1. Details of Module and its structure

Module Detail							
Subject Name	Chemistry						
Course Name	Chemistry 01 (Class XI, Semester 01)						
Module Name/Title	Structure of Atom: Part 5						
Module Id	kech_10205						
Pre-requisites Knowledge of Orbitals, quantum number, atomic number, d, f notation							
Objectives	 After going through this module you will be able to: Describe the energies of orbitals Understand Pauli's exclusion principle and Hund's rule of maximum multiplicity Write the electronic configuration of different atoms Discuss the stability of completely filled and half filled orbitals 						
Keywords	Electronic Configuration, Aufbau Principle, Pauli's Exclusion Principle, Hund's Rule of Maximum Multiplicity, Degenerate, Effective Nuclear Charge						

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1.0 INTRODUCTION

In the previous module you have studied about the quantum numbers, their significance and the shapes of different orbitals. Now we shall learn about the energies of orbitals and the rules according to which electrons are filled in these orbitals.

2.0 ENERGIES OF ORBITALS

The energy of an electron in a hydrogen atom is determined solely by the principal quantum number. Thus the energy of the orbitals increases as follows:

This is depicted in Fig. 1. Although the shapes of 2s and 2p orbitals are different, an electron has the same energy when it is in the 2s orbital as when it is present in 2p orbital. The orbitals having the same energy are called **degenerate**. The 1s orbital in a hydrogen atom, as said earlier, corresponds to the most stable condition and is called the **ground state** and an electron residing in this orbital is most strongly held by the nucleus. An electron in the 2s, 2p or higher orbitals in a hydrogen atom is in **excited state**.



Fig. 1 Energy level diagrams for the few electronic shells of (a) hydrogen atom and (b) multi-electronic atoms. Note that orbitals for the same value of principal quantum number, have the same energies even for different azimuthal quantum number for hydrogen atom. In case of multi-electron atoms, orbitals with same principal quantum number possess different energies for different azimuthal quantum numbers.

The energy of an electron in a multi-electron atom, unlike that of the hydrogen atom, depends not only on its principal quantum number (shell), but also on its azimuthal quantum number (subshell). That is, for a given principal quantum number, s, p, d, f... all have different energies. The main reason that the subshells have different energies is the mutual repulsion among the electrons in a multi-electron atom. The only electrical interaction present in hydrogen atom is the attraction between the negatively charged electron and the positively charged nucleus. In multi-electron atoms, besides the presence of attraction between the electron and nucleus, there are repulsion terms between every electron and other electrons present in the atom. Thus, the stability of an electron in multi-electron atom is because the total attractive interactions are more than the repulsive interactions. In general, the repulsive interaction of the electrons in the outer shell with the electrons in the inner shell are more important. On the other hand, the attractive interactions of an electron increases with increase of positive charge (Ze) on the nucleus. Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge of the nucleus (Ze). The effect will be lowered due to the partial screening of positive charge on the nucleus by the inner shell electrons. This is known as the shielding of the outer shell electrons from the nucleus by the inner shell electrons, and the net positive charge experienced by the outer electrons is known as effective nuclear charge ($Z_{eff}e$).

Despite the shielding of the outer electrons from the nucleus by the inner shell electrons, the attractive force experienced by the outer shell electrons increases with the increase of nuclear charge. In other words, the energy of interaction between the nucleus and electron (that is orbital energy) decreases (that is, becomes more negative) with the increase of atomic number (\mathbf{Z}).

Both the attractive and repulsive interactions depend upon the shell and shape of the orbital in which the electron is present. For example, electrons present in spherical shaped s orbital shield the outer electrons from the nucleus more effectively as compared to electrons present in p orbital. Similarly electrons present in p orbitals shield the outer electrons from the nucleus more than the electrons present in d orbitals, even though all these orbitals are present in the same shell. Further within a shell, due to spherical shape of s orbital, the s orbital electron spends more time close to the nucleus in comparison to p orbital electron which spends more time in the vicinity of nucleus in comparison to d orbital electron. In other words, for a given shell (principal quantum number), the Z_{eff} experienced by the electron decreases with increase of azimuthal quantum number (1). This means that the s orbital electron will be more tightly bound to the nucleus than p orbital electron which in turn will be more tightly bound than the d orbital electron. The energy of electrons in s orbital will be lower (more negative) than that of p orbital electron which will have less energy than that of d orbital electron. Since the extent of shielding from the nucleus is different for electrons in different orbitals, it leads to the splitting of energy levels within the same shell (or same principal quantum number). That is, the energy of electron in an orbital, as mentioned earlier, depends upon the values of n and l. Mathematically, the dependence of energies of the orbitals on n and 1 are quite complicated but one simple rule is that, the lower the value of (n (n + l) for an orbital, the lower is its energy. If two orbitals have the same value of (n + l), the orbital with lower value of *n* will have the lower energy. The Table 1 illustrates the (n + l) rule and Fig. 2 depicts the energy levels of multi-electrons atoms. It may be noted that different subshells of a particular shell have different energies in case of multi-electrons atoms. However, in hydrogen atom, these have the same energy. Lastly it may be mentioned here that the energies of the orbitals in the same subshell decrease with increase in the atomic number (\mathbb{Z}_{eff}). For example, energy of 2s orbital of hydrogen atom is greater than that of 2s orbital of lithium and that of lithium is greater than that of sodium and so on, that is, $\mathbb{E}_{2s}(\mathbf{H}) > \mathbb{E}_{2s}(\mathbf{Na}) > \mathbb{E}_{2s}(\mathbf{K})$.

Orbital	Value of n	Value of <i>l</i>	Value of (n + l)	
15	1	0	1 + 0 = 1	
2s	2	0	2 + 0 = 2	
2p	2	1	2 + 1 = 3	2p (n=2) has lower energy than
3s	3	0	3 + 0 = 3	3s (n=3)
Зр	3	1	3 + 1 = 4	3p (n =3) has lower energy than
4s	4	0	4 + 0 = 4	4s (n =4)
3d	3	2	3 + 2 = 5	3d (n =3) has lower energy than
4p	4	1	4 + 1 =5	4p (n =4)

Table 1 Arrangement of Orbitals with Increasing Energy on the Basis of (n+l) Rule

3.0 FILLING OF ORBITALS IN ATOM

The filling of electrons into the orbitals of different atoms takes place according to the aufbau principle which is based on the Pauli's exclusion principle, the Hund's rule of maximum multiplicity and the relative energies of the orbitals.

3.1 Aufbau Principle

The word 'aufbau' in German means 'building up'. The building up of orbitals means the filling up of orbitals with electrons. The principle states: **In the ground state of the atoms, the orbitals are filled in order of their increasing energies.** In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled.

The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s...

The order may be remembered by using the method given in Fig. 2. Starting from the top, the direction of the arrows gives the order of filling of orbitals, that is starting from right top to bottom left.



Fig.2 Order of filling of orbitals

3.2 Pauli Exclusion Principle

The number of electrons to be filled in various orbitals is restricted by the exclusion principle, given by the Austrian scientist Wolfgang Pauli (1926). According to this principle **no two** electrons in an atom can have the same set of four quantum numbers. Pauli exclusion principle can also be stated as: "Only two electrons may exist in the same orbital and these electrons must have opposite spin." This means that the two electrons can have the same value of three quantum numbers n, l and m_l , but must have the opposite spin quantum number. The restriction imposed by Pauli's exclusion principle on the number of electrons in an orbital helps in calculating the capacity of electrons to be present in any subshell. For example, subshell 1s comprises of one orbital and thus the maximum number of electrons can be 6 and 10, respectively. Thus, the maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.

3.3 Hund's Rule of Maximum Multiplicity

This rule deals with the filling up of electrons into the orbitals belonging to the same subshell (orbitals of equal energy, called **degenerate orbitals**). It states that **the pairing of electrons** in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each, i.e., it is singly occupied.

Since there are three p, five d and seven f orbitals, therefore, the pairing of electrons will start in the p, d and f orbitals with the entry of 4th, 6th and 8th electron, respectively. It has been observed that half filled and completely filled degenerate set of orbitals acquire extra stability due to their symmetry.

3.4 Electronic Configuration of Atoms

The distribution of electrons into orbitals of an atom is called its **electronic configuration**. If one keeps in mind the basic rules which govern the filling of different atomic orbitals, the electronic configurations of different atoms can be written very easily.

The electronic configuration of different atoms can be represented in two ways. For example:

(i) $s^a p^b d^c$ notation

(ii) Orbital diagram



In the first notation, the subshell is represented by the respective letter symbol and the number of electrons present in the subshell is depicted, as the super script like a, b, c, The similar subshell represented for different shells is differentiated by writing the principal quantum number before the respective subshell. In the second notation each orbital of the subshell is represented by a box and the electron is represented by an arrow (\uparrow) for a positive spin or an arrow (\downarrow) for a negative spin. The advantage of second notation over the first is that it represents all the four quantum numbers.

The hydrogen atom has only one electron which goes in the orbital with the lowest energy, namely 1s. The electronic configuration of the hydrogen atom is $1s^1$ meaning that it has one electron in the 1s orbital. The second electron in helium (He) can also occupy the 1s orbital. Its configuration is, therefore, $1s^2$. As mentioned above, the two electrons differ from each other with opposite spin, as can be seen from the orbital diagram.



The third electron of lithium (Li) is not allowed in the 1s orbital because of Pauli exclusion principle. Therefore, it takes the next available choice, namely the 2s orbital. The electronic configuration of Li is $1s^22s^1$. The 2s orbital can accommodate one more electron. The configuration of beryllium (Be) atom is, therefore, $1s^2 2s^2$ (see Table 2, for the electronic configurations of elements).

In the next six elements-boron (B, $1s^22s^22p^1$), carbon (C, $1s^22s^22p^2$), nitrogen (N, $1s^22s^22p^3$), oxygen (O, $1s^22s^22p^4$), fluorine (F, $1s^22s^22p^5$) and neon (Ne, $1s^22s^22p^6$), the 2p orbitals get progressively filled. This process is completed with the neon atom. The orbital picture of these elements can be represented as follows:



The electronic configuration of the elements sodium (Na, $1s^22s^22p^63s^1$) to argon (Ar, $1s^22s^22p^63s^23p^6$), follow exactly the same pattern as the elements from lithium to neon with the difference that the 3s and 3p orbitals are getting filled now. This process can be simplified if we represent the total number of electrons in the first two shells by the name of element neon (Ne). The electronic configuration of the elements from sodium to argon can be written as (Na, [Ne]3s¹) to (Ar, [Ne] $3s^23p^6$). The electrons in the completely filled shells are known as core electrons and the electrons that are added to the electronic shell with the highest principal quantum number are called **valence electrons.** For example, the electrons in Ne are the core electrons and the electrons from Na to Ar are the valence electrons. In potassium (K) and calcium (Ca), the 4s orbital, being lower in energy than the 3d orbitals, is occupied by one and two electrons respectively.

A new pattern is followed beginning with scandium (Sc). The 3d orbital, being lower in energy than the 4p orbital, is filled first. Consequently, in the next ten elements, scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn), the five 3d orbitals are progressively occupied. We may be puzzled by the fact that chromium and copper have five and ten electrons in 3d orbitals rather than four and nine as their position would have indicated with two-electrons in the 4s orbital. The reason is that fully filled orbitals and half-filled orbitals have extra stability (that is, lower energy). Thus p^3 , p^6 , d^5 , d^{10} , f^7 , f^{14} configurations, which are either half-filled or fully filled, are more stable. Chromium and copper therefore adopt the d^5 and d^{10} configuration (caution: exceptions do exist)

With the saturation of the 3d orbitals, the filling of the 4p orbital starts at gallium (Ga) and is completed at krypton (Kr). In the next eighteen elements from rubidium (Rb) to xenon (Xe),

the pattern of filling the 5s, 4d and 5p orbitals are similar to that of 4s, 3d and 4p orbitals as discussed above. Then comes the turn of the 6s orbital. In caesium (Cs) and the barium (Ba), this orbital contains one and two electrons, respectively. Then from lanthanum (La) to mercury (Hg), the filling up of electrons takes place in 4f and 5d orbitals. After this, filling of 6p, then 7s and finally 5f and 6d orbitals takes place. The elements after uranium (U) are all short-lived and all of them are produced artificially. The electronic configurations of the known elements (as determined by spectroscopic methods) are tabulated in Table 2.

One may ask what is the utility of knowing the electron configuration? The modern approach to the chemistry, infact, depends almost entirely on electronic distribution to understand and explain chemical behaviour. For example, questions like why two or more atoms combine to form molecules, why some elements are metals while others are non-metals, why elements like helium and argon are not reactive but elements like the halogens are reactive, find simple explanation from the electronic configuration. These questions have no answer in the Daltonian model of atom. A detailed understanding of the electronic structure of atom is, therefore, very essential for getting an insight into the various aspects of modern chemical knowledge.

4.0 STABILITY OF COMPLETELY FILLED AND HALF FILLED SUBSHELLS

The ground state electronic configuration of the atom of an element always corresponds to the state of the lowest total electronic energy. The electronic configurations of most of the atoms follow the basic rules given above. However, in certain elements such as Cu, or Cr, where the two subshells (4s and 3d) differ slightly in their energies, an electron shifts from a subshell of lower energy (4s) to a subshell of higher energy (3d), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half filled. The valence electronic configurations of Cr and Cu, therefore, are $3d^5 4s^1$ and $3d^{10} 4s^1$ respectively and not $3d^4 4s^2$ and $3d^9 4s^2$. It has been found that there is extra stability associated with these electronic configurations.

Causes of Stability of Completely Filled and Half Filled Sub-shells

The completely filled and completely half filled sub-shells are stable due to the following reasons:

1. Symmetrical distribution of electrons: It is well known that symmetry leads to stability. The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable. Electrons in the same subshell (here 3d) have equal energy but different spatial distribution. Consequently, their shielding of one-another is relatively small and the electrons are more strongly attracted by the nucleus.

2. Exchange Energy: The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled (Fig. 2.18). As a result the exchange energy is maximum and so is the stability.

You may note that the exchange energy is at the basis of Hund's rule that electrons which

enter orbitals of equal energy have parallel spins as far as possible. In other words, the extra stability of half-filled and completely filled subshell is due to: (i) relatively small shielding, (ii) smaller coulombic repulsion energy, and (iii) larger exchange energy. Details about the exchange energy will be dealt with in higher classes.



Element Z	15	2s	2 p	35	3 <i>p</i>	3đ	4 s	4 <i>p</i>	4d	4 <i>f</i>	5 <i>s</i>	5 <i>p</i>	5d 5f	6 <i>s</i>	6 p	6d	7s
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 Table 2 Electronic Configurations of the Elements

* Elements with exceptional electronic configuration

Elem	ent Z	15	2s	2 <i>p</i>	35	Зр	3d	4s	4p	4d	4 <i>f</i>	5 <i>s</i>	5p	5d 5f	6 <i>s</i>	6 <i>p</i>	6d	7s
Cs Ba La* Ce* Pr Nd Pm Sm Eu Gd* Tb Dy Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt* Au* Hg Tl Pb Bi Po At Rn	$\begin{array}{c} 55\\ 56\\ 57\\ 58\\ 59\\ 60\\ 61\\ 62\\ 63\\ 64\\ 65\\ 66\\ 67\\ 68\\ 69\\ 70\\ 71\\ 72\\ 73\\ 74\\ 75\\ 76\\ 77\\ 78\\ 79\\ 80\\ 81\\ 82\\ 83\\ 84\\ 85\\ 86\end{array}$	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	$egin{array}{cccccccccccccccccccccccccccccccccccc$	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	666666666666666666666666666666666666666	10 10 10 10 10 10 10 10 10 10 10 10 10 1	$\begin{array}{c} 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ $	6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	10 10 10 10 10 10 10 10 10 10 10 10 10 1	$\begin{array}{c}2&3\\4&5\\6&7\\7&9\\10&11\\12&13\\14&14\\14$	$\begin{array}{c} 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ $	666666666666666666666666666666666666666	$ \begin{array}{c} 1\\1\\2\\3\\4\\5\\6\\7\\9\\10\\10\\10\\10\\10\\10\\10\\10\\10\\10\\10\\10\\10\\$	$\begin{array}{c}1\\1\\2\\2\\2\\2\\2\\2\\2\\2\\2\\2\\2\\2\\2\\2\\2\\2\\2\\2$	123456		
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5.0 SUMMARY

- For hydrogen and hydrogen like systems (such as He⁺ and Li²⁺ etc.) all the orbitals within a given shell have the same energy.
- The energy of the orbitals in a multi-electron atom depends upon the values of *n* and *l*.

- The lower the value of (n+l) for an orbital, the lower is its energy. If the two orbitals have the same (n+l) value, the orbitals with the lower value of n has the lower energy.
- In an atom mant such orbitals are possible and electrons are filled in those orbitals in order of increasing energy.
- Pauli's Exclusion Principle: No two electrons in an atom have the same set of four quantum numbers.
- Hund's Rule of Maximum Multiplicity: Pairing of electrons in the orbitals of the same subshell does not take place until each orbital belonging to that subshell has got one electron each.