodic table

The Modern periodic table is divided into 4 blocks based on the subshell in which the last electron enters. They are s block, p block, d block and f block.

1. The s block elements

These are elements in which the last electron enters in the outer most s sub shell. They include elements of the groups 1 and 2. Their general outer electronic configuration is ns^1 or ns^2 . They are all reactive metals with low ionization enthalpies. They lose their outer most electrons readily to form +1 and +2 ions. Their metallic character and reactivity increases down the group. They mainly form ionic compounds (except Li and Be).

2. The p block elements

These are elements in which the last electron enters in the outer most p sub shell. They include elements of the groups 13 to 18. They are also called **Representative elements**. Their general outer electronic configuration is $ns^2 np^{1 \text{ to } 6}$. The 18th group elements are called Noble gases. They have completely filled orbitals. Their non-metallic character increases from left to right in a period and metallic character increases from top to bottom in a group.

3. The d block elements

These are elements in which the last electron enters in the penultimate d sub shell. They include elements of the groups 3 to 12. They are also called **Transition elements**, since they show a transition (change) from the most electropositive s block elements to the least electropositive p block elements. Their general outer electronic configuration is $(n-1)d^{1 \text{ to } 10} ns^{0 \text{ to } 2}$. They are all metals, form coloured compounds or ions, show variable oxidation states and valencies, paramagnetism and catalytic properties.

4. The f block elements

These are elements in which the last electron enters in the anti-penultimate f sub shell. They include *lanthanides of 6th period and actinides of 7th period*. They are also called **Inner transition elements**. Their general outer electronic configuration is $(n-2)f^{1 \text{ to } 14} (n-1)d^{0 \text{ to } 1} ns^2$. They are all metals. Within each series the properties of these elements are similar. Actinoid elements are radioactive. Elements after Uranium ($z=92$) in the actinide series are called trans-uranium elements or trans-uranic elements or artificial elements.

Periodic properties of Elements

The properties which repeat after a regular interval are called periodic properties. Some of the important periodic properties of elements are atomic and ionic radii, ionization enthalpy, electron gain enthalpy, electropositivity, electronegativity etc.

1. Atomic Radius

It is defined as the distance from the centre of the nucleus to the outermost shell having electrons. Atomic radius of individual atoms cannot be determined. So it is expressed in any of the following methods:

- Covalent radius:** It is half of the inter nuclear distance between two covalently bonded (single bonded) atoms. It is used to express the atomic radius of non-metal atoms. For e.g. the bond distance of Cl_2 molecule is 198 pm. So the covalent radius is 99 pm.
- Metallic radius:** It is the half of the inter nuclear distance between two metallic ions in a metal crystal.
- van der Waal's radius:** It is defined as the half of the inter nuclear distance between two non bonded atoms of separate molecules in the solid state.

Atomic radius is commonly expressed in picometre (pm) or angstrom (Å). It is measured by x-ray diffraction method or by spectroscopic methods.

Variation of atomic radius along a group and period

The atomic size decreases from left to right in a period. This is because in a period, the electrons are added to the same valence shell. Thus the number of shells remains same, but the effective nuclear charge increases. So the atomic radius decreases. In a given period, alkali metals (group 1) have the maximum size and halogens (group 17) have the minimum size.

Down a group, the atomic radius increases from top to bottom. This is because of the increase in no. of shells and shielding effect. (in atoms with higher atomic number, the inner electrons partially shield the attractive force of the nucleus. So the outer electrons do not experience the full attraction of the nucleus and this is known as shielding effect or screening effect).

Atomic radius of noble gases is larger than that of halogens. This is because noble gases are monoatomic. So van der Waal's radius is used to express the atomic radius which is greater than covalent radius or metallic radius.

2. Ionic radius

It is defined as the half of the inter nuclear distance between cations and anions of an ionic crystal. The variation of ionic radius is same as that of atomic radius.

Generally a cation is smaller than its parent atom (e.g. Na^+ is smaller than Na atom). This is because a cation has fewer electrons, but its nuclear charge remains the same as that of the parent atom.

An anion is larger than its parent atom (e.g. Cl^- is larger than Cl atom). This is because the addition of one or more electrons would result in an increased electronic repulsion and a decrease in effective nuclear charge.

Isoelectronic species:

Atoms and ions having the same number of electrons are called isoelectronic species. E.g. O^{2-} , F^- , Ne, Na^+ , Mg^{2+} etc. (All these contain 10 electrons)

Among isoelectronic species, *the cation with greater positive charge will have the smaller radius*. This is because of the greater attraction of electrons to the nucleus. *The anion with greater negative charge will have the larger radius*. Here the repulsion between electrons is greater than the attraction of the nucleus. So the ion will expand in size.

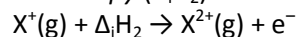
3. Ionisation enthalpy ($\Delta_i H$)

It is defined as the energy required to remove an electron from the outer most shell of an isolated gaseous atom in its ground state. It may be represented as: $\text{X}_{(\text{g})} + \Delta_i H \rightarrow \text{X}_{(\text{g})}^+ + \text{e}^-$

Its unit is kJ/mol or J/mol.

The energy required to remove the first electron from the outer most shell of a neutral atom is called *first ionisation enthalpy* ($\Delta_i H_1$) $\text{X}_{(\text{g})} + \Delta_i H_1 \rightarrow \text{X}_{(\text{g})}^+ + \text{e}^-$

Second ionisation enthalpy ($\Delta_i H_2$) is the amount of energy required to remove an electron from a unipositive ion.



Energy is always required to remove an electron from an atom or ion. So $\Delta_i H$ is always positive.

The second ionisation enthalpy is always higher than first ionization enthalpy. This is because it is more difficult to remove an electron from a positive charged ion than from a neutral atom.

Similarly third ionisation enthalpy is higher than second ionisation enthalpy and so on.

i.e. $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3 \dots$

As the ease of removal of electron increases, the ionisation enthalpy decreases.

Factors affecting ionisation enthalpy

The important factors which affect ionisation enthalpy are:

- Atomic size:** Greater the atomic size (atomic radius), smaller will be the ionisation enthalpy.
- Nuclear charge:** The value of ionisation enthalpy increases with nuclear charge.
- Shielding effect:** As the shielding effect increases, the electrons can easily be removed and so the ionisation enthalpy decreases.
- Presence of half filled or completely filled orbitals** increases ionisation enthalpy.

Variation of $\Delta_i H$ along a period and a group

Along a *period*, ionisation enthalpy *increases* from left to right. This is because of the *decrease in atomic radius and increase in nuclear charge*. Thus alkali metals have the least $\Delta_i H$ and noble gases have the most.

Down a *group*, $\Delta_i H$ *decreases* due to *increase in atomic radius and shielding effect*. Thus among alkali metals, lithium has the least $\Delta_i H$ and francium has the most.

In the second period of modern periodic table, *the first ionisation enthalpy of Boron is slightly less than that of Beryllium*. This is because of the completely filled orbitals in Be ($1s^2 2s^2$).

Similarly *the first ionisation enthalpy of N is greater than that of Oxygen*. This is because N has half filled electronic configuration ($1s^2 2s^2 2p^3$), which is more stable and so more energy is required to remove an electron.

4. Electron gain enthalpy ($\Delta_{eg} H$)

It is the heat change (enthalpy change) when an electron is added to the outer most shell of an isolated gaseous atom. It can be represented as $X_{(g)} + e^- \rightarrow X^-_{(g)}$

Its unit is kJ/mol. It may be positive or negative depending on the nature of the element. For most of the elements, energy is released when electron is added to their atoms. So $\Delta_{eg} H$ is negative. Noble gases have large positive electron gain enthalpy because of their completely filled (stable) electronic configuration.

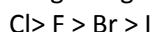
Electron gain enthalpy also depends on atomic size, nuclear charge, shielding effect etc. As the atomic size increases $\Delta_{eg} H$ decreases. When nuclear charge increases, electron gain enthalpy increases and become more negative. Shielding effect decreases $\Delta_{eg} H$. Presence of half filled or completely filled orbitals makes $\Delta_{eg} H$ less negative.

Periodic variation of $\Delta_{eg} H$

From left to right across a *period*, $\Delta_{eg} H$ become *more negative*. This is *because of decrease in atomic radius and increase in nuclear charge*. So the ease of addition of electron increases and hence the $\Delta_{eg} H$.

Down a *group*, $\Delta_{eg} H$ becomes less negative. This is *due to increase in atomic radius and shielding effect*. *Electron gain enthalpy of fluorine is less negative than chlorine*. This is because, when an electron is added to F, it enters into the smaller 2nd shell. Due to the smaller size, the electron suffers more repulsion from the other electrons. But for Cl, the incoming electron goes to the larger 3rd shell. So the electronic repulsion is low and hence Cl adds electron more easily than F. Due to the same reason $\Delta_{eg} H$ of Oxygen is less negative than S.

Thus in modern periodic table, alkali metals have the least –ve $\Delta_{eg} H$ and halogens have the most –ve $\Delta_{eg} H$. Among halogens, the negative $\Delta_{eg} H$ decreases as follows.



The negative electron gain enthalpy is also called electron affinity.

5. Electronegativity

Electronegativity of an atom in a compound is the ability of the atom to attract shared pair of electron of electrons. It is not a measurable quantity and so it has *no* unit. There are different scales for measuring the Electronegativity of elements. The most commonly used is the **Pauling Electronegativity scale** developed by Linus Pauling.

Electronegativity depends on atomic size and nuclear charge. As the atomic radius increases, electronegativity decreases. Greater the nuclear charge, greater will be the electronegativity. Generally electronegativity increases across a period and decreases along a group. So in modern periodic table, F has the maximum electronegativity and Fr has the minimum electronegativity. *In Pauling Scale, electronegativity of F is 4.0 and that of Oxygen is 3.5.*

The electronegativity of an element is *not constant*. It varies depending on the element to which it is bound. It is directly related to the non-metallic character of elements. *An increase in electronegativity across a period indicates an increase in non-metallic character and decrease in metallic character.*

6. Electropositivity

It is the tendency of an atom to lose the most loosely bound electron (valence electron). It is directly related to the metallic character of elements. It depends on atomic size and nuclear charge. As the atomic radius increases, electropositivity increases.

Along a period, electropositivity decreases from left to right. But down a group, it increases. So francium is the most electropositive element and fluorine is the least electropositive element.

7. Valency

It is the combining capacity of an element. Or, it is the number of electrons lost or gained by an atom during a chemical reaction.

Along a period, valency first increases upto the middle and then decreases (for s and p block elements only). In a group, valency remains constant. Transition elements can show variable valency.

Valency is numerically equal to oxidation number of the element. The difference is that oxidation number has a positive or negative sign but the valency doesn't.



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