

Chapter No. 1

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Periodic Classification of Elements and Periodicity

Introduction:

To achieve a thorough understanding of a complex subject like chemistry, it would be highly desirable to fit all the facts into a simple logical pattern. The periodic table of elements has served the purpose to systematize the properties of the elements for well over 100 years. The development of periodic table is one of the most significant achievements in the history of chemical sciences.

Periodic table:

A table obtained by the arrangement of elements into period's and groups is called periodic table.

Usefulness of periodic table:

The periodic table provides a basic framework to study the periodic behaviour of physical and chemical properties of elements as well as their compounds.

Historical Background:

The early history of ideas leading up to the periodic classification of elements is fascinating, but will not be treated here in detail. Those who made memorable contributions in this field are:

- **Al-Razi:**

He organized the known elements and compounds. His classification was based upon the physical and chemical properties of elements and compounds

- **Dobereiner's Triads:**

In 1829, a German Chemist, Dobereiner arranged then known elements in groups called Triads, as each contained three elements with similar properties. According to his Law of Triads.

"The atomic mass of middle element is the average of atomic masses of other two elements of triads"

Demerits:

Dobereiner's idea of classification failed because only a few elements could be covered under triads.

Some Dobereiner's Triads

Triad	Li	Na	K	Atomic mass of Na = $(7 + 39) \div 2$ = 23
Atomic mass	7	23	39	
Triad	Ca	Sr	Ba	Atomic mass of Sr = $(40 + 137) \div 2$ = 88.5
Atomic mass	40	88	137	
Triad	Cl	Br	I	Atomic mass of Br = $(35.5 + 127) \div 2$ = 81.25
Atomic mass	35.5	80	127	

Newland's Law of Octave:

In 1864, an English chemist, John Newland classified 62 elements, known at that time, increasing order of their atomic masses. According to his Law of Octave:

“If the elements are arranged in the increasing order of their atomic masses, every eighth (8th) element had some properties in common with the first one.”

Newland's Octaves

Li (7)	Be (9)	B (11)	C (12)	N (14)	O (16)	F (19)
Na (23)	Mg (24)	Al (27)	Si (28)	P (31)	S (32)	Cl (35.5)
K (39)	Ca (40)	Cr (52)	Ti (48)	Mn (55)	Fe (56)	Ni & Co

Demerits:

- It was found that the Law of Octaves was applicable only upto calcium, as after calcium every eighth element did not possess properties similar to that of the first.
- It was assumed by Newlands that only 62 elements existed in nature and no more elements would be discovered in the future. But, later on, several new elements were discovered, whose properties did not fit into the Law of Octaves.
- The above sequence of elements was disturbed with the discovery of noble gases.

Mendeleev's Periodic Table:

In 1871, Russian Chemist, Dmitri Mendeleev, gave a more useful and comprehensive scheme for the classification of elements. He presented the first regular periodic table in which elements of similar chemical properties were arranged in eight vertical columns called Groups. The horizontal rows, of the table were called Periods.

Mendeleev's Periodic Law:

“If the elements are arranged in ascending order of their atomic masses, their chemical properties repeat in a periodic manner.”

Characteristics of Mendeleev's periodic table:

The main features of the periodic table are discussed briefly as follows:

- Study of elements:**
The periodic table simplified the study of elements and made it very systematic
- Discovery of new elements:**
Mendeleev laid more stress on similarity in properties, rather than increasing atomic masses of the elements. He left gaps for undiscovered elements but predicted their properties; **For example**, he predicted that after zinc, there should be two elements, which have properties similar to aluminium and silicon, respectively. He named them as eka aluminium and eka-silicon. The elements were discovered later on. Eka-aluminium was named as gallium, whereas eka-silicon was named as germanium.
- Determination of correct atomic masses:**
Mendeleev corrected the atomic masses of certain elements on the basis of their properties. **For example**, beryllium was assigned atomic mass of 13.5 and hence, should be placed in between carbon (at mass 12) and nitrogen (at mass 14). But on the basis of the properties, it should be placed above magnesium. Hence, the atomic mass of beryllium was changed to 9 (from 13.5) which actually is also its correct atomic mass.

Improvements in Mendeleev's Periodic Table:

(1) Atomic Number:

The elements were arranged in ascending order of their atomic number instead of their atomic masses.

(2) Extra Group:

For the arrangement of Noble gases, one extra group (VIII-A) was added at the extreme right of the periodic table. These gases had not been discovered in Mendeleev's time.

(3) Sub-group:

In Mendeleev's Periodic table, the elements like Be, Mg, Ca, Sr, Ba, and Zn, Cd, Hg were placed in a single vertical group although they possess different properties. This confusion was removed by dividing the elements in two types of vertical group A and B.

(4) Position of Isotopes:

If the elements are arranged in the order of their increasing atomic masses, it is not possible to accommodate a large number of isotopes. This problem was solved by arranging elements in ascending order of their atomic numbers.

The Modern Periodic Table:

In modern periodic table, all the elements are arranged in ascending order of their atomic numbers.

Modern Periodic Law:

"If the elements are arranged in ascending order of their atomic numbers, their chemical properties repeat in a periodic manner."

This law was introduced by Moseley in 1911. Later on Bohr introduced modern periodic table based on modern periodic. Following are the essential features of the periodic table.

(1) Groups:

Elements with similar properties are placed in vertical columns called groups.

- There are eight (8) groups, which are usually numbered by Roman numerals I to VIII.
- Each group is divided into two subgroups

A Subgroups containing representative or normal elements.

B Subgroups contain less typical elements called **transition elements** and are arranged in the centre of periodic table.

- Elements of same group have similar chemical properties due to same valence shell electronic configuration.
- Usually number of valence electrons is same as that of group number.

(2) Periods:

"The horizontal rows of elements in periodic table are called periods."

The essential features of periods are as follows.

- There are 7 periods in the periodic table numbered by Arabic numerals 1 to 7.
- The period 1 contains only two elements, hydrogen and helium.
- The periods 2 and 3 contain eight elements each and are called **periods**. All the elements in these periods are representative elements and belong to **A** subgroup. In these periods, every

eight element resembles in properties with the first element. As lithium and beryllium in the 2nd period resemble in most of their properties with sodium and magnesium of the 3rd period, respectively. Similarly, boron and aluminum both show oxidation state of +3 fluorine in 2nd period has close resemblances with chlorine of 3rd period.

- The period 4 and 5 contain eighteen elements each and are called long periods. Out of these, 8 are representative elements which belong to **A** sub group. Whereas the other 10 elements, placed in the centre of the table, belong to **B** subgroup and are known as outer transition elements. In these periods, the repetition of properties among the elements occurs after 18 elements. As after $_{19}\text{K}$ (having atomic number 19) the, next element with similar properties is $_{37}\text{Rb}$.
- The period 6 contains thirty-two elements and is called very long period. In this period there are eight representative elements, ten transition elements and a new set of fourteen elements called. Lanthanides as they start after $_{57}\text{La}$ Lanthanides have remarkably similar properties usually shown separately at the bottom of the periodic table.
- The period 7 is incomplete so far. It contains only two normal elements Fr and $_{88}\text{Ra}$, ten transition elements and 14 elements. The inner transition elements of this period are called Actinides, as they follow $_{89}\text{Ac}$. The actinides are also shown at the bottom of the periodic table under the Lanthanides. Due to their scarcity, the inner transition elements are also called rare earth elements.

(3) Some more Families in the Periodic Table:

- **Families in periods:**

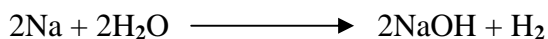
While studying about periods, it is observed that certain rows of elements with similar properties have assigned common names such as transition elements, Lanthanides, Actinides or Rare Earth elements.

- **Families in groups:**

Due to their peculiar characteristics, some typical elements belonging to sub-groups A and B have been assigned family names.

- **Alkali Metals:**

Elements of group IA (Li, Na, K., Rb, Cs, Pr) are called alkali metals because of their property to form strong alkalies with water.



- **Alkaline Earth metals:**

Elements of group IA (Be, Mg, Ca, Sr, Ba, Ra) are known as alkaline earth metals because of their presence in Earth's crust and alkaline character.

- **Halogens:**

Elements of group VIIA (F, Cl, Br, I, At) are called halogens due to their salt forming properties.

- **Noble gases:**

The gases of VIIIA group (He, Ne, Ar, Kr, Xe, Rn) are called noble gases because of their least reactivity.

(4) Blocks in Periodic Table:

Upon the basis of valence orbital of the element involved in chemical bonding, elements in the periodic table can be classified into following four blocks.

The vertical columns in periodic table are called groups. There are 18 vertical columns in the extended or long form of the periodic table. Every column contains a series of elements whose atoms have same outer most electronic configurations, thereby similar chemical properties.

- **s-block:**

Elements of IA and IIA subgroups including Helium (He) are called s-block element because their valence electrons available in “s” orbital. e.g. $11\text{Na} = 1\text{S}^2, 2\text{S}^2, 2\text{P}^6, 3\text{S}^1$ so, sodium belongs to s-block.

- **p-block:**

The elements of IIIA to VIIIA except Helium (He) are known as p-block elements as their valence electrons are present in p-orbital $17\text{Cl} = 1\text{S}^2, 2\text{S}^2, 2\text{P}^6, 3\text{S}^2, 3\text{P}^5$ so, chlorine belongs to p-block.

- **d-block:**

In transition elements, electrons in d-orbital are responsible for their valency hence they are called d-block elements $26\text{Fe} = 1\text{S}^2, 2\text{S}^2, 2\text{P}^6, 3\text{S}^2, 3\text{P}^6, 4\text{S}^2, 3\text{d}^6$

- **f-block:**

In Lanthanides and Actinides valence electrons are present in f-orbital hence these elements are called f-block elements $58\text{Ce} = 1\text{S}^2, 2\text{S}^2, 2\text{P}^6, 3\text{S}^2, 3\text{P}^6, 4\text{S}^2, 3\text{d}^{10}, 4\text{P}^6, 5\text{S}^2, 4\text{d}^{10}, 5\text{P}^6, 6\text{S}^2, 4\text{f}^2$.

(5) Metals, Non-metals and Metalloids:

Another basis for classifying the elements in the periodic table is their metallic character.

Metals:

- The elements on the left hand side, in the centre and at the bottom of the periodic table are metals.
- All the remaining elements except hydrogen, non-metals and metalloids.

Non-metals:

- Elements in the upper right corner of the periodic table are nonmetals.
- In the periodic table elements of groups IVA to VIIIA, at the top right hand corner above the stepped line, are non-metals.

Metalloids:

- Some elements, especially lower members of groups, IIIA, IVA and VA have properties of both metals as well as non-metals. These elements are called semi-metals or metalloids.
- The elements, just under the “stepped line” such as Si, As, and Te are the metalloids.

Periodic Trends in Physical Properties:

In modern periodic table the elements are arranged in ascending order of their atomic numbers and their classification in groups and periods is based on the similarity in their properties. Yet, due to the gradual increase in the number of protons in the nucleus and electrons in outer shells the physical &

chemical properties of the elements steadily vary within a group or a period. Following are the periodic trends in some physical properties of elements.

1. Atomic size:

(i) Atomic Radius:

The half of the distance between the centres of two bonded atoms of any element is called atomic radius.

OR

The average distance between the nucleus of an atom and its outermost shell is called atomic radius.

Periodic Trend:

(a) Across the Period:

Atomic radius decreases left to right in a period. This is because of:

- Increase in atomic number.
- Increase in the positive charge in the nucleus. As positive nuclear charge increases, the negatively charged electrons in the shells are pulled closer to the nucleus.

(b) Down the Group:

Atomic radius increases down the group. This is because of:

- Increase in number of shells.
- Increase in shielding effect down the group due to increase in intervening electrons. Thus atomic radius increases.

✦ Lanthanide Contraction:

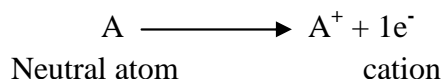
In lanthanide series, there is a regular decrease in the atomic as well as ionic radii of trivalent ion (M^{3+}) as the atomic number increases from cerium to lutetium. This decrease in size of atoms and ions is known as Lanthanide contraction. The reason is that as we proceed from one element to the next element in the lanthanide series, the nuclear charge, i.e. atomic number increases by one unit and the addition of one electron occurs at the same time in 4f energy shell. Due to diffuse shapes of f orbitals, the 4f electrons shield each other quite poorly from the nuclear charge. Thus the effect of nuclear charge increase is somewhat more than the change-shielding-effect. This brings the valence shell nearer to the nucleus and hence the size of atom goes on decreasing as we move in the series.

(ii) Ionic Radius:

The size of an ion when it is supposed to be spherical is called ionic radius.

Formation of cation:

Cation is formed when an atom loses electron or electrons.

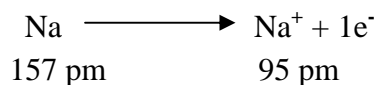


Size of cation is always smaller than parent atom:

A cation is formed by the loss of one or more electrons from a neutral atom. The size of cation is always smaller than its parent atom. This is because of:

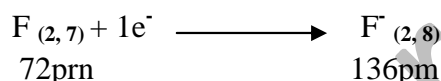
- Removal of one or more electrons from neutral atom usually results in the loss of outermost shell.

- Removal of electrons causes an imbalance in proton electron ratio. Due to greater attraction of nuclear charge, the remaining electrons of ions are drawn closer to the nucleus.

Example:**Ionic radius of –ve ions are larger than the size of their parent atoms:**

When a neutral atom gains one or more electrons, it becomes a negative ion. The size of the ion is increased because of two reasons given below:-

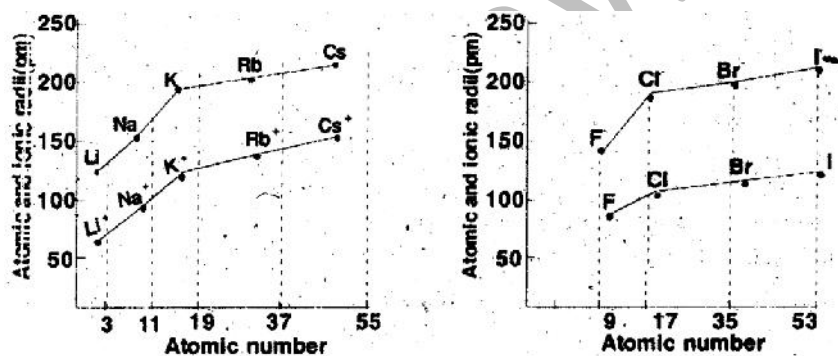
- Incoming electron is repelled by the valence electron. So in order to add this incoming electron, the expansion of the shell takes place which ultimately reduces the repulsion.
- Imbalance in electron and proton ratio occurs. As a result, the ionic radius of negative ion becomes greater than the size of its parent atom.

Example:

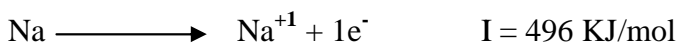
The radius of F-atom is 72 pm while that of Fluoride ion (F) is 136 pm

Periodic Trend:**(a) Across the Period:**

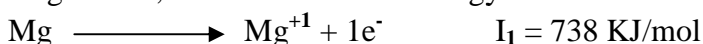
Within a period isoelectronic positive ions show decrease in ionic radius from left to right because of increasing nuclear charge. $\text{Na}^{+1} < \text{Mg}^{+2} < \text{Al}^{+3}$

**2. Ionization Energy:**

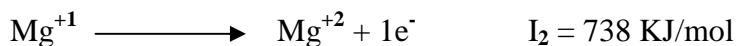
The minimum amount of energy which is required to remove an electron from the outermost shell of its isolated gaseous atom is called ionization energy.

Examples:

Elements with greater number of electrons have more than one values of ionization energy. So for magnesium, the first ionization energy value is the energy required to remove the first electron:



Similarly, the second ionization energy value is the energy required to remove the second electron:



Factors Effecting the Ionization Energy:

- **Atomic Size:** Atomic size $\propto 1/I.E$
- **Nuclear charge:** Nuclear charge $\propto I.E$
- **Shielding effect:** Shielding effect $\propto 1/I.E$
- Stable electronic configuration

Periodic Trend:

(a) Down the group:

The value of ionization energy decreases from top to bottom in a group due to:

- Addition of an extra shell successively in each period hence more number of electrons shields the nucleus.
- The nuclear charge increases but as the size of the atom and the number of electrons causing the shielding effect also increases therefore ionization energy decreases from top to bottom.

That is why in alkali metals, for example it is easier to remove an electron from caesium atom than from lithium atom.

Across the period:

The value of ionization energy increases from left to right in a period due to:

- Due to decrease in atomic radius nuclear charge increases, more strongly electrons are bound to the nucleus and hence higher the ionization energy of the atom.
- Nuclear charge increases effectively that makes removal of electron difficult and hence value of ionization energy increases.
- Shielding effect almost remains constant.

The figure also reveals that inert gases have the highest values of ionization energy because due to complete outermost shell in them, the removal of electron is extremely difficult.

3. Electron Affinity (E.A):

The energy released or absorbed, when an electron is added to a valence shell of isolated gaseous atom to form a negative ion is called electron affinity.



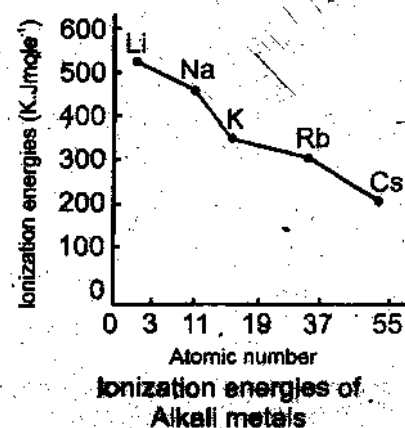
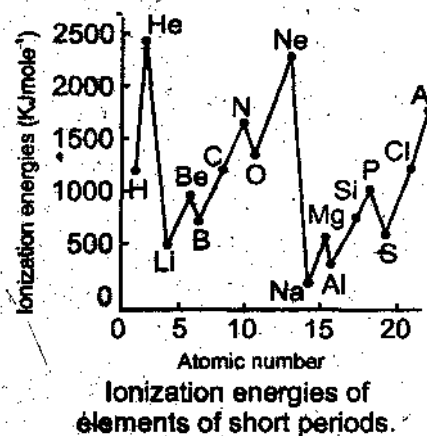
Factors Effecting the Electron Affinity:

Following are the factors which effect the electron affinity.

- **Atomic size:** Atomic size $\propto 1/E.A$
- **Nuclear charge:** Nuclear charge $\propto E.A$
- **Shielding effect:** Shielding effect $\propto 1/E.A$
- **Vacancies in the outermost shell:** Relatively smaller atoms with one or two vacancies in the outermost shell show large values of electron affinity.

Second value of electron affinity:

Usually the electronegative elements release energy when first electron is added into them. But when a second electron is added in a



uni-negative ion, the incoming electron is repelled by the already present - ve ion (charge). In order to overcome this repulsion, energy is absorbed during the process. Thus the formation of a di-negative ion is an endothermic process and its E.A. is shown with positive sign.



Periodic Trend:

(i) Across the Period:

Across the period electron affinity increases due to:

- Increase in atomic number.
- Decrease in atomic radius.
- Shielding effect almost remains same.

(ii) Down the group:

When move from top to bottom in the group, electron affinity decreases due to increase in atomic radius and shielding effect.

✦ Important Point:

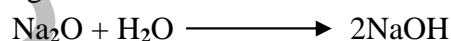
Knowledge of electron affinities can be combined with the knowledge of ionization energies to predict which atoms can easily lose electrons and which can accept electrons more readily.

4. Metallic and Non-metallic:

Elements in periodic table can be divided into metals, non-metals and metalloids.

Characteristics of Metals:

- Metals are good conductor of heat and electricity.
- They have tendency to form cation by losing electrons.
- They form basic oxides which give bases when dissolved in water.



Periodic Trend of Metallic Character:

The tendency of an element to lose electron and form a positive ion is called metallic character.

- **Down the group:**

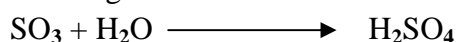
As it becomes easier to remove the electron of an atom bigger in size, therefore metallic character increase from top to bottom in a given group of elements.

- **Across the period:**

Metallic character decreases from left to right across a period. The elements of group VIIA (the halogens) are least metallic in nature.

Non-Metals Characteristics:

- Non metals are poor conductor of heat and electricity.
- They, have tendency to form negative ion (anion) by gaining electron.
- Non-metals form acidic oxides which yield acids when dissolved in water.
- All the gases are non metals.



Periodic Trend of Non-Metallic Character:

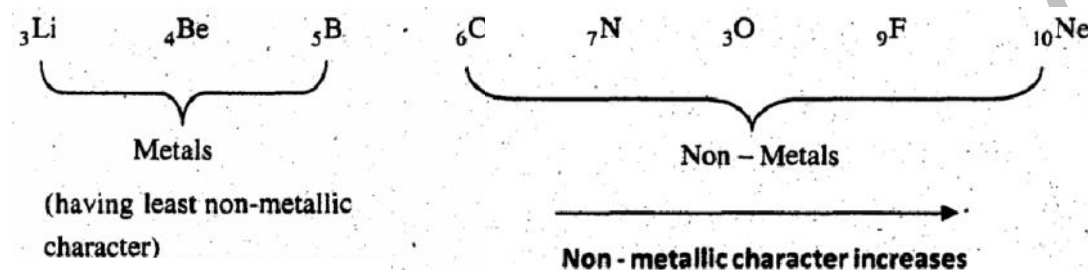
(i) Down the group:

- Non-metallic character of an element decreases as the atomic size increases. Therefore in a group of non-metals like halogens, the non-metallic character decreases from top to bottom. The member at the top, fluorine, is the most non-metallic element of the periodic table.
- In the elements of groups VA and VIA, nitrogen and oxygen are pure non-metals and usually exist in gaseous state while bismuth and polonium, the members at the bottom of these groups, are fairly metallic in nature.

(ii) Across the period:

Due to decrease in atomic size, gain of electron increases as a result non-metallic character increases.

2nd Period:



5. Melting and Boiling:

Melting and boiling points of elements tell us something about how strong the atoms or molecules in them are bound together.

✧ Variation in Melting and Boiling Points

Melting and boiling points of elements are the index for the strength of binding forces existing between atoms & molecules. As we move from left to right in a period up to group IVA, the number of binding electrons goes on increasing. As these elements form three dimensional lattices and greater energy is required to break their intramolecular molecular forces of attraction and have high melting and boiling points. In case of groups VA, VIA, VIIA and VIIIA elements exist as small, covalent molecules which have very weak inter molecular forces of attraction. So less energy is required to break them. Consequently their melting and boiling are extremely low.

Periodic Trend:

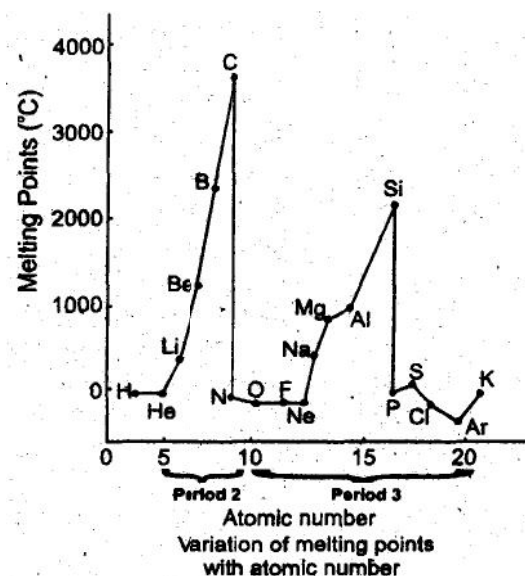
(a) Variation in Period:

- Across the short periods**, melting and boiling points of elements increase with the number of valence electron up to group IVA.
- The melting points** of group IA elements have low melting and boiling point because each atom in them provides only one electron to form a bond with other atom.
- Melting points** of group IIA elements are considerably higher than those of group IA elements because each atom in them provides two binding electrons.
- Carbon** has the maximum number of binding electrons, thus it has a very high melting point in diamond in which each carbon is bound to four other carbon atom. In general, the elements which exist as giant covalent structures have very high melting and boiling points.

- **Melting point of group IVA to VIIA:** When we move from group IVA to group V'A, VIA and VIIA as the lighter elements of these groups exist as small discrete covalent molecules, rather than as three dimensional lattices. **For instance**, nitrogen, oxygen, and fluorine exist as individual molecules which have very weak intermolecular forces and hence they have extremely low melting and boiling points.

(b) Variation in a Group:

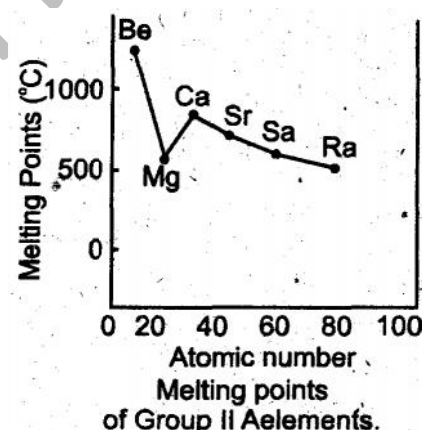
- **The melting and boiling points of IA and IIA group elements decrease from top to bottom** due to increase in their atomic sizes. The binding forces present between large sized atoms are relatively weaker as compared to those between smaller atoms.
- **Group VIIA elements** which exist in the form of molecules, the melting and boiling points increase down the group. This is because large molecule exerts stronger force of attraction due to their higher polarizabilities.



6. Oxidation State:

The Oxidation number of an atom in a compound is the charge (with the sign) which it would carry in the compound.

- **In ionic compounds** it equal to the number of electrons gained or lost by the atom. e.g. In sodium chloride oxidation state of Na is +1 and chlorine is -1 Na^{+1} , Cl^{-1} .
- **In covalent compounds** it decided on the basis of difference in their relative electronegativities. e.g. SnCl_4 is a covalent compound in which oxidation state of Sn is +4 and of Cl is -1.
- **In free state**, (Cl_2 , Br_2 , O_2 , H_2 etc.) oxidation state of elements is zero.



Periodic Trend:

(a) Across the Period:

Typical elements (Subgroup A):

The oxidation state of a typical element is directly or indirectly related to the group number to which the elements belong in the periodic table.

- The elements of IA to VIIA have the same oxidation states as their group numbers just as B, Al and Ga belong to group IIIA, hence, they always show oxidation state of +3. So, for the elements of these groups, the oxidation state is same as the number of electrons present in the valence shells of the elements.
- For the elements of group VA, the oxidation states are either the number of electrons present in the valence shell (which is same as their group number) or the number of vacancies available in these shells. For example, N, P, As and Sb frequently show +3 as well as +5 oxidation states.

- Elements of group VIA show almost similar behaviour. In H_2SO_4 , sulphur shows the oxidation state of +6, which is the number of electrons in its outermost shell whereas its oxidation state is -2 in H_2S , which is the number of electrons in its outermost shell.
- In group VIIA elements oxidation state is always -1, which is again the number of vacancies in their outermost shells.
- Group VIIIA elements, which are also called zero group elements, usually show zero oxidation state because there is no vacancy in their outermost shells.

Due to same outer most shell electronic configuration, the elements of same group have same oxidation state.

Transition Elements (Subgroup-B):

Transition elements, which are shown in B subgroups of the periodic table, also show the oxidation states equal to their group number as it can be seen for Cu (I), Zn (II), V (V), Cr (VI) and Mn (VII). But due to greater number of valence electrons available in partly filled d-orbital these elements usually showed more than one oxidation states in their compounds.

7. Electrical Conductance:

One of the most familiar properties of metals is their ability to conduct electricity. This property is mainly due to the presence of relatively loose electrons in the outermost shell of element and ease of their movement in solid lattice.

Periodic Trend:

- The electrical conductance of metals in groups IA and IIA, generally increases from top to bottom. However, the trend is not free from the individual variation in different atoms.
- Metals of group IB, which are known as coinage metals, have extraordinary high values of electrical conductance.
- Non metals especially of groups VIA and VIIA, show such low electrical conductance that they can be considered as nonconductors.
- In these series of transition metals, the values of electrical conductance vary so abruptly that no general trend can be assigned to them.
- Carbon, in the form of diamond is non-conductor because its valence electrons are tetrahedrally bound and unable to move freely, while in the form of graphite, carbon is a fairly good conductor because one of its four valence electrons is relatively free to move.
- The lower elements of group IVA tin and lead, are fairly good conductors and their values of electrical conductivity are comparable with those of their counterparts in group IA.

8. Hydration Energy:

The hydration energy is the heat absorbed or evolved when one mole of gaseous ions dissolve in water to give an infinitely dilute solution is called hydration energy. e.g.

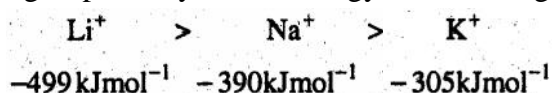


Factor:

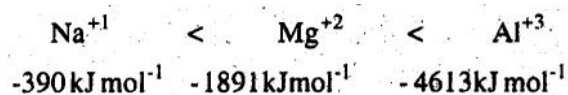
Hydration energy highly depends upon charge density (charge to size ratio) of the ions. Greater the charge density higher will be the hydration energy.

Periodic Trend:

- For a given set of ions, for example of group IA, charge to size ratio decreases from top to bottom in a group, the hydration energy increases significantly.



- On the contrary, the hydration energy increases significantly by moving from left to right in a period as the charge size ratio increases, as found in the metal ions of third period.



Periodic Relationship in Compounds:

Halides:

Binary compounds of halogens with other elements are called halides.

Classification of Halides:

The physical properties of halides are largely determined by the nature of bonding present in them. On the basis of nature of bonding, halide are of following types.

- Ionic halides.
- Polymeric halides.
- Covalent halides.

(i) Ionic halides:

Strongly electropositive elements (IA and hA groups except Be) having greater electronegativity difference with halogen atom, form ionic halides. The halides of group IA are considered purely ionic compounds.

Examples: NaCl, MgCl₂, CaCl₂, KBr etc.

Properties:

- They have high melting and boiling points.
- They have three dimensional lattices consisting of discrete ions.
- They exist in solid state.
- They are conductor of electricity in molten state or aqueous solution.

Variation with halogens:

Among the pure ionic compounds, the fluorides have the highest lattice energies due to the small size of fluoride ion. Thus for ionic halides, the fluorides have the highest melting and boiling points which decrease in the order.

Fluoride > Chloride > Bromide > Iodide

(ii) Polymeric halides:

In between the ionic or covalent halides, there is another class of halides called polymeric halides. In these halides, the halogen atom acts as a bridge between two atoms of other element. Less electropositive elements such as Be, Ga and Al form polymeric halides having partly ionic bonding with layer or chain lattices.

Examples: BeCl_2 , AlCl_3 , GaCl_3 etc.

Properties:

- Their properties are intermediate between the covalent and ionic halides.
- The lattice of SiCl_4 consists of discrete molecules which are highly polar the bonds in PCl_3 and S_2Cl_2 are less than those of SiCl_4

(iii) Covalent halides:

Least electropositive elements of IVA, VA, VIA groups, having less electronegativity difference with halogen atom, form covalent halides.

Examples: CCl_4 , NF_3 , PCl_3 , S_2Cl_2 etc.

Properties:

- The intermolecular forces in covalent halide molecules are weak van der Waal's forces.
- They often exist in gases, liquids or low melting point solids.
- They have low melting and boiling points.
- Non-conductor of electricity.

Variation with halogens:

Physical properties of covalent halides are influenced by the size and polarizability of the halogen atom iodides, as being the largest and more polarizable ions possess the strongest van der Waal's forces and therefore have higher melting and boiling points than those of other covalent halides.

Periodic Trend:

Across the period:

Ionic character of halides depends on the electronegativity difference between the halogen and the other atom.

Elements on the left side of the periodic table (Group I-A and 11-A elements) are highly electropositive. They have low ionization energy and thus possess the tendency to lose electron easily. They will form ionic bond with the halogens, which are in turn highly electronegative on the right side of periodic table. So, on moving from left to right along the period, elements become less electropositive. Thus, electronegativity difference reduces and the trend is shifted towards covalent halides. That's why NaCl is a pure ionic compound while PCl_3 is partly covalent in nature or Cl_2 is 100% covalent in nature.

Melting points of chlorides of Period Three Elements and their bonding character

Name of compound	Property	
	Melting point $^{\circ}\text{C}$	Type of bonding
NaCl	808	Ionic
MgCl_2	715	Partly ionic
AlCl_3	192	Partly ionic
SiCl_4	-88	Partially covalent
PCl_3	-93	Partially covalent
S_2Cl_2	-80	Partially covalent

Down the Group:

The variation in bonding character is also present in descending from top to bottom in the halogen group. In general, for a metal the order of decreasing ionic character of the halides is:

Fluoride > chloride > bromide > Iodide

Example:

For example, AlF_3 is purely ionic compound having melting point 1290°C and fairly a good conductor. Whereas, AlI_3 is predominantly covalent with melting point 198°C and electrically a non-conductor.

Variation due to Oxidation State:

In case of an element forming more than one, halides the metal halide in its lower oxidation state tends to be ionic while that in the higher oxidation state is covalent. **For example** PbCl_2 mainly ionic and PbCl_4 is fairly covalent. This can be explained by the higher polarizing power of Pb^{4+} as compare to that of Pb^{2+} .

$$\text{Charge density} \propto \frac{\text{charge}}{\text{size}} \propto \text{Polarizing Power} \propto \text{Polarization}$$

Hydrides:

The binary compounds of hydrogen with other elements are called hydrides.

Classification of Hydrides:

According to the nature of bonding, hydrides may be broadly classified into three classes.

- 1) Ionic hydrides
- 2) Intermediate hydrides
- 3) Covalent hydrides

(i) Ionic hydrides:

The elements of group IA and the heavier members of group IIA form ionic hydrides. They have ionic bond.

Examples: NaH , CaH_2 , KH etc.

Properties:

- Ionic hydrides contain H^- (Hydride) ion.
- These hydrides are crystalline solid compounds, with high melting and boiling points.
- These hydrides are conductor of electricity in molten state and aqueous solution.

(ii) Intermediate Hydrides:

The elements like Be, Mg, Zn, Cd and In, combine with hydrogen to form intermediate hydrides.

Examples: BeH_2 , MgH_2 , ZnH_2 etc.

Properties:

- Their properties are in between ionic and covalent hydrides.
- They have polymeric structures and covalent in nature.

Hydrides of the elements of IA to VIIB and IIB sub-groups:

IA	IIA	IIB	IIIA	IVA	VA	VIA	VIIA
LiH	BeH ₂		BH ₃	CH ₄	NH ₃	H ₂ O	HF
NaH	MgH ₂		AlH ₃	SiH ₄	PH ₃	H ₂ S	HCl
KH	CaH ₂	ZnH ₂	GaH ₃	GeH ₄	AsH ₃	H ₂ Se	HBr
RbH	SrH ₂	CdH ₂	InH ₃	SnH ₄	SbH ₃	H ₂ Te	HI
CsH	BaH ₂			PbH ₄	BiH ₃		
Ionic		Intermediate		Covalent			

(iii) Covalent Hydrides:

The elements having electronegativity more than 1.8 form covalent hydrides. These hydrides have covalent bond.

Examples: HCl, BH₃, CH₄, H₂O, NH₃ etc.

Properties:

- They are usually gases or volatile liquids.
- These hydrides are non-conductor of electricity.
- They are soluble in organic solvents.
- Their bond energies depend on the size and the electronegativity of the elements.
- Stability of covalent hydrides increases from left to right in a period and decreases from top to bottom in a group e.g Fluorine forms the most stable hydrides and the least stable hydrides are formed by thallium (Tl), lead (Pb) and bismuth (Bi).
- Since electronegativity of hydrogen is 2.1, most of these hydrides have polar covalent bonds in which hydrogen is carrying a slight positive charge. Due to high polarity, the hydrides like H₂O and NH₃ are capable of forming hydrogen bonds between their molecules.
- The boiling points of covalent hydrides generally increase on descending a group except the hydrides like H₂O, HF and NH₃ which, due to hydrogen bonding have higher boiling points than might be expected.

Melting and boiling points of Hydrides of Groups IVA and VIA

Hydrides (Group IVA)	Property	
	Melting point (°C)	Boiling point (°C)
CH ₄	-184	-164
SiH ₄	-185	-112
GeH ₄	-165	-90
SnH ₄	-150	-52
(Group VIA)		
H ₂ O	0.00	100
H ₂ S	-82.9	-59.6
H ₂ Se	-65.7	-41.3
H ₂ Te	-48	-1.8

Periodic Trend:

Across the period:

In ionic hydrides, the tendency towards covalent character increases by moving from left to right in the Periodic table. Stability of covalent hydrides increase from left to right in a period. On moving left to right across a period the electronegativity of the other element increases and the hydrogen element becomes more polar.

Down the Group:

Stability of the covalent hydrides decrease down the group. Boiling points of covalent hydrides are due to increase in London dispersion forces except H₂O, HF and NH₃ which have boiling points on the top of their groups.

Oxides:

The binary compounds of oxygen with other elements in the periodic table are called oxides. Since, many of these have quite unusual properties there is an extensive and varied chemistry of the compounds of oxygen.

Classification of Oxides:

Oxides can be classified in more than one ways

- 1) On the basis of nature of bonding.
- 2) On the basis of oxidation state of oxygen.
- 3) On the basis of acidic and basic character.

On the basis of oxidation state

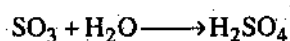
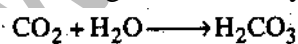
Oxides	Oxidation state of oxygen	Example
Normal oxides	-2	Li ₂ O, MgO, ZnO, Al ₂ O ₃ , Cl ₂ O ₇
Peroxides	-1	H ₂ O ₂ , Na ₂ O ₂
Super oxides	-1/2	KO ₂ , RbO ₂ , CsO ₂ etc.
Sub oxides	+2, +4	C ₃ O ₂ (highly unstable)

1) On the basis of acidic or basic behavior:

There are three types of oxides

(i) Acidic oxides:

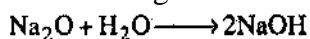
- Non-metals like C, N, O, P etc. form acidic oxides
- On adding in water, they give, acidic solutions.



Examples: CO₂, P₄O₁₀, SO₃, Cl₂O₇ etc.

(ii) Basic Oxides:

- Metals of IA & IIA groups (except Be) form basic oxides.
- On adding in water they give basic solutions.



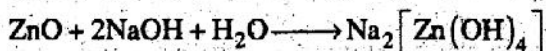
The O^{2-} ion has great affinity for proton (H^+) and cannot exist alone in an aqueous solution. Therefore, it immediately takes proton (H^+) from water and forms OH^- ion. In this way the concentration of OH^- increases and solution become basic.

Example: Li_2O , MgO , CaO etc.

iii) Amphoteric Oxides:

The less electropositive elements (Be, Al, Zn, Ga, In) form amphoteric oxides. They behave as bases when react. It strong acids and behave as acids with strong bases.

Example: BeO , Al_2O_3 , ZnO , Bi_2O_3 etc.



Classification of Oxides based on their Acid and Base Character

IA	IIA	IIB	IIIA	IVA	VA	VIA	VIIA
Li	Be		B	C	N	O	F
Na	Mg		Al	Si	P	S	Cl
K	Ca	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Cd	In	Sn	Sb	Te	I
Cs	Ba	Hg	Pb	Pb	Bi	Po	At
Basic Oxides		Amphoteric oxides		Covalent oxides			

Periodic Trend:

Across the period:

In a given period the oxides progress from strongly basic through weakly basic, amphoteric and weakly acidic to strongly acidic.

Exampmles: Na_2O , MgO , Al_2O_3 , SiO_2 , P_4O_{10} , SO_3 , Cl_2O_7
 strongly basic basic amphoteric weakly acidic acidic strongly acidic

Down the Group:

The basicity of main group metal oxides increases on decreasing a group of the periodic table.

Examples: $BeO < MgO < SrO < BaO$

The basicity of traisition metal oxides (Sub group B) decrease from top to-bottom

Variation due to Oxidation State:

The oxidation state of the metal also affects the acid / base character of its oides. The acidity increases with increasing oxidation state e.g. the acidity of $MnO < Mn_2O_3 < MnO_2 < Mn_2O_7$

✧ The Position of Hydrigen:

Position of an element in periodic table depends upon its electronic configuration and properties. Hydrogen is resembles the elements of group I-A, II-A and VII-A in some respects. Properties of hydrogen do not completely match any one of the above mentioned groups. That is why position of hydrogen is still undecided.

Hydrogen and IA group (Alkali Metals):**Similarities:**

- Hydrogen and alkali metals have one electron in their valence “s” sub-shell, (ns^1).
- Valence shell electronic configuration of hydrogen and alkali metal is same.
- Both hydrogen and alkali metals by losing their valence electron, form uni-positive ion.

$$\text{H} \longrightarrow \text{H}^+ + 1\text{e}^-$$

$$\text{M} \longrightarrow \text{M}^+ + 1\text{e}^-$$
- Both hydrogen and alkali metals have a strong tendency to combine with electronegative elements such as halogens.
- Both form ionic compounds which dissociate in water (ionize in water).
- Both hydrogen and alkali metals are good reducing agents.

Dissimilarities:

IA Group	Hydrogen
1. The elements of IA group are metals.	1. It is a non-metal.
2. Alkali metals are solid at room temperature.	2. Hydrogen is a gas at room temperature.
3. Due to low I.E they lose electron easily.	3. Hydrogen does not lose electron as easily as most of the alkali metals.
4. They do not gain electron.	4. It gains electron.
5. They do not exist, in the molecular form	5. Hydrogen exists as H_2 (molecular form) in open atmosphere.
6. Na^+ and K^+ are stable in Water.	6. H^+ is unstable in water and forms H_3O^+ ion.

Hydrogen and VIIA group (Halogens):**Similarities:**

- Both hydrogen and halogens gain one electron to complete their valence shell. In this way both form uni-negative ions.

$$\text{H} + 1\text{e}^- \longrightarrow \text{H}^-$$

$$\text{X} + 1\text{e}^- \longrightarrow \text{X}^-$$
- Both hydrogen and halogens are non-metals in true sense.
- Both exist as molecular form in open atmosphere. (H_2 , F_2 , Cl_2 , Br_2).
- Hydrogen is the gas like that of most halogens (F, Cl).
- Both hydrogen and halogens form ionic compound with alkali metals.

$$\text{H}_2 + 2\text{Na} \longrightarrow 2\text{NaH}$$

$$\text{Cl}_2 + 2\text{Na} \longrightarrow 2\text{NaCl}$$

Dissimilarities:

VIIA Group (Halogens)	Hydrogen
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1. Halogens have seven electrons in their valence shells.	1. Hydrogen has one electron in its valence shell.
2. They cannot lose electrons.	3. It loses its valence electron to form hydrogen ion. $\text{H} \longrightarrow \text{H}^+ + 1\text{e}^-$
3. They belong to p-block.	4. It is a s-block element.
4. They cannot form stable oxides.	5. It combines with oxygen to form stable oxides.
5. Br is a liquid while Iodine is solid at room temp.	6. It is a gas at room temperature.

Hydrogen and IVA group (Carbon family):

Similarities:

- Hydrogen has half-filled outermost shell like that of elements IVA group.
- Both hydrogen and elements of IVA group combine with other elements through covalent bonding.
- Like carbon, hydrogen also shows remarkable reducing property.

$$\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O}$$

$$\text{SnO}_2 + \text{C} \longrightarrow \text{Sn} + \text{CO}_2$$
- Ionization energy and electron affinity of hydrogen and carbon are comparable.
- Electronegativity of hydrogen and carbon family is almost similar. (H = 2.1, C = 2.5, Si = 2.4).

Dissimilarities:

IVA Group (Carbon Family)	Hydrogen
1. The elements of IVA group belong to p-block.	1. Hydrogen belongs to s-block.
2. IVA group elements are solid at room temperature.	3. It is gas at room temperature.
4. Elements of IVA group need 4 electrons to complete their valence shell.	5. It needs one electron to complete its valence shell.
4. Carbon and Si form long chain compounds when they combine with their atoms. (Catenation).	6. It does not form long chain compounds.
5. Carbon can simultaneously form bonds with more than one elements.	7. Due to one electron in the valence shell, hydrogen can combine with only one element at a time.

Conclusion:

Some of the properties of hydrogen are similar to those of the elements of IA, IVA and VIIA groups. But this is an act that hydrogen is a unique element whose properties do not match exactly with any of the groups in the periodic table. However due to partial resemblance in properties with alkali metals and monovalent nature, hydrogen is usually placed at the top of the elements in group IA.