INTRODUCTION TO PERIODIC CHEMISTRY

Periodic chemistry involves the study of how **physical** and **chemical properties** of elements **vary** with their different **electron arrangement**. Atomic number is the number of protons in the nucleus of an atom and it equal to the number of electrons in a neutral atom.

Atoms of different element have different atomic number and hence have different number of electrons. Different number of electrons means different electron arrangements. Hence, elements with different electron arrangement have different properties and element with similar electron arrangement have similar properties.

ARRANGEMENT OF ELECTRON IN THE SHELL

1. Electrons in an atom can **orbit** in a maximum of seven shells or energy levels. The shells are represented by K,L,M,N,O,P and Q.
2. A shell is a volume of space around the nucleus in which there is high probability of locating and electron.
3. The maximum number of electrons that a shell can accommodate is known by using the formula $\mathbf{2n^2}$ where n is the shell number.
4. The maximum number of electrons possible in an outermost shell of an atom is 8
5. The electrons in the outermost shell are called **valence electrons** and the shell is called **valence shell.**
6. The **valence electrons** are responsible for the chemical properties of elements.
7. **Core electrons (inner electrons)** are electrons between the nucleus and the valence electrons. They do not participate in chemical reactions but do influence the behaviour of valence electron.

ELEMENT AND THEIR SYMBOLS

Name of the Element	Symbol of the Element	Atomic Number
Hydrogen	H	1
Helium	He	2
Lithium	Li	3
Beryllium	Be	4
Boron	B	5
Carbon	C	6
Nitrogen	N	7
Oxygen	O	8
Fluorine	F	9
Neon	Ne	10
Sodium	Na	11

Magnesium	Mg	12
Aluminium	Al	13
Silicon	Si	14
Phosphorus	P	15
Sulfur	S	16
Chlorine	Cl	17
Argon	Ar	18
Potassium	K	19
Calcium	Ca	20
Scandium	Sc	21
Titanium	Ti	22
Vanadium	V	23
Chromium	Cr	24

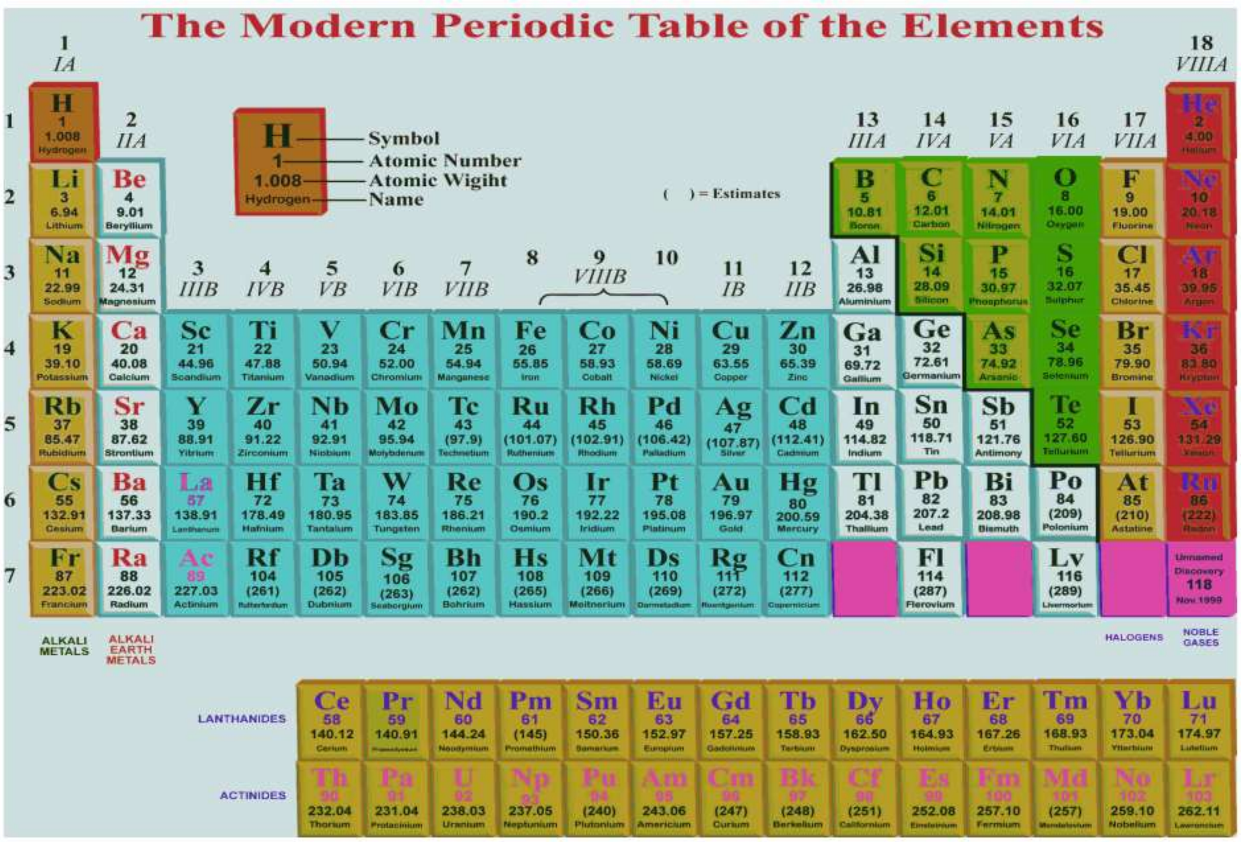
Manganese	Mn	25
Iron	Fe	26
Cobalt	Co	27
Nickel	Ni	28
Copper	Cu	29
Zinc	Zn	30
Gallium	Ga	31
Germanium	Ge	32
Arsenic	As	33
Selenium	Se	34
Bromine	Br	35
Krypton	Kr	36
Rubidium	Rb	37

Strontium	Sr	38
Yttrium	Y	39
Zirconium	Zr	40
Niobium	Nb	41
Molybdenum	Mo	42
Technetium	Tc	43
Ruthenium	Ru	44
Rhodium	Rh	45
Palladium	Pd	46
Silver	Ag	47

PERIODIC LAW: it states that the properties of element are a periodic function of their atomic number.

THE PERIODIC TABLE

- ✓ This is a table showing all the known elements arrange systematically in order of increasing atomic number such that their outer electron configuration and recur at interval.
- ✓ Elements with the same number of valence electron constitute a group.



Physical States of Elements

The physical state and heat of fusion or vaporization of elements reflect the relative strength of bonding and/or interparticle forces within the element.

- *Metals are solids* (except mercury): strong metallic bonding holds atoms in their crystal structures.

- *Metalloids and carbon are hard solids* because of strong covalent bonds holding atoms together in extensive covalent networks;
- Nonmetals such as sulfur, phosphorus, and iodine are “soft” solids because of relatively *strong dispersion forces* holding their molecules together. Bromine is a liquid.
- Other nonmetals are gases because dispersion forces between small molecules are weak.

- *The hardness and melting points of metals increase as the number of valence electrons increases from left to right across periods*;
- In Groups 1A(1) and 2A(2), *melting point, boiling point,* $\mathrm{D}H_{\mathrm{fus}}$, and $\mathrm{D}H_{\mathrm{vap}}$ decrease from top to bottom down the groups;
- In Groups 7A(17) and 8A(18), *melting point, boiling point,* $\mathrm{D}H_{\mathrm{fus}}$, and $\mathrm{D}H_{\mathrm{vap}}$ increase from top to bottom down the groups.
- Among transition metals, the hardest metals are found approximately in the middle of the series. Thus, Cr and Mn are the hardest metals in the first transition series.

Metallic & Nonmetallic Characteristics

General Properties of Elements in the Periodic Table:

	Metals	**Nonmetals**
Atomic Properties	Have fewer valence electrons	Have more valence electrons
	Larger atomic size	Smaller atomic size
	Lower ionization energy	Higher ionization energy
	Lower electronegativity	Higher electronegativity
Physical Properties	Solid at room temperature (except Hg)	Mostly gases, Br_2 is a liquid, others are solids
	Good conductors of electricity and heat	Generally nonconductors (except graphite)
	Lustrous, malleable & ductile	None of these

Chemical Properties	Lose electrons to become cations Reacts with nonmetals to form ionic compounds (salts) Metals do not react with one another	Gain electrons to become anion Reacts with metals to form ionic compounds Nonmetals (except noble gases) reacts to form covalent compds.

Characteristics of the groups

GROUP ONE (I) ELEMENT (**Alkali Metals)**

- Less dense than other metals
- One loosely bound valence electron
- Highly reactive, with reactivity increasing moving down the group
- The largest atomic radius of elements in their period
- Low ionization energy
- Low electronegativity
-

GROUP TWO (II) ELEMENT (**Alkaline Earth Metals)**

- Two electrons in the valence shell
- Readily form divalent cations
- Low electron affinity
- Low electronegativity

Transition Metals

The lanthanides (rare earth) and actinides are also transition metals. The basic metals are similar to transition metals but tend to be softer and to hint at nonmetallic properties. In their pure state, all of these elements tend to have a shiny, metallic appearance. While there are radioisotopes of other elements, all of the actinides are radioactive.

- Very hard, usually shiny, ductile, and malleable
- High melting and boiling points
- High thermal and electrical conductivity
- Form cations (positive oxidation states)

- Tend to exhibit more than one oxidation state
- Low ionization energy

Metalloids or Semimetals

- Electronegativity and ionization energy intermediate between that of metals and nonmetals
- May possess a metallic luster
- Variable density, hardness, conductivity, and other properties
- Often make good semiconductors
- Reactivity depends on the nature of other elements in the reaction

Non-metals

The halogens and noble gases are nonmetals, although they have their own groups, too.

- High ionization energy
- High electronegativity
- Poor electrical and thermal conductors
- Form brittle solids
- Little if any metallic luster
- Readily gain electrons

GROUP SEVEN (VII) ELEMENTS **(Halogens)**

The halogens exhibit different physical properties from each other but do share chemical properties.

- Extremely high electronegativity
- Very reactive
- Seven valence electrons, so elements from this group typically exhibit a -1 oxidation state

GROUP EIGHT (VIII) ELEMENTS **(Noble Gases)**

The noble gasses have complete valence electron shells, so they act differently. Unlike other groups, noble gasses are unreactive and have very low electronegativity or electron affinity.

PERIODIC PROPERTIES

A periodic property is a periodic variation in physical and chemical properties of elements with increasing in atomic number OR it is any property of elements (either physical or chemical) which changes regularly with increase in atomic number. Examples of periodic properties to be considered for study are,

i. Atomic radius or ionic radius
ii. Electronegativity
iii. Ionization energy
iv. Electron affinity

ATOMIC RADIUS OR SIZE

Atomic radius is half the internuclear distance between two Identical atoms in a covalent bond. Size of an atom depends on

a. Number of protons (i.e nuclear charge)
b. Number of core shells

Atomic radius depends on how strongly the proton in the nucleus attract or pull the outermost electrons. Given two atoms with the same number of core shell, the one with greater number of protons will have greater pull of its outermost electrons to the nucleus leading to smaller size. The Inner or core electrons in the core shells which are negatively charged tend to shield or screen the outermost shell electrons from the full impact of attraction by the positively charged protons in the nucleus. The attraction by the positive protons (also called nuclear charge) for electrons in the outermost shell is usually reduced due to the presence of the core electrons in the core shells which cause **screening** or **shielding effects.**

Effective nuclear charge is therefore is the **net positive** charge which is felt by electrons in the outermost shell through attraction by the positive proton (i.e effective nuclear charge = Nuclear charge – Shielding effects). *Atomic radii decrease across the period from Lithium to Fluorine and increase down the group from Lithium to Rubidium.*

Electrons in inner levels or *shells* tend to *shield* outer electrons from the full nuclear charge, which is reduced to *effective nuclear charge* (Z_{eff}). Electrons that have a greater *penetration* shield others more effectively. For example, electrons in level n = 1 shield those in level n = 2 very effectively, and those in n = 1 and n = 2 shield electrons in level n = 3. Electrons at the same level, but in different sublevels, also *shield* other electrons to some extent. The extent of *penetration* and *shielding effect* is in the order: $s > p > d > f$.

The *effective nuclear charge* (Z_{eff}) greatly influence atomic properties. In general,

- Z_{eff} increases significantly across a period (left-to-right)
- Z_{eff} increases slightly down a group.

In the periodic table, elements are divided into:

- the *s-block* (contains reactive metals of Group 1A (1) and 2A (2)),
- the *p-block* (contains *metals* and *nonmetals* of Group 3A (13) through 8A (18)),
- the *d-block* (contains transition metals (Group 3B (3) through Group (2B (12)), and
- the *f-block* (contains *lanthanide* and *actinide series* or *inner transition* metals).

Elements within the same *group* have the same number of electrons in their *valence* (outermost) shells, and they have *similar electron configurations*. They exhibit *similar chemical properties.* Elements within the same *period* have different number of electrons in their *valence shells* (the number is *increasing from left to right*) and *different valence shell electron configuration*. Therefore, elements in the same period are chemically different.

Example: arrange the following in order of increasing size K, Li, and Na. give reason for your order.

IONIC RADIUS OR SIZE

CATIONS: positive ion or cation has smaller ionic radius than its original neutral atom.

ANIONS: A negative ion or anion has a larger radius than that of the parent atom.

IONIZATION ENERGY

It is the minimum energy required to remove an electron from the outermost shell of a free or isolated gaseous atom to form a gaseous singly charge cation. *Generally, ionization energy increase across the period from left to right and decrease down the group*.

Factors that influence ionization energy

a. Atomic radius or distance of the outermost electron to the nucleus.
b. Stability of the electron configuration
c. Shielding effects of inner electrons
d. Size of the positive nuclear charge

Example: Arrange the following elements in decreasing order of first ionization energies of their atoms. Give reason for your answer. Na, Cl, and K.

ELECTRON AFFINITY E.A.

First electron affinity is the energy lost or gained when 1 mole of atoms in the free gaseous state gain 1 mole of electrons into the outermost shells to form 1 mole of gaseous singly charge anions. Generally, electron affinity increases across the period from left to right and decrease down the group.

Factors influencing EA.

a. Atomic size or effective nuclear charge
b. Stability of the electron configuration
c. Charge carried by the anion

ELECTRONEGATIVITY

It is the ability or power of an atom to attract or pull the shared pair of electrons to itself when it is in a bonded molecule. The smaller the atomic size the higher the electronegativity. Electronegativity therefore increases across the period from left to right and decrease down the group.

ELECTRON CONFIGURATION

Quantum Numbers

Principal Quantum Number (n)

The principal quantum number n indicates the shell or energy level in which the electron is found. The value of n can be set between 1 to n, where n is the value of the outermost shell containing an electron. This quantum number can only be positive, non-zero, and integer values. That is, n=1,2,3,4,..

For example, an Iodine atom has its outmost electrons in the 5p orbital. Therefore, the principal quantum number for Iodine is 5.

Orbital Angular Momentum Quantum Number (l)

The orbital angular momentum quantum number, l, indicates the subshell of the electron. You can also tell the shape of the atomic orbital with this quantum number. An s subshell corresponds to l=0, a p subshell = 1, a d subshell = 2, a f subshell = 3, and so forth. This quantum number can only be positive and integer values, although it can take on a zero value. In general, for every value of n, there are n values of l. Furthermore, the value of l ranges from 0 to n-1. For example, if n=3, l=0,1,2.

So in regards to the example used above, the l values of Iodine for n = 5 are l = 0, 1, 2, 3, 4.

Magnetic Quantum Number (m_l)

The magnetic quantum number, m_l, represents the orbitals of a given subshell. For a given l, m_l can range from $-l$ to $+l$. A p subshell (l=1), for instance, can have three orbitals corresponding to m_l = -1, 0, +1. In other words, it defines the p_x, p_y and p_z orbitals of the p subshell. (However, the m_l numbers don't necessarily correspond to a given orbital. The fact that there are three orbitals simply is indicative of the three orbitals of a p subshell.) In general, for a given l, there are $2l+1$ possible values for m_l; and in a n principal shell, there are n^2 orbitals found in that energy level.

Continuing on from out example from above, the m_l values of Iodine are m_l = -4, -3, -2, -1, 0 1, 2, 3, 4. These arbitrarily correspond to the 5s, $5p_x$, $5p_y$, $5p_z$, $4d_x2_{-y}2$, $4d_z2$, $4d_{xy}$, $4d_{xz}$, and $4d_{yz}$ orbitals.

Spin Magnetic Quantum Number (m_s)

The spin magnetic quantum number can only have a value of either +1/2 or -1/2. The value of 1/2 is the spin quantum number, s, which describes the electron's spin. Due to the spinning of the electron, it generates a magnetic field. In general, an electron with a m_s=+1/2 is called an alpha electron, and one with a m_s=-1/2 is called a beta electron. No two paired electrons can have the same spin value.

Out of these four quantum numbers, however, Bohr postulated that only the principal quantum number, n, determines the energy of the electron. Therefore, the 3s orbital (l=0) has the same energy as the 3p (l=1) and 3d (l=2) orbitals, regardless of a difference in l values. This postulate, however, holds true only for Bohr's hydrogen atom or other hydrogen-like atoms.

When dealing with multi-electron systems, we must consider the electron-electron interactions. Hence, the previously described postulate breaks down in that the energy of the electron is now determined by both the principal quantum number, n, and the orbital angular momentum quantum number, l. Although the Schrödinger equation for many-electron atoms is extremely difficult to solve mathematically, we can still describe their electronic structures via electron configurations

General Rules of Electron Configuration

There are a set of general rules that are used to figure out the electron configuration of an atomic species: Aufbau Principle, Hund's Rule and the Pauli-Exclusion Principle. Before continuing, it's important to understand that each orbital can be occupied by *two* electrons of opposite spin (which will be further discussed later). The following table shows the *possible* number of electrons that can occupy each orbital in a given subshell.

subshell	number of orbitals	total number of possible electrons in each orbital
s	1	2
p	3 (p_x, p_y, p_z)	6
d	5 ($d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{xz}, d_{yz})	10
f	7 (f_{z^3}, f_{xz^2}, f_{xyz}, $f_{x(x^2-3y^2)}$, f_{yz^2}, $f_{z(x^2-y^2)}$, $f_{y(3x^2-y^2)}$)	14

Using our example, iodine, again, we see on the periodic table that its atomic number is 53 (meaning it contains 53 electrons in its neutral state). Its complete electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$. If you count up all of these electrons, you will see that it adds up to 53 electrons. Notice that each subshell can only contain the max amount of electrons as indicated in the table above.

Aufbau Principle

The word 'Aufbau' is German for 'building up'. The Aufbau Principle, also called the building-up principle, states that electron's occupy orbitals in order of increasing energy. The order of occupation is as follows:

1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<7s<5f<6d<7p

Another way to view this order of increasing energy is by using **Madelung's Rule**:

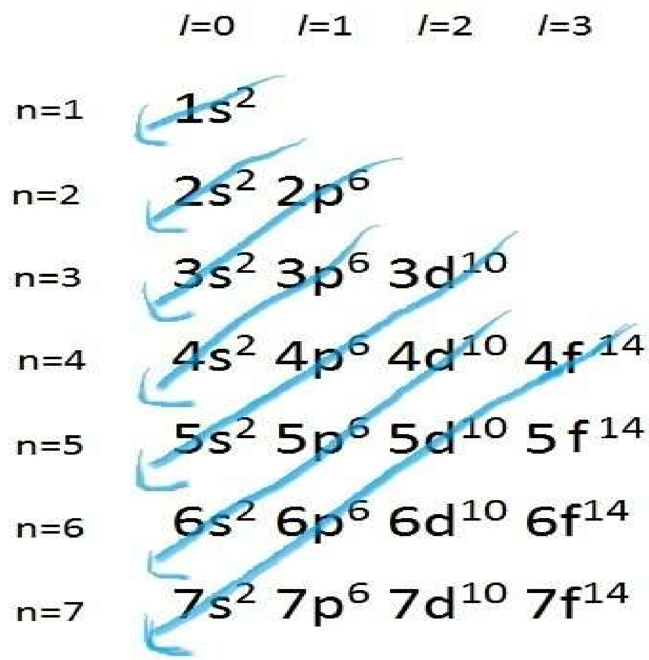


Figure 1. Madelung's Rule is a simple generalization which dictates in what order electrons should be filled in the orbitals, however there are exceptions such as copper and chromium

This order of occupation roughly represents the increasing energy level of the orbitals. Hence, electrons occupy the orbitals in such a way that the energy is kept at a minimum. That is, the 7s, 5f, 6d, 7p subshells will not be filled with electrons unless the lower energy orbitals, 1s to 6p, are already fully occupied. Also, it is important to note that although the energy of the 3d orbital has been mathematically shown to be lower than that of the 4s orbital, electrons occupy the 4s orbital first before the 3d orbital. This observation can be ascribed to the fact that 3d electrons are more likely to be found closer to the nucleus; hence, they repel each other more strongly. Nonetheless, remembering the order of orbital energies, and hence assigning electrons to orbitals, can become rather easy when related to the periodic table.

To understand this principle, let's consider the bromine atom. Bromine (Z=35), which has 35 electrons, can be found in Period 4, Group VII of the periodic table. Since bromine has 7 valence electrons, the 4s orbital will be completely filled with

2 electrons, and the remaining five electrons will occupy the 4p orbital. Hence the full or expanded electronic configuration for bromine in accord with the Aufbau Principle is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$. If we add the exponents, we get a total of 35 electrons, confirming that our notation is correct.

Hund's Rule

Hund's Rule states that when electrons occupy degenerate orbitals (i.e. same n and *l* quantum numbers), they must first occupy the empty orbitals before double occupying them. Furthermore, the most stable configuration results when the spins are parallel (i.e. all alpha electrons or all beta electrons). Nitrogen, for example, has 3 electrons occupying the 2p orbital. According to Hund's Rule, they must first occupy each of the three degenerate p orbitals, namely the $2p_x$ orbital, $2p_y$ orbital, and the $2p_z$ orbital, and with parallel spins (Figure 2). The configuration below is incorrect because the third electron occupies does not occupy the empty $2p_z$ orbital. Instead, it occupies the half-filled $2p_x$ orbital. This, therefore, is a violation of Hund's Rule (Figure 2).

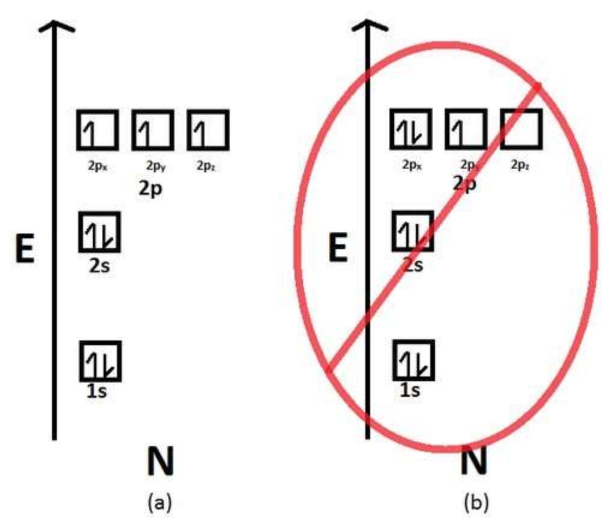


Figure 2. A visual representation of the Aufbau Principle and Hund's Rule. Note that the filling of electrons in each orbital (p_x, p_y and p_z) is arbitrary as long as the electrons are singly filled before having two electrons occupy the same orbital. (a)This diagram represents the correct filling of electrons for the nitrogen atom. (b) This diagram represents the incorrect filling of the electrons for the nitrogen atom.

Pauli-Exclusion Principle

Wolfgang Pauli postulated that each electron can be described with a unique set of four quantum numbers. Therefore, if two electrons occupy the same orbital, such as the 3s orbital, their spins must be paired. Although they have the same principal quantum number (n=3), the same orbital angular momentum quantum number (l=0), and the same magnetic quantum number (m_l=0), they have different spin magnetic quantum numbers (m_s=+1/2 and m_s=-1/2).

Electronic Configurations of Cations and Anions

The way we designate electronic configurations for cations and anions is essentially similar to that for neutral atoms in their ground state. That is, we follow the three important rules: Aufbau Principle, Pauli-exclusion Principle, and Hund's Rule. The electronic configuration of cations is assigned by removing electrons first in the outermost p orbital, followed by the s orbital and finally the d orbitals (if any more electrons need to be removed). For instance, the ground state electronic configuration of calcium (Z=20) is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. The calcium ion ($Ca^{2+}$), however, has two electrons less. Hence, the electron configuration for Ca^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6$. Since we need to take away two electrons, we first remove electrons from the outermost shell (n=4). In this case, all the 4p subshells are empty; hence, we start by removing from the s orbital, which is the 4s orbital. The electron configuration for Ca^{2+} is the same as that for Argon, which has 18 electrons. Hence, we can say that both are isoelectronic.

The electronic configuration of anions is assigned by adding electrons according to Aufbau Principle. We add electrons to fill the outermost orbital that is occupied, and then add more electrons to the next higher orbital. The neutral atom chlorine (Z=17), for instance has 17 electrons. Therefore, its ground state electronic configuration can be written as $1s^2 2s^2 2p^6 3s^2 3p^5$. The chloride ion (Cl^-), on the other hand, has an additional electron for a total of 18 electrons. Following Aufbau Principle, the electron occupies the partially filled 3p subshell first, making the 3p orbital completely filled. The electronic configuration for Cl^- can, therefore, be designated as $1s^2 2s^2 2p^6 3s^2 3p^6$. Again, the electron configuration for the chloride ion is the same as that for Ca^{2+} and Argon. Hence, they are all isoelectronic to each other.

Examples

Write the electron configuration of the following