

Chapter 5 - Periodic Classification of Elements

Introduction

Initially scientists had classified elements into metal and non-metals. However, some elements possessed properties which could neither be classified as metals nor non-metals called metalloids. This classification was found to be insufficient for scientific study. Later on, a number of chemists attempted to make a rational and systematic classification of the physical and chemical properties of elements and tabulate the results in the form of a table.

Periodic table – The table giving the arrangement of the known elements according to their properties so that similar elements fall within the same vertical column and dissimilar elements are separated.

Dobereiner's Triads

In the year 1829, Johann Wolfgang Dobereiner, a German scientist, was the first to classify elements into groups based on John Dalton's assertions. He grouped the elements with similar chemical properties into clusters of three called 'Triads'. The distinctive feature of a triad was the atomic mass of the middle element. When elements were arranged in order of their increasing atomic mass, the atomic mass of the middle element was approximately the arithmetic mean of the other two elements of the triad.

Examples of Dobereiner's Triads

Element	Lithium	Beryllium	Potassium	Arithmetic mean
Atomic mass	7.0	9.0	11.0	9.0
Element	Lithium	Beryllium	Boron	Arithmetic mean
Atomic mass	7.0	9.0	11.0	9.0
Element	Lithium	Sodium	Potassium	Arithmetic mean
Atomic mass	7.0	23.0	39.0	23.0
Element	Carbon	Nitrogen	Oxygen	Arithmetic mean
Atomic mass	12.0	14.0	16.0	14.0
Element	Calcium	Strontium	Barium	Arithmetic mean
Atomic mass	40.0	87.5	137	88.1
Element	Chlorine	Bromine	Iodine	Arithmetic mean
Atomic mass	35.0	80.0	127.0	80.6

Defects of Triad Classification

- A large number of similar elements could not be grouped into triads e.g., iron, manganese, nickel, cobalt, zinc and copper are similar elements but could not be placed in the triads.
- It was possible that quite dissimilar elements could be grouped into triads.
- Dobereiner could only classify 3 triads successfully (highlighted in the table).

Since he failed to arrange the then known elements in the form of triads his attempt at classification was not very successful.

Newlands' Law of Octaves

Newland arranged many of the known elements in the increasing order of their atomic masses. He started with the element having the lowest atomic mass (hydrogen) and ended at thorium which was the 56th element.

He arranged many of the known elements in the increasing order of their atomic masses. It was noticed that the eighth element was similar in properties to the first element, just like the eighth note in music - Western as well as Indian.

Western	Indian	
Re	Re	Beryllium, Magnesium, Calcium
Do	Sa	Lithium, Sodium, Potassium
Me	Ga	Boron, Aluminium
Fa	Ma	Carbon, Silicon
So	Pa	Nitrogen, Phosphorus
La	Da	Oxygen, Sulphur
Ti	Ni	Fluorine, Chlorine
Do	Sa	- -

Groups of the 8th elements

The eighth element after lithium is sodium. In many of its chemical properties it is similar to lithium. Similarly, the eighth element after sodium is potassium, whose properties are similar to sodium. The eighth element from fluorine is chlorine both of which are similar in their properties. The eighth element from nitrogen is phosphorus and both these elements are similar in properties.

Based on this observation, Newland stated his law of octaves thus 'when elements are arranged in increasing order of their atomic mass, the eighth element resembles the first in physical and chemical properties just like the eighth note on a musical scale resembles the first note'. As a result a very important conclusion was made that there is some systematic relationship between the order of atomic masses and the repetition of properties of elements. This gave rise to a new term called 'periodicity' which signifies the recurrence of characteristic properties of elements arranged in a table, at regular intervals of a period.

Achievements of the Law of Octaves

- The law of octaves was the first logical attempt to classify elements on the basis of atomic weights.
- Periodicity of elements was recognized for the first time.

In 1860, there was a conference of chemists in Karl Sruhe, Germany. A young Russian chemist, Dmitri Mendeleev, attending this conference, was deeply influenced by a thesis presented by Stanislao Cannizzaro, which described Cannizzaro's method of determining atomic mass of elements. Mendeleev then started working on this aspect of atomic mass and periodicity. He later on stated the law of chemical periodicity.

Defects of Law of Octaves

- This law could be best applied, only up to the element calcium.
- Newly discovered elements could not fit into the octave structure.
- The feature of resemblance of the 8th element when arranged in increasing order of their atomic mass was not successful with heavier elements.

Lothar Meyer's Curves: In 1870, the German chemist plotted the atomic volumes of the elements against their atomic masses. From this graph he was able to produce a table showing periodic arrangement of elements.

Mendeleev's Periodic Table

In 1869, Mendeleev classified the then known 56 elements on the basis of their physical and chemical properties in the increasing order of the atomic masses, in the form of a table. Mendeleev had observed that properties of the elements orderly recur in a cyclic fashion. He found that the elements with similar properties recur at regular intervals when the elements are arranged in the order of their increasing atomic masses. He concluded that 'the physical and chemical properties of the elements are periodic functions of their atomic masses'. This came to be known as the law of chemical periodicity and stated: that the physical and chemical properties of elements are periodic function of their atomic weights.

Based on this law all the known elements were arranged in the form of a table called the 'Periodic Table'. Elements with similar properties recurred at regular intervals and fell in certain groups or families. The elements in each group were similar to each other in many properties. The elements with dissimilar properties from one another were separated. Mendeleev's periodic table contains eight vertical columns of elements called 'groups' and seven horizontal rows called 'periods'. Each group has two sub-groups A and B. The properties of elements of a sub-group resemble each other more markedly than the properties of those between the elements of the two sub-groups.

Achievements of Mendeleev's Periodic Table

Mendeleev's periodic table was one of the greatest achievements in chemistry with some of its important contributions as follows:

Systematic Study of Elements

Mendeleev's Periodic table simplified the study of elements. As the arrangements of elements showing similar properties were classified into groups, it was very useful in studying and remembering the properties of a large number of elements in a systematic way.

Prediction of New Elements

Based on the positions in the periodic table, Mendeleev could predict the properties of some undiscovered elements. He left three blanks for elements that were not discovered at that time. He was able to predict the properties of these unknown elements more or less accurately. He named them eka-boron, eka-aluminium and eka-silicon. He named them so, as they were just below boron, aluminium and silicon in the respective sub-groups. Eka-boron was later named as scandium, eka-aluminium as gallium and eka-silicon as germanium. A Comparative Study of the Properties of Elements Predicted and later Discovered

Property	Eka-boron	Scandium
Atomic weight	44	43.79
Oxide	Eb_2O_3	Sc_2O_3
Specific gravity	3.5	3.864
Sulphate	$\text{Eb}_2(\text{SO}_4)_3$	$\text{Sc}_2(\text{SO}_4)_3$
Property	Eka-aluminium	Gallium
Atomic weight	68	69.9
Specific gravity	5.9	5.94
Melting point	Low	303.15°K
Formula of oxide	Ea_2O_3	Ga_2O_3
Solubility in acid and alkali	Dissolves slowly in both acid and alkali	Dissolves slowly in both acid and alkali

Correction of Atomic Masses

Mendeleev's periodic table helped in correcting the atomic masses of some of the elements, based on their positions in the periodic table. For example, atomic mass of beryllium was corrected from 13.5 to 9.0. Atomic masses of indium, gold and platinum were also corrected.

Limitations of Mendeleev's Classification

Position of Hydrogen

The position of hydrogen was not correctly defined. It was placed in Group I although its properties resembled both the Group I elements (the alkali metals) and the group VII elements (the halogens).

Grouping of Some Elements

In some cases Mendeleev placed elements according to their similarities in properties and not in increasing order of their atomic masses, while some dissimilar elements were grouped together. Thus, the position of these elements was not justified. For example, cobalt (at. mass 58.9) was placed before nickel (at. mass 58.6); copper and mercury are similar in their properties but were placed separately. Copper was placed in group I although it did not resemble the elements of this group.

Anomalous Pair

In certain pairs of elements like, Ar (40) and K (39); Co (58.9) and Ni (58.6); Te (127.6) and I (126.9) the arrangement was not justified. For example, argon was placed before potassium whereas its atomic mass is more than potassium.

Isotopes

Isotopes are atoms of the same element having different atomic mass but same atomic number. For e.g., there are three isotopes of hydrogen with atomic mass 1, 2, and 3. According to Mendeleev's periodic table these should be placed at three separate places. However isotopes have not been given separate places in the periodic table.

Lanthanides and Actinides

Fourteen elements that follow lanthanum called lanthanides and fourteen elements following actinium called actinides were not given proper places in Mendeleev's periodic table.

Long Form of the Periodic Table or Modern Periodic Table

Modern Periodic Law

The modern periodic law states that "the physical and chemical properties of the elements are periodic function of their atomic numbers". Thus, when the elements were arranged in the order of their increasing atomic numbers, the elements of similar properties recur at regular intervals.

Cause of Periodicity of Elements

The modern periodic table is based on the electronic configuration of the elements. The properties of an element are determined largely by the electrons in its outermost or valence shell. Valence electrons interact with other atoms and take part in all chemical reactions, while inner shell electrons have little influence on the properties of elements. When elements are placed in the order of their increasing atomic number, the elements having the same number of valence shell electrons is repeated in such a way, so as to fall under the same group. Since, the electronic configuration of the valence shell electrons is same they show similar properties. Members of the same group have similar electronic configuration of the valence shell and thus show same valency.

Magic Numbers – When the elements are arranged in the order of increasing atomic number, it is observed that the elements with similar properties recur after intervals of either 2 or 8 or 18 or 32 elements. These numbers(2,8,18,32) are called magic numbers.

The Modern Periodic Table

It is based on modern periodic law.

Structural Features of the Modern Periodic Table

This table consists of horizontal rows called as 'periods' and vertical columns called as 'groups'.

Periods

There are seven periods in the periodic table and each period starts with a different principal quantum number.

The first period corresponding to ' n ' = 1 consists of only two elements hydrogen and helium .This is because the first energy shell can accommodate only two electrons.

In the second period corresponding to ' n ' = 2, with a capacity of eight electrons and so contains eight elements. This period starts with lithium ($Z = 3$) ends with neon ($Z = 10$) where the second shell is complete.

In the third period corresponding to ' n ' = 3, contains eight elements. It starts with sodium ($Z = 11$) and ends with argon ($Z = 18$) where the third shell is partially complete.

The fourth period corresponding to ' n ' = 4, consists of eighteen elements in this period starting from potassium ($Z = 19$) to krypton ($Z = 36$) where the third shell gets completed.

In the fifth period there are 18 elements like the fourth period. It begins with rubidium ($Z = 37$) and ends with xenon ($Z = 54$).

The sixth period contains 32 elements ($Z=55$ to 86) .It starts with caesium and ends with radon.

The seventh period, though expected to have 32 elements is incomplete and contains only 19 elements at present.

The first three periods are called short periods while the other three periods are called long periods.

Groups

The vertical column in the periodic table is called as group. There are 18 groups in the long form of the periodic table and they are numbered from 1 to 18 in the IUPAC system. In the old system of naming they are numbered as I to VIII with A and B groups. This convention is followed in many places.

The number of elements present in each period is given in the following table.

Period	Valence shell	Type of period	No of elements	Atomic No of the elements
1 st Period	n = 1	Short period	2	Atomic number 1 and 2
2 nd Period	n = 2	Short period	8	Atomic number 3 to 10
3 rd Period	n = 3	Long period	8	Atomic number 11 to 18
4 th Period	n = 4	Long period	18	Atomic number 19 to 36
5 th Period	n = 5	Long period	18	Atomic number 37 to 54
6 th Period	n = 6	Long period	32	Atomic number 55 to 86
7 th Period	n = 7	Incomplete	23	Atomic number 87 to 109

The number of elements in these periods is based on the way electrons are filled into various shells. The maximum number of electrons that can be accommodated in a shell depends on the formula $2n^2$ where 'n' is the number of the given shell from the nucleus.

For example,

K Shell - $2 \times (1)^2 = 2$, 1st period = 2 elements.

L Shell - $2 \times (2)^2 = 8$, 2nd period = 8 elements.

M Shell - $2 \times (3)^2 = 18$, but the outermost shell can have only 8 electrons, so the third period also has only 8 elements.

The position of an element in the Periodic table tells us about its chemical reactivity.

Position of Elements in the Modern Periodic Table

Types of Elements

On the basis of electronic configuration, the elements of the periodic table are classified into:

- Noble gases
- Normal elements
- Transition elements
- Inner-transition elements
- Alkali metals
- Halogens

Noble Gases

Noble gases are also known as inert gases and do not take part in chemical reactions. They have their outermost shell complete and thus remain stable. They do not generally combine with other substances, nor are they affected by oxidising agents or by reducing agents. They are placed in the 18 or VIIIA group. Since, the outermost shell is complete, the valency is zero, hence VIIIA group is also referred to as zero group.

Normal Elements

In the case of these elements, all shells except the outermost shell are completely filled. Elements belonging to 1 (IA), 2 (IIA), 3 (IIIA), 4 (IVA), 5 (VA), 6 (VIA) and 7 (VIIA) are normal elements. Elements of the second period are known as typical elements [Li ($Z = 3$) to Ne ($Z = 10$)] because each element is placed in a group whose number matches with the number of valence electrons. The elements of the IIIrd period are representative elements [Na ($Z = 11$) to Ar ($Z = 18$)] as each of them is a representative of its group. Groups 1 (IA) and 2 (IIA) are strongly metallic and are called group of 'alkali metals and alkaline earth metals', while group 7 (VIIA) are halogens.

Alkali Metals

Elements of group I A of the periodic table constitute a family of very reactive metals called alkali metals. They are lithium, sodium, potassium, rubidium, caesium and francium. All of them have one electron in the valence shell. They are called alkali metals because their hydroxides are strong alkalis. These metals are soft, light and easily fusible. In fact, sodium and potassium are lighter than water. At room temperature they readily get oxidised in air and so are preserved under kerosene in the laboratory.

Lithium	3	2, 1	+1	Li_2O	LiOH
Sodium	11	1, 8, 1	+1	Na_2O	NaOH
Potassium	19	2, 8, 8, 1	+1	K_2O	KOH
Rubidium	37	2, 8, 18, 8, 1	+1	Rb_2O	RbOH
Caesium	55	2, 8, 18, 18, 8, 1	+1	Cs_2O	CsOH
Francium	87	2, 8, 18, 32, 18, 8, 1	+1	-	-

Halogens

The elements placed in group 7 (VIIA) of the periodic table are called halogens or salt producers. All these elements form salts called halides, e.g. NaCl , NaI , KCl , KI etc. Halogen is an ancient Greek word meaning 'salt producer'. Halogens have seven electrons in their valence shell and so are monovalent.

Fluorine	9	2, 7	-1	Greenish but more yellow
Chlorine	17	2, 8, 7	-1	Greenish yellow Liquid
Bromine	35	2, 8, 18, 7	-1	Dark red liquid
Iodine	53	2, 8, 18, 18, 7	-1	Solid Dark purple
Astatine	85	2, 8, 18, 32, 18, 7	-1	- -

Bromine is the only Liquid non-metal. Iodine when heated undergoes sublimation.

Transition Elements

All the elements belonging to 3 to 12 groups are called transition elements. They resemble each other in several physical and chemical properties. They are all metals. They are called transition elements because they are placed between the most reactive metals on the left and non-metals on the right. Their compounds are coloured. They exhibit variable valency.

Inner-transition Elements

The 6th period consists of elements that have atomic numbers 58 to 71. They are called Lanthanides. The 7th period consists of elements that have atomic numbers 90 to 105. They are called Actinides. Both of them are called inner transition elements. Lanthanides and actinides are not accommodated in the main body of the periodic table but are placed in separate rows in form of two series at the bottom of the modern periodic table. The 7th period is an incomplete period as it has only 23 elements.

Position of an Element

In a period, the number of valence shell remains the same for all elements. However, the number of electrons in the valence shell increases from left to right.

The position of an element in the periodic table is determined by its electronic configuration e.g. electronic configuration of sodium is 2, 8, 1 i.e., it has three shells and one electron in the outermost shell. Hence, it is placed in period number 3 and group number 1. However, in the case of transition elements this pattern is not followed.

Merits of the Long Form of the Periodic Table

- This classification is based on the most fundamental property of the
- Elements - the atomic number, so it is more accurate.
- With the atomic number as the basis of this classification, the position of isotopes in one place is justified.
- The electronic configuration determines the properties of the elements. The position of elements governed by this feature is useful in studying the properties of elements.
- The position of the elements, which were misfit on the basis of atomic mass is now justified on the basis of atomic number.
- The lanthanides and actinides have been placed separately due to their properties being different from other groups.
- The whole table is easy to remember and reproduce in terms of electronic configuration and properties of the elements.

Demerits of the Long Form of the Periodic Table

Although the long form of the period table has been able to help in systematic studying the elements to a great extent, it has some minor defects:

- Hydrogen resembles both the alkali metals and halogens. But it has been placed with the alkalis and with the halogens.
- The lanthanides and actinides have not been placed in the main body of the table.

Periodic Properties

1. Valency

Valency is the combining capacity of an element. For metals it is the number of electrons lost during chemical combination while for nonmetals it is the number of electrons gained during chemical combination.

When metals combine with hydrogen, they show a valency corresponding to group number, & nonmetals show a valency equal to (8 – group number).

Thus, valency of an element with respect to hydrogen increases from 1 to 4 and then falls from 4 to 1 across a period.

All elements when combining with oxygen can show a valency corresponding to group number. For example, phosphorus forms phosphorus pentoxide (P_2O_5), where the valency of P is 5 & corresponds to its group number (V A). While combining with hydrogen, phosphorus forms phosphine (PH_3) where it shows a valency of 3 (8- group number)

Thus, valency of an element with respect to oxygen increases from 1 to 7 along a period.

2. Atomic Volume

It is defined as the volume occupied by one mole atoms of the element at its melting point, in solid state.

Variation along the Group – increases on moving down the group.

Variation along the period – decreases along the period, reaches a minimum in the middle and then starts increasing. Alkali metals have maximum atomic volume in a period.

3. Atomic Size and Atomic Radius

Atomic Radius – The distance between the centre of the nucleus and the outermost shell of an isolated atom.

Covalent radius of an element – half the internuclear distance between the two atoms of the element held by a single covalent bond.

Metallic radius of an element – half the internuclear distance between the two nearest metal atoms in a metallic crystal.

Atomic radii increases down the group and increases across the period.

4. Ionisation Energy

The minimum energy needed to remove the outermost electron from the neutral atom in the gaseous state.

It increases across a period in general and decreases down the group.

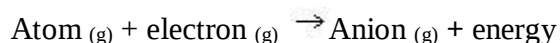
Factors affecting ionization Energy

1. Size of the atom
2. Magnitude of Nuclear Charge
3. Screening Effect of the inner electrons
4. Electronic Configuration

Electron Affinity

Electron affinity is the amount of energy released when an electron is added to an isolated gaseous atom.

Element	Electron affinity
Fluorine	3.62eV
Chlorine	3.79eV
Bromine	3.56eV
Iodine	3.28eV



Electron affinity is the ability of an atom to hold an additional electron. If the atom has more tendency to accept an electron then the energy released will be large and consequently the electron affinity will be high. Electron affinities can be positive or negative. It is taken as positive when an electron is added to an atom. It is expressed as electron volts per atom (eV per atom) or kilo joules per mole.

Electron affinity depends on:

- Extent of nuclear charge
- Size of the atom
- Electronic configuration

As a result of the gain in electrons, the atom gains one negative charge. In the case of halogens, all the elements have a high electron affinity, as they need one electron to complete the octet of their outermost shell.

Electron Affinity of the Halogens

From chlorine to iodine, which ionize by accepting one electron there is a decrease in the electron affinity or the energy released. The lower electron affinity of fluorine when compared to chlorine is not fully understood.

If the electron affinity is low, the electron is weakly bound; if the electron affinity is high, the electron is strongly bonded, e.g., electron affinity of chlorine is 3.79 which is higher than that of iodine i.e., 3.28. Hence, chlorine accepts the electrons more easily than iodine.

- Electron affinity increases from left to right across the period because of increase in nuclear charge and decrease in atomic size. This causes the incoming electron to experience a greater pull of the nucleus thus giving a higher electron affinity.
- Electron affinity decreases down the group because the number of shells increases i.e., the atomic size increases and the effective nuclear charge decreases. This causes the incoming electron not to experience much attraction of the nucleus thus giving a lower electron affinity.
- The electron affinity of completely filled atoms is almost zero. An atom does not accept an electron in its outermost shell if it already has a stable configuration i.e. a duplet or octet, as in the case of inert gases.

Electronegativity

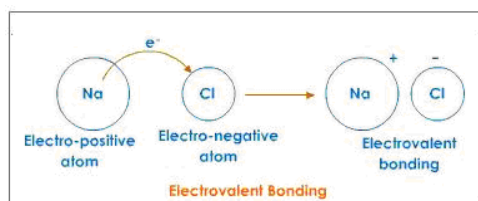
Electronegativity is the tendency of an atom to attract electrons towards itself in a molecule of a compound. The value of electronegativity of an element describes the ability of its atom to compete for electrons with the other atom to which it is bonded. Electronegativity is however not the property of an isolated atom.

Electronegativity increases from left to right in each period ending at group 17.

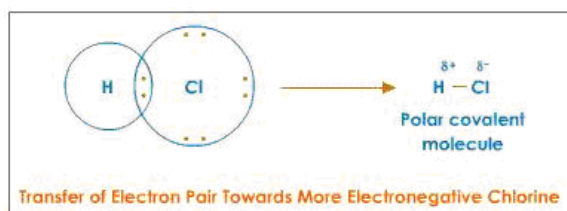
In the 3rd period, electronegativity increases from sodium to chlorine i.e., chlorine can accept electrons most easily in that period followed backwards by sulphur, phosphorus, silicon, aluminium, magnesium and sodium. All the atoms of the above mentioned elements have three shells but chlorine has the smallest atomic radii. Hence chlorine experiences more positive charge from the nucleus than all other atoms in that period. So, if one electron is available, chlorine can attract it most easily.

Types of Electronegativity

When the molecule is formed by transfer of electrons (ionic bonding) the transfer takes place from electropositive atom to electronegative atom. In the example below, Na is electropositive and Cl is electronegative.

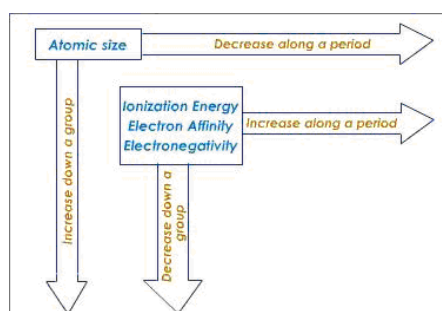


If the molecule is formed by sharing of electrons (covalent bond) the bonded pair of electrons shifts towards more electronegative atom resulting in the formation of polar molecule. In the example below, chlorine atom is more electronegative as compared to hydrogen atom, resulting in a covalent bond where the shared pair of electron shifts towards the more electronegative atom. This results in polar molecules.



The electron pair is closer to the chlorine atom and so the molecule gets polarized i.e., the chlorine atom gets a negative charge while the hydrogen atom gets a positive charge.

A summary of periodic properties and their variation in groups and periods is given below:



Metallic and Non-metallic Character

The tendency of an element to lose electrons and form positive ions (cations) is called electropositive or metallic character. For example, alkali metals are the most electropositive elements.

"The tendency of an element to accept electrons to form an anion is called its non-metallic or electronegative character." For example, chlorine, oxygen and phosphorous show greater electronegative or non-metallic character.

In each period, metallic character of elements decreases as we move to the right. Elements to the left of the periodic table have a pronounced metallic character while those to the right have a non-metallic character. Conversely, non-metallic character increases from left to right.

In the third period, sodium on the extreme left is most metallic. The metallic character decreases towards magnesium and aluminium, which are to the right. Silicon is midway between metals and non-metals. From phosphorus to sulphur to chlorine, non-metallic character gradually increases, chlorine being the most non-metallic in behaviour. In the 18 or zero group, argon does not exhibit either metallic or non-metallic character.

The elements to the left of the periodic table have a tendency of losing electrons easily as compared to those to the right. As we move from left to right of the period, the electrons of the outer shell experience greater pull of the nucleus. This greater force of attraction is because the nuclear charge increases and the size of the atom decreases from left to right. Thus, electrons of the elements to the right of the table do not lose electrons easily so are non-metallic in nature.

Metals usually have 1, 2 or 3 electrons in the outermost shell and ionize by giving out these electrons. Thus they gain positive charges equal to the number of electrons lost. Germanium, tin and lead with four electrons each in the valence shell are also included among the metals.

Non-metals usually have 5, 6 or 7 electrons in the outermost shell and ionize by accepting electrons. Thus they gain a negative charge equal to the number of electrons gained. Although carbon and silicon have four electrons each in the valence shell, they are included in the non-metals. Boron is an exception; it has three electrons in the outermost shell but is still included among non-metals.

As we move down the group the number of shells increases. This causes the effective nuclear charge to decrease due to the outer shells being further away: in effect the atomic size increases. The electrons of the outermost shell experience less nuclear attraction and so can lose electrons easily thus showing increased metallic character.