

Electronic Configuration of Elements

APPLICATION OF QUANTUM MECHANICAL MODEL OF THE ATOM FOR UNDERSTANDING CHEMISTRY

The theoretical basis of our understanding chemistry today is based on our understanding of the behaviour of the electrons in an atom. It is therefore necessary to know exactly how the electrons are located around the nucleus and what their energies are. The electronic configuration of atoms (or ions) gives us this information.

Aufbau is a German word which means 'building up.' The principles of quantum mechanical governing the electronic configuration of atoms and ions are therefore sometimes referred to collectively as the **Aufbau principle**.

The Rules Governing the Electronic Configuration of Atoms (*Aufbau* Principle)

(a) Electrons in an atom tend to go to the lowest energy orbital available.

(b) **Pauli's exclusion principle** forbids **more than two electrons** to populate one orbital. Hence when the lower energy orbitals are 'filled up', electrons go to higher energy orbitals.

(b) **Hund's rule of maximum spin multiplicity** does not allow **more than one electron** to occupy any orbital as long as other vacant degenerate orbitals (i.e. equal energy orbitals belonging to the same subshell) are available. This rule also states that all electrons in singly occupied degenerate orbitals have the

same $m_s = +\frac{1}{2}$ or, all of them have $m_s = -\frac{1}{2}$.

(c) The relative energies of orbitals are **not** simply determined by their principal quantum number n but it depends on both **n and l** .

No single rule can be used to 'theoretically' predict the relative energy of orbitals for 'all' atoms or ions! This is amply clear from the '**experimentally**' determined graph showing the variation of orbital energies with atomic numbers as given in a previous section.

Luckily for us, a way out exists only for the purpose of determining electronic configurations in the form of the $(n + l)$ rule, which also constitutes the **central theme of the Aufbau principle**.

According to this rule:

- (i) orbitals with higher values of $(n + l)$ have higher energy, and
- (ii) among any two orbitals having the same value of $(n + l)$, the one having a higher value of n has the higher energy.

The different orbitals may now be arranged in increasing order of energy (i.e. in the order that they are filled up) using the $(n + l)$ rule.

Orbital	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p	6s	4f	5d	6p	7s	5f	6d
n	1	2	2	3	3	4	3	4	5	4	5	6	4	5	6	7	5	6
l	0	0	1	0	1	0	2	1	0	2	1	0	3	2	1	0	3	2
$(n + l)$	1	2	3	3	4	4	5	5	5	6	6	6	7	7	7	7	8	8

Thus, **according to this**, a 3d orbital ($n + l = 5$) has higher energy than a 4s orbital

($n + l = 4$). Also, of the three orbitals having the same ($n + l$) values of 5, the order of energy depends on the principal quantum number:
 $3d < 4p < 5s$

Example

If the relative energy of orbitals can be different for different atomic number, how reliable is the ($n + l$) rule?

Solution

The utility of the ($n + l$) rule ends with the successful prediction of most of the atoms. Once the electronic configurations has been determined you must **remember one simple rule for predicting the energies of electrons in an atom:**

An electron in an atom having a higher value of n always has a higher energy. If two electrons in an atom have the same n , then the one with a higher level of l has the higher energy.

The following example will clarify it further:

An atom of K ($Z = 19$) has no electrons in $3d$ ($n + l = 5$) but one electron in $4s$ ($n + l = 4$) as predicted correctly by the ($n + l$) rule.

An atom of Sc ($Z = 21$) has only one electron in $3d$ whereas its $4s$ is filled first, as predicted correctly by the ($n + l$) rule.

Now consider this, if we ionise an atom, we know that we take out the highest energy electron of the atom. When we ionise a Scandium atom, however, it has been experimentally observed that the $4s$ and **not the $3d$ electron** is removed! The ($n + l$) rule cannot explain this fact. On the other hand from Sc ($Z = 21$) onwards, $4s > 3d$.

N.B.: We thus have two different rules for two different purposes:

(a) **To predict the electronic configuration of a neutral atom**

- (i) higher ($n + l$) \Rightarrow higher energy.
- (ii) If ($n + l$) is the same, then higher $n \Rightarrow$ higher energy.

(b) **To predict the energy of an electron in an atom**

- (i) Higher $n \Rightarrow$ higher energy.
- (ii) If n is the same, then higher ($n + l$) \Rightarrow higher energy.

(c) **Half-filled or fully-filled subshells have extra stability**

This rule not only helps us explain some configurations which are exceptions to the ($n + l$) rule, it also has a physical basis.

The electrical field due to the nucleus of an atom is spherically symmetrical and one may speculate that a spherical electron cloud should imply extra stability. However, there is no reason to expect extra stability for spherical symmetry. For both half-filled and fully-filled subshells, the extra stability is because the exchange is maximum, and those electrons having parallel spins avoid each other.

In conjunction with Hund's rule, this would mean that p^3 , p^6 , d^5 , d^{10} , f^7 and f^{14} configurations have extra stability.

Depicting Electronic Configurations

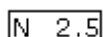
In the preceding sub-sections we studied the theory of how to go about determining electronic configurations. Electronic configuration can be depicted in many ways - each has different levels of convenience and each convey different levels of chemically meaningful information.

We will review them here by **assuming** (i.e. not asking why), for the time being, that the electronic configurations of the atoms of some elements, nitrogen in particular.

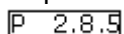
How to depict electronic configurations?

(a) **Shell description:** Here we simply shown how many electrons there are in each shell of the atom beginning with the K, or the 1st shell.

Nitrogen ($Z = 7$) has two electrons in the K shell and five electrons in the L shell. We show it as



Similarly phosphorous ($Z = 15$) is shown as

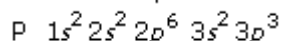
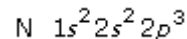


Chemical information: In chemistry, we find it useful to divide different elements into periods and groups on the basis of similarities and graded variation of their properties. The shell description gives us, (a) **The number of shells:** This corresponds to the **period** to which the element belongs and

(b) **The number of electrons in the outermost shell** which tells us a lot about the **group** to which the element belongs. The outermost shell electrons are also called valence shell electrons.

(b) **Subshell description (*spdf* notation):**

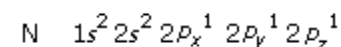
The electronic configurations of nitrogen and phosphorus are:



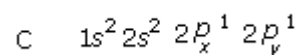
Chemical information: In addition to classifying elements into periods and groups, we find it useful, in chemistry, to classify elements into blocks (such as *s*-block elements or *p*-block elements, etc.) on the basis of which subshell is in the process of getting filled up. The subshell description provides all this information. For example, we can immediately say that both nitrogen and phosphorus are *p*-block elements.

(c) **Orbital description:**

For nitrogen, we write



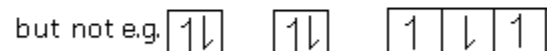
For carbon ($Z = 6$), we write



(note that for carbon $1s^2 2s^2 2p_y^1 2p_z^1$ would also be a valid description. Can you say why?)

Chemical information: In addition to the information provided by the subshell description also have information regarding the number of unpaired electrons in the atom and also the 'spin only' magnetic moment. Since covalent bonds are formed by unpaired electrons, this description tells us something (not all) about the possible number of bonds.

man-filled or unfilled. For nitrogen we may write,



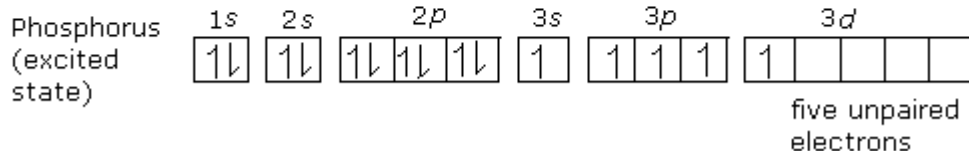
For carbon we may write



$1s$ $2s$ $2p$ $3s$ $3p$ $3d$

These are called 'low lying vacant orbitals'.

corresponding excited state configuration would be



(e) **Noble gas core description - a matter of convenience:**

Though the descriptions (b)-(d) progressively provide additional chemical information, all these descriptions become tedious and cumbersome.

Chemists have therefore used the following 'chemical' knowledge to develop a short hand notation for conveniently displaying the '**relevant**' chemical information

(i) The chemical property of any atom is **primarily** determined by the configuration of the outermost, or valence shell, electrons.

(ii) Wherever applicable, the configuration of the penultimate and the pre-penultimate shell electrons, respectively affect the chemical properties only secondarily or tertiarily.

(iii) Filled inner shell electrons, or **core** electrons, do not affect chemical properties and hence their depiction is not **relevant** except for the purpose of counting the number of inner shells.

(iv) The noble gases have an electronic configuration with completed shells and they can be used to denote the number of completed inner shells.

Thus, in this notation,

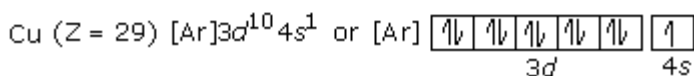
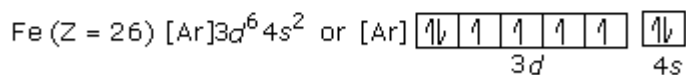
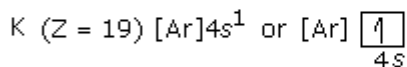
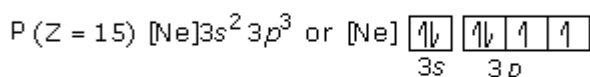
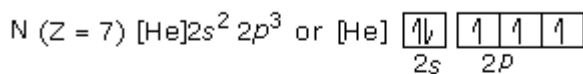
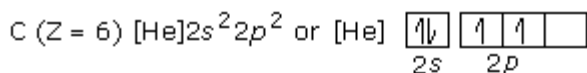
$1s^2$ is replaced by $[\text{He}] \Rightarrow$ one inner shell.

$1s^2 2s^2 2p^6$ is replaced by $[\text{Ne}] \Rightarrow$ two inner shells.

$1s^2 2s^2 2p^6 3s^2 3p^6$ is replaced by $[\text{Ar}] \Rightarrow$ three inner shells.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ is replaced by $[\text{Kr}] \Rightarrow$ four inner shells. etc.

Accordingly we may write the electronic configurations as follows:



Such a description brings out the **essential** similarity of the configurations of pairs such as N and P, or K and Cu it gives us a great amount of detailed information and is yet convenient to use. We usually stick to such representations.

The Electronic Configuration of Atoms for the Elements $Z = 1$ to $Z = 36$

When it comes to applying the *Aufbau* principle, a problem may arise as to how to **remember** the order of filling up. Most chemistry books provide a mnemonic for this purpose. We will provide you, however, with an alternative mnemonic which incorporates the chemically relevant concept of the periodic table, by telling you how the periods are filled up.

How to remember the order of filling of orbitals by applying the *Aufbau* principle?

If you look at the order of orbitals you will find a very simple rhythm:
s sp sp sdp sdp sfdp sfd

Now if you put the principal quantum numbers.

s orbitals will be numbered 1, 2, 3

p orbitals will be numbered 2, 3, 4

d orbitals will be numbered 3, 4

f orbitals will be numbered 4, 5

you will have

1s 2s2p 3s3p 4s3d 4p 5s4d 5p 6s4f5d6p 7s5f6d

1s 2s2p 3s3p 4s3d 4p 5s4d 5p 6s4f5d6p 7s5f6d

The advantages of this alternative mnemonic are manifold as will be apparent from the table below.

Sets	Filled as	Represented by core	Marks end of	Number of elements in period	Upto atomic number
1s	$1s^2$	[He]	1 st period	2	2
2s2p	$2s^2 2p^6$	[Ne]	2 nd period	8	10
3s3p	$3s^2 3p^6$	[Ar]	3 rd period	8	18
4s3d4p	$4s^2 3d^{10} 4p^6$	[Kr]	4 th period	18	36
5s4d5p	$5s^2 4d^{10} 4p^6$	[Xe]	5 th period	18	54
6s4f5d6p	$6s^2 4f^{14} 5d^{10} 6p^6$	[Rn]	6 th period	32	86
7s5f6d7p *		*	7 th period	*	*

* This period is not completed.

The moment you are given an atomic number you can immediately identify which noble gas core is there and which period it belongs to. For example

$Z = 13 \Rightarrow$ [Ne] core + 3 electrons.

$Z = 25 \Rightarrow$ [Ar] core + 7 electrons and so on.

The table which follows gives you the electronic configuration of atoms of elements 1 to 36 with details of subshell wise distribution. You may now depict the configurations using any of the descriptions.

(a) The configuration should show the orbitals ordered according to their actual energies. Thus, vanadium ($Z = 23$) should be shown as

$[\text{Ar}] 3d^3 4s^2$ and **not** $[\text{Ar}] 4s^2 3d^3$

Element	Atomic Number	Population of sub shell								
		1s	2s	2p	3s	3p	3d	4s	4p	4d
H	1	1								
He	2	2								
Li	3		1							
Be	4		2							
B	5		2	1						
C	6		2	2						
N	7		2	3						
O	8		2	4						
F	9		2	5						
Ne	10	2	2	6						
Na	11				1					
Mg	12				2					
Al	13				2	1				
Si	14				2	2				
P	15				2	3				
S	16				2	4				
Cl	17				2	5				
Ar	18	2	2	6	2	6				
K	19							1		
Ca	20							2		
Sc	21						1	2		
Ti	22						2	2		
V	23						3	2		
Cr	24						5	1	Exception	
Mn	25						5	2		
Fe	26						6	2		
Co	27						7	2		
Ni	28						8	2		
Cu	29						10	1	Exception	
Zn	30						10	2		
Ga	31						10	2	1	
Ge	32						10	2	2	
As	33						10	2	3	
Se	34						10	2	4	
Br	35						10	2	5	
Kr	36	2	2	6	2	6	10	2	6	

Special note should be made of the configurations of Cr ($Z = 24$), and Cu ($Z = 29$). The configuration are exceptions to the $(n + l)$ rule but consistent with the stability of half-filled and fully-filled subshells. Thus we have

Cr $[\text{Ar}] 3d^5 4s^1$, and **NOT** $[\text{Ar}] 3d^4 4s^2$

Cu $[\text{Ar}] 3d^{10} 4s^1$, and **NOT** $[\text{Ar}] 3d^9 4s^2$

(c) The electronic configuration of atomic cations needs some special consideration.

Writing electronic configurations of atomic cations

We must first write down the electronic configuration of the neutral atom in the ground state. The required number of electrons must be removed subsequently. This is particularly important for writing the configuration of cations of transition elements.

Example

Write down the configuration of Fe ($Z = 26$) and Ni^{2+} ($Z = 28$)

Solution

Both **Fe** and **Ni^{2+}** have **26 electrons**.

Configuration of Fe $[\text{Ar}] 3d^6 4s^2$ ($26 = 18 + 8 = [\text{Ar}] + 8$ electrons)

Configuration of Ni $[\text{Ar}] 3d^8 4s^2$

Configuration of Ni^{2+} $[\text{Ar}] 3d^8 4s^0$ (electrons are removed from 4s!)

N.B.: Fe and Ni^{2+} do not have the same configuration.

All the configurations shown in the table correspond to the lowest energy states (ground states) for each atom.

Any configuration **other than the ground state configuration** would represent an atom in its excited state.