ELECTRONIC CONFIGURATION OF ELEMENTS SECTION - 7

Quantum numbers can now characterise the electrons in an atom. To describe the arrangements and distribution of electrons for different elements, following rules and selective principles are used. The distribution of electrons in an atom is known as *the electronic configuration of that element.*

Electronic configuration of an element is represented by the notation $n\,\ell^x$:

n : principal quantum number ℓ : denotes the sub-shell x : number of electrons present in an orbital

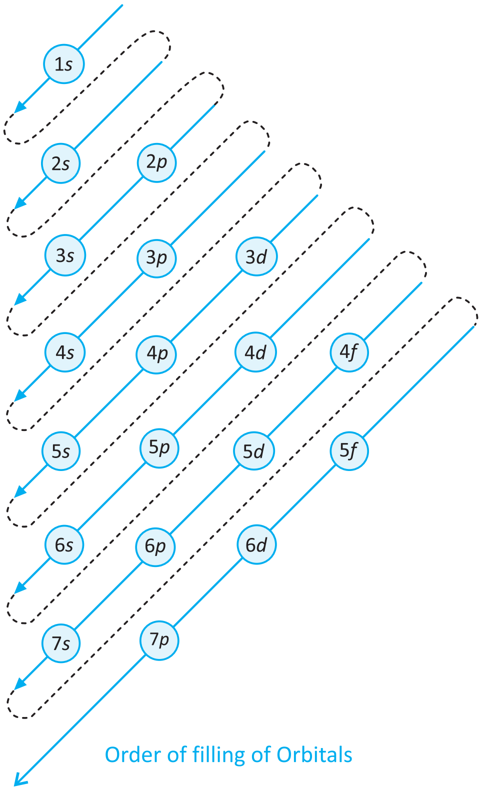
Aufbau Principle

An atom in its lowest state of energy is said to be in *ground state*. The ground state is the most stable state in an atom. According to Aufbau principle:

> ***"electrons are added progressively to the various orbitals in their order of increasing energy starting with the orbital of lowest energy"***

The order of increasing energy may be summed up as : 1s, 2s, 2p, 3s, 3p, **4s, 3d**, 4p, **5s, 4d**, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d,.....

As a working rule, a new electron enters an empty orbital for which the value of $(n + \ell)$ is minimum. If the value of $(n + \ell)$ is same for two or more orbitals, the new electron enters an orbital having lower value of n.



Order of filling of Orbitals

Pauli Exclusion Principle

According to this principle :

" no two electrons in an atom can have the same set of all the quantum numbers. or one can say that no two electrons can have the same quantised states."

Consider an electronic arrangement in Ist energy level (n = 1). For $n = 1$, $\ell = 0$, and $m_\ell = 0$. Now m_s can have two values corresponding to each value of m_ℓ i.e. $m_s = +1/2, -1/2$. Hence the possible designation of an electron in a state with n = 1 is $(1, 0, 0, +1/2)$ and $(1, 0, 0, -1/2) \equiv (n, \ell, m_\ell, m_s)$ i.e., two quantised states. This implies that an orbital can accommodate (for $n = 1, m_\ell = 0$, i.e., one orbital) maximum of two electrons having opposite spins.

The maximum number of electrons in the different sub-shells are :

s sub-shell = 2, *p sub-shell* = 6, *d sub-shell* = 10 *and* *f sub-shell* = 14.

Hund's Rule Of Maximum Multiplicity

According to this rule : *" electrons never pair until no available empty degenerate orbitals are left to them."*

This means an electron always occupies a vacant orbital in the same sub-shell (degenerate orbital) and pairing starts only when all of the degenerate orbitals are filled up. This means that the pairing starts with 2nd electron in *s* sub-shell, 4th electron in *p* sub-shell, 6th electron in *d* sub-shell and 8th electron in *f* sub-shell.

By doing this, the electrons stay as far away from each other as possible. This is highly reasonable if we consider the *electron-electron repulsion*. Hence electrons obey Hund's rule as it results in lower energy state and hence more stability.

Extra Stability of Half And Fully Filled Orbitals

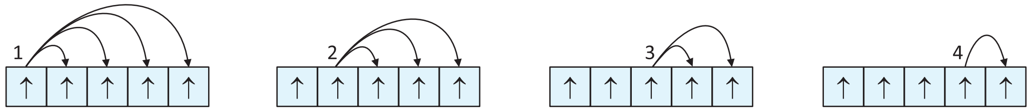
A particularly stable system is obtained when a set of equivalent orbitals (degenerate orbitals) is either fully filled or half filled, i.e., each containing one or a pair of electrons. This effect is more dominant in *d* and *f* sub-shells.

This means three or six electrons in *p* sub-shell, five or ten electrons in *d* sub-shell, and seven or fourteen electrons in *f* sub-shell forms a stable arrangement. Note this effect when filling of electrons takes place in *d* sub-shells (*for atomic numbers* $Z = 24, 25$ *and* $29, 30$).

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 atoms follow the basic rules given in the sections written above. However, in certain elements such as Cr and Cu where the two lower 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 subshells of higher energy getting either completely filled or half filled. The valence electronic configuration of Cr and Cu therefore are $4s^1 3d^5$ and $4s^1 3d^{10}$ respectively and not $4s^2 3d^4$ and $4s^2 3d^9$. It has been found that there is extra stability associated with these electronic configurations. This stabilization is due to the following factors:

- **Symmetrical Distribution of electrons:** It is well known that symmetry leads to stability. The completely filled or half filled sub shells have a symmetric 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 electrons are more strongly attracted by the nucleus.
- **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 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. As a result the exchange energy is maximum and so is the stability.



4 exchanges by electron 1 3 exchanges by electron 2 2 exchanges by electron 3 1 exchanges by electron 4

Possible exchanges for a d^5 configuration

Illustration - 17 *A compound of Vanadium has a magnetic moment of 1.73 B.M. Work out the electronic configuration of vanadium in the compound.*

SOLUTION :

The magnitude of magnetic moment (μ) of a compound/species/ion is given by : $\mu = \sqrt{n(n+2)}\, B.M$

(n = number of unpaired electrons ; BM : unit of magnetic moment in Bohr's Magneton)

$$\Rightarrow \qquad 1.73 = \sqrt{n(n+2)}$$

On solving for n, we get $n = 1$. This means that vanadium ion $(Z = 23)$ in the compound has one unpaired electron.

3d : (↑)( )( )( )( )

So its electronic configuration (e.c.) must be :

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$$

i.e., vanadium exists as V^{4+} ion in the compound since the ground state e.c. of $_{23}V$ is :

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$$

3d : (↑)(↑)(↑)( )( ) 4s : (⇅)

Note : In these kind of questions, keep on removing e^- from the outermost orbitals.

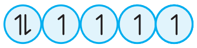
Illustration - 18 *Write down the electronic configuration of following species. Also find the number of unpaired electrons in each.* **(a)** Fe, Fe^{2+}, Fe^{3+} (Z of Fe = 26) , **(b)** Br, Br^- (Z of Br = 35) , **(c)** V, V^{3+} (Z of V = 23)

SOLUTION :

Follow the order of increasing energy (Aufbau Rule) :
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d……..

(a) Fe(Z = 26): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

Note that 3d orbital are not fully filled.

$3d^6 \equiv$ 

Orbitals filled as per Hund's Rule.

Clearly the number of unpaired electrons is 4.

- Fe^{2+} : (Z = 26) [No. of electrons = 24]

While writing electronic configuration (e.c.) of cations, first write e.c of neutral atom and then "remove desired number of electrons from outermost orbital".

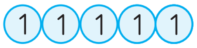
In Fe^{2+}, remove $2e^-$ from $4s^2$ since 4s orbital (through lower in energy then 3d) is the outermost. Hence e.c. of Fe^{2+} is: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^0$

Note that number of unpaired electrons remains same as that in Fe, i.e. 4.

- Fe^{3+} (Z = 26) [No. of electrons = 23]

Now remove $2e^-$ from $4s^2$ and $1e^-$ from $3d^6$ to get e.c. as : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^0$

Note that, now all 'd' orbits have an odd electron (i.e. are half filled).

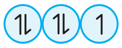


Hence number of unpaired electrons in Fe^{3+} = 5.

(b) Br (Z = 35) [No. of electron = 35]

Following Aufbau rule, e.c. is :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$

Clearly one of $4p^5$ orbitals contains unpaired electrons: $4p^5 \equiv$ 

Orbitals filled as per Hund's Rule.

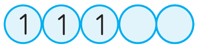
Hence Br has only one unpaired electron.

- Br^- (Z = 35) [No. of electron = 36]

Since anion(s) is(are) formed by adding electron(s), so simply write e.c. as per total number of electrons finally.
For Z = 35, e.c. is : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$
Clearly there are no unpaired electrons.

(c) Following on pattern in (a), we can write e.c. for V as follows.

V(Z = 23) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$

$3d^3 \equiv$ 

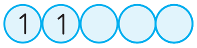
Orbitals filled as per Hund's Rule.

⇒ 3 unpaired electrons.

- V^{3+} (Z = 23) [No. of electron = 20]

Remove $3e^-$ from outermost orbitals successively i.e., '$2e^-$' from $4s^2$ and $1e^-$ from $3d^3$. Hence e.c. of V^{3+} is :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^2$

$3d^2 \equiv$ 

Orbitals filled as per Hund's Rule.

⇒ 2 unpaired electrons.