CHM 101

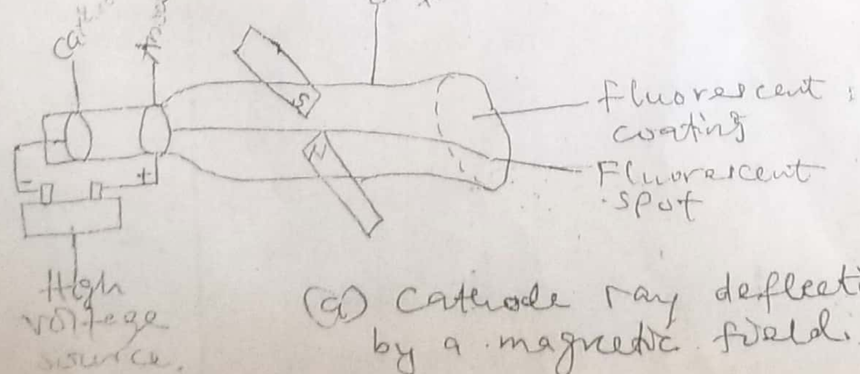
1st DEC, 2019.

ATOMIC STRUCTURE

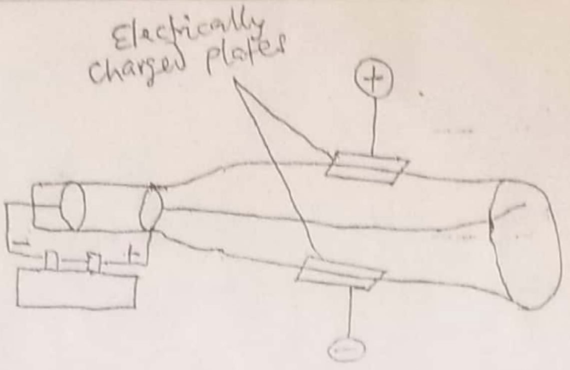
By the end of the 19th century, scientist had concluded that atoms were not the smallest particles of matter but were themselves made up of even smaller units, called subatomic particles. This realization came as a result of studies with a device called a cathode ray tube by British scientist Joseph John Thompson (J.J Thompson), 1856-1940.

When electricity is passed through a glass tube from which most of the air has been removed, a beam of cathode rays is generated. The rays are invisible, but if the end of the tube is coated with a fluorescent material, a glowing spot appears where the ray contact it.

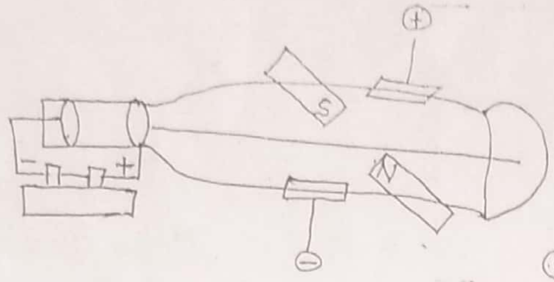
Thompson showed that cathode rays were deflected in one direction by a magnetic field (a) and in the opposite direction by an electric field (b). The direction of these deflections established that the charge on the particle was <u>negative</u>. By adjusting the strength of the electric and magnetic field, Thompson was able to balance out the deflections (C).



(a) Cathode ray deflection by a magnetic field.



(b) Cathode ray in an electric field



(C) Electric and magnetic fields to balance out the deflections

From the strength of the two opposing fields he was able to calculate the mass to charge ratio (m/e) of the particles in the ray. This observation established that particles in the cathode ray are electrons and are the fundamental particles of all matter.

In 1909, the American physicist Robert Millikan advanced the work of thompson where he determined the ~~exact~~ charge on the electron. Millikan's value was within 1% of the modern value of -1.602×10^{-19} C. He used Thompson value of m/e of electron and was able to calculate the mass of electron as 9.19×10^{-28} g.

In 1903, Rutherford discovered that the path of an α-particle could be deflected by a combination of electric and magnetic fields. Because it was deflected in the opposite direction from that of a β-particle, the charge on an α-particle had to be positive. The β-particle (an electron) was assigned a charge of 1-, based on its ~~observation~~ observed behaviour in both fields, the α-particle was assigned a charge of 2+, α-particles were found to have nearly the mass of Helium (He) atom.

Thompson formulated the "plum pudding" model, based on the hypothesis that an atom was a diffuse sphere of +ve charge with -vely charged electrons embedded in the sphere like raisins in a plum pudding.

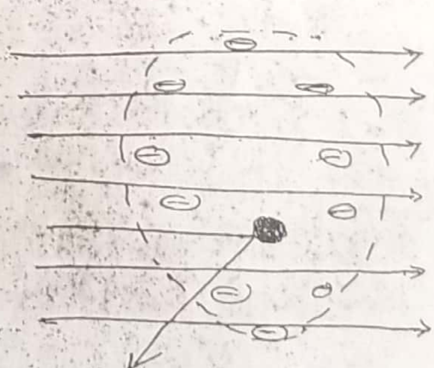
Fig 4: Rutherford Model of atom.

The plum pudding model formulated by ~~Rutherford~~ Thompson was discarded because of the results of an experiment Rutherford directed his students Han Geiger (for whom geiger counter was named) and Ernest Marsden. They bombarded a thin foil of gold with α-particles emitted from a radioactive source. They measured how many α-particles were deflected from their original path and to what extent they were deflected.

Rutherford hypothesis was that, if thompson's model were correct, most of the α particle would pass straight through the diffuse +ve spheres of gold atoms but a few of the particles would interact with the tiny electrons embedded in these spheres and be deflected slightly.

⊖: Electrons
⟶: path of α-particles
( ): region of diffuse +ve charge

Fig 5: (a)



●: Nucleus; region of [con]trated +ve charge

Fig 6: (b)

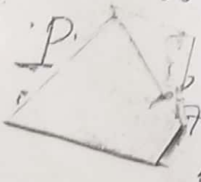
There observation was completely different from ... work.

The gold-foil experiment suggested that the plum-pu... model be rejected because it could not account f... large-angle of deflections. Rutherford concluded that ... large deflections of +vely charged α-particles occurred wh... particles encountered small regions characterized by ... concentrations of +ve charge and high mass (the nuclei of gold atoms). Rutherford determined that the region of +ve charge was only about 1/10,000 of the size of the gold a... Rutherford model of atoms showed above fig 4. became the ... for our current understanding of atomic structure. "It assu... that atoms consist of massive but tiny +vely charged nucle... that are far apart from each other and are surrounded by -vely charged electrons". This gives rise to the description ... atoms as being mostly empty space occupied by electrons plus tiny centre called the nucleus, which contains all of the at... +ve charge and nearly all its mass.

By 1920 a concensus was growing that hydrogen nuclei which Rutherford called protons were fundamental buildi... blocks of all nuclei eg to account for the mass and charg... of an α-particle, Rutherford assumed that it was made of four protons, two of which had combined with two electrons to form two neutral particles, which he called neutrons.

Neutrons, according to Chadwick (Rutherford student) in 1932 bombarded a thin sheet of Be with α-particle. He discovered particles which have the same mass as the protons but have no charge. The particles are called the neutrons. They ... found in the nucleus.

P.



... according to R.A Millikan found out that the charg... ...ton is $+1.6 \times 10^{-19}$C which is same as that of the ... electron but with opposite charge. ... was ...tuting the value of the charge in the e/m ratio, the ... to mass of proton is calculated to be 1.67×10^{-27} kg. Comparing the mass of the proton with that of the electron, the proton is approximately 1840 times heavier than the electron.

PROPERTIES OF SUBATOMIC PARTICLES

Particle	Symbol	In atomic mass unit (AMU)	In grams (g)	Relative value	charge (e^-)
Neutron	^1_0n	$1.00867 \simeq 1$	1.67494×10^{-24}	0	0
Proton	^1_1P	$1.00728 \simeq 1$	1.67263×10^{-24}	1+	$+1.602 \times 10^{-19}$
Electron	$^0_{-1}e$	$5.485799 \times 10^{-4} \simeq 0$	9.10939×10^{-28}	1 —	-1.602×10^{-19}

Thompson repeated his experiment and observed rays moving in the opposite direction to that of the catode rays.
He made the following observations that
- The rays travel in straight line
- They are +vely charged.

He determined the m/e and obtained a value 9.58×10^7 C/kg.
He called it proton.

Rutherford model of atomic structure is that the electrons are moving in circular orbits round the nucleus.

The development of the quantum theory and the interpretation of the atomic emission spectra helps us to understand the arrangement of electrons in the atom.

QUANTUM THEORY

Max planck proposed a model based on the view that light behave like a wavelike and particle-like properties. He called the particles of radiant energy quanta. In his model, called quantum theory, quanta are the smallest amount of radiant energy in nature, such that a single atom molecule might absorb or emit

The quantum theory is based on the ~~assumption~~ idea that energy absorbed and emitted in discrete quanta.

A quantum is the smallest discrete quantity of a particular form of energy while he proposed that the energy (E) of a quantum was related to the frequency (ν) of the corresponding wave of radiation by a constant (h), $E = h\nu$

When metals such as Na, Ca, K, Cu or their compound are heated and examined using spectrophometer they gave out the following colours Na — golden yellow flame, Ca — Brick red, K — lilac & Cu — greenish blue and composed of descrete lin ~~lines~~ of different colours in the visible region of the spectrum of white light ranging from red to violet. *This kind of ~~[illegible]~~ spectrum is called the line emission spectrum. The wavelen of the lines are characteristics of the elements.*

FEATURES OF BOHR'S HYDROGEN MODEL

1. The electron in a hydrogen atom occupies a discrete energy leve and may exist only in the available energy levels.
2. The electron may move from one energy level to another by either acquiring or releasing an amount of energy equal to the differences in the energies of the two le
3. Each energy level is designated by a specific value for n called the principal quantum number. The level closes to the nucleus has the lowest value for n; that is n = 1, next level 2 and so on.

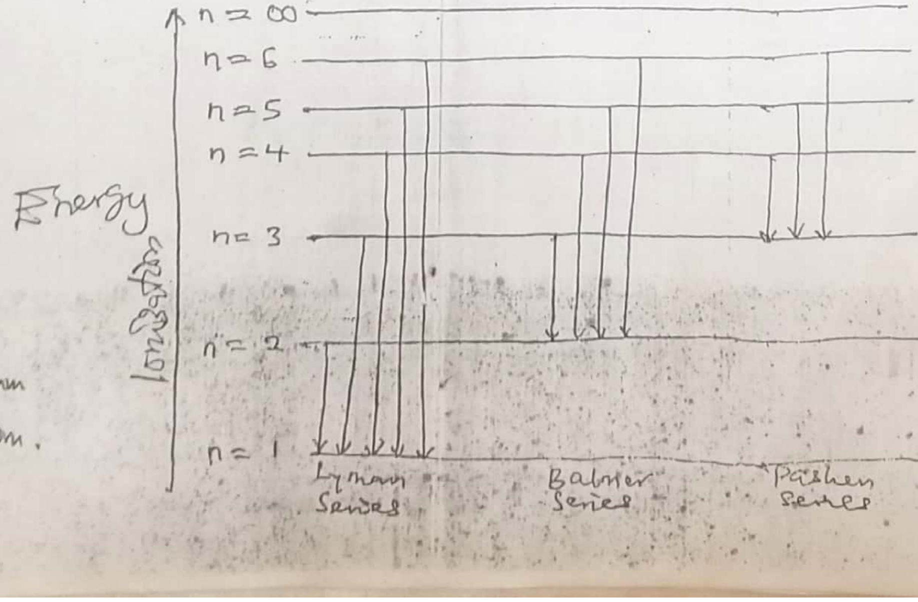


Fig: Emission spectrum of Hydrogen atom.

The energy level diagram shows the allowed states for an electron in the atom. An energy level is an allowed state that an electron can occupy in an atom while electron transitions is the movement of electrons between energy levels.

Bohr model proposed that electron can move from the ground state to one of the excited states (e.g $n_1 \rightarrow n_3$), from one excited state to another (e.g $n_5 \rightarrow n_4$) or from an excited state back to the ground state ($n_2 \rightarrow n_1$).

Hydrogen electron can make this transition if only it absorbs or emits a quantum of energy that exactly matches the energy difference (ΔE) between the two states i.e.

$$\Delta E = E_f - E_i$$

One of the strength of the Bohr model is that it accurately predicts the energy needed to remove the electron. This energy is called the ionization energy of the hydrogen atom.

As the value of n increases, the energy of the orbit increases. These orbits are called shells and are designated as K, L, M, N etc. The maximum number of electrons in a shell is given as $2n^2$.

Value of n	Name of electron shell	No of electrons
1	K	2
2	L	8
3	M	16
4	N	32

The Bohr model has now been replaced by the wave mechanics or quantum mechanics (developed by Schrodinger which describes the wavelike behaviour of particles on the atomic level) to explain the spectrum of more completed atom.

Wave mechanics regards electrons as having wave-like properties. This properties makes it difficult to locate electron. It does not restrict the electron to certain energy level but describes a region around the nucleus where there is a possibility of finding an electron with a certain amount of energy.

This is called orbitals or wave functions of electrons in
Orbital is identified by the quantum number
- Principal quantum number (n)
- Angular momentum quantum number (l)
- Magnetic quantum number (m)
- Spin quantum number.

1. Angular momentum/Azimuthal quantum number: Describe possibility of locating an electron within a region in a shell with a certain amount of energy. It is given as l is an integer, the value starts from from 0 to $n-1$.

If $n = 1$
Then $l = 0$: This describes an s- orbital.

If $n = 2$
Then $l = 0$ and 1
$l = 0$ describes an s- orbital
$l = 1$ describes a p- orbital

If $n = 3$, then $l = 0, 1$ and 2
$l = 0$ describes an s- orbital
$l = 1$ " a p- orbital
$l = 2$ " " d- orbital

If $n = 4$, then $l = 0, 1, 2, 3$ ~~&~~ 4
$l = 0$ describes s - orbital
$l = 1$ " p - orbital
$l = 2$ " d - "
$l = 3$ " f - "

2. Magnetic quantum number: Describes splitting of orbital in the magnetic field. It is denoted by letter m and the values of m depends on the value of l. m starts from $-l$ to 0 $-+l$. ($-l$ to $+l$).

0000.

3.7×10^{10}

37000000000

If $l = 0$, $m = 0$

$l = 0$ is an s-orbital and there is only one value for m which is 0. Therefore, s-orbital does not split in the magnetic field.

If $l = 1$

$m = -1, 0$ and $+1$

$l = 1$ is an p-orbital and it splits into three sub-~~atomic~~ orbitals orbitals in the magnetic field as P_x, P_y and P_z

If $l = 2$

$m = -2, -1, 0, +1$ and $+2$

$l = 2$ is a d-orbital and d-orbitals splits into five sub-atomic orbitals in the magnetic field.

If $l = 3$, $m = -3, -2, -1, 0, +1, +2, +3$.

$l = 3$ is an f-orbital & it splits into seven sub-~~atomic~~ orbitals in the magnetic field. Each sub-orbitals can accomodate maximum of two electrons.

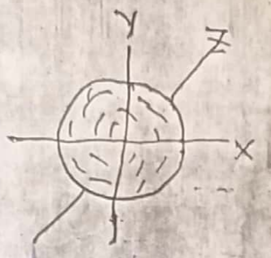
3. Spin quantum number: Describes the rotation of electron in it axis. Negatively charged particles repel each other in the orbital. To attain stability, they spin on their axis in opposite directions to generate force of attraction, therefore spin quantum no. They are represented by the value of S and is either $+\frac{1}{2}$ or $-\frac{1}{2}$

This is in agreement with the pauli Exclusion principle which states that no two electrons in an atom can have the same values for all four four quantum numbers i.e they have opposite spins eg 2He ($1s^2$) $\boxed{1L}$

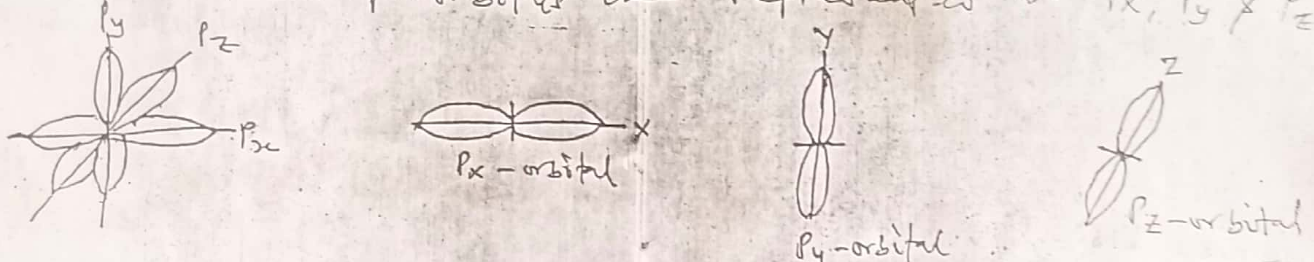
4. Principal quantum number: Describes the main energy level of an atom and is designated by n, n = 1, 2, 3, 4 to infinity referred to as K, L, M, N etc, shell ~~number~~ n is an integer. The lowest energy state or level is (ground state) ranged from 1 to infinity.

Shapes of orbitals.

The shape of s- orbital is symmetrically spherical

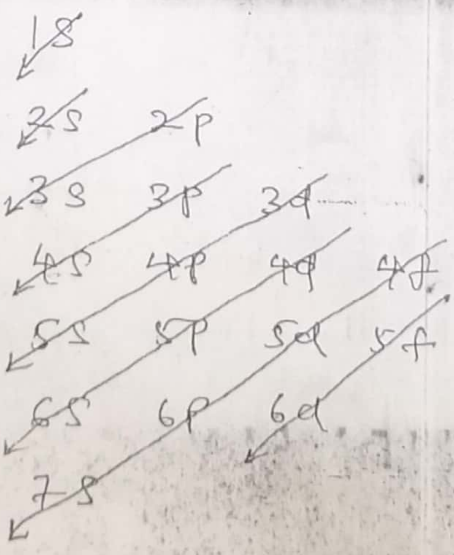


The shape of P- orbitals is dumb-bell. Its electrons can m about three axis, X, Y and Z which are at angle 90°C to ea other. The three P-orbitals are represented as P_x, P_y & P_z



Orbital electronic configuration

Arrangement of electrons in the atom is in accordance with the Aufbau principle, " orbitals are arranged in an incr easing order of energy. Electron enter into orbital of lower en ergy, first until it is completely filled before it can occupy orbital of higher energy.



Qs: Write the electronic configuration of the 1st 30 element.

Degenerate orbitals

p, d & f orbitals are called degenerate orbitals because they split in the magnetic field and ~~have~~ are energetically equivalent. Degenerate orbitals are filled according Hund's rule which states that when electrons enter into degenerate orbitals, they do so singly with the same spin until the orbitals are completely half filled before pairing start taking place e.g.

$^{14}_{7}N \quad 1s^2 2s^2 2p^3$

$\boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \quad \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

S- orbital is not degenerate because it is not affected by magnetic field, so do not split.

p- orbital splits into three sub-orbitals as $\boxed{\ }\boxed{\ }\boxed{\ }$

d- " " " five " " " $\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }$

f- " " " seven " " " $\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }$

Note that S = orbital takes only two electrons maximum.

p = " " " six " "

d = " " " ten " "

f = " " " fourteen " "

THE MODERN PERIODIC TABLE

4TH DEC 2019.

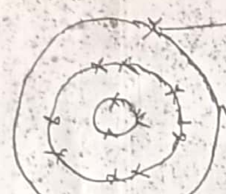
The arrangement of elements in vertical columns and horizontal rows forms a table known as the periodic table.

The periodic table makes it easier to study the physical and chemical properties of an element in a group.

* The vertical column are called groups while the horizontal rows are called periods. We have eight or eighteen groups and seven periods.

* The group is the number of electrons in the outermost shell of the atom while the period is the number of shells in the atom. e.g

$^{23}_{11}Na$



This means that sodium is found in group 1, Period 3.

The periodic table is categorise according to blocks. We have four major blocks of elements.

1. **The S – block elements**

This comprises of element in which their outer electrons are in S – orbital. They are element in group 1 and 2. They are called alkali and alkaline earth metals

2. **The P – block elements**

They are made up of element in which the outer electrons are in P – block orbital. They are usually found in group 13 to 18.

3. The d- block elements

They comprised of element whose d- orbital is be filled with electrons. They are found between the group 3 to 12 and in the period 4 to 7. They are called the transition elements.

4. The f- block elements

Element that their f-orbital is being filled with electrons. They are also known as the Lanthanide and Actinide series or the inner transition elements.

Assignment: Write short notes on the families of elements; group 1 to 8.

Features of the d- block (transition elements) elements.

1. They have variable oxidation states
2. Their compounds or ions are coloured
3. They form complex ions
4. They are catalytic in nature
5. They are paramagnetic

1. Variable oxidation states.

The elements can easily lose electrons from the 3d and 4s orbitals to form compounds with different oxidation states because ~~there is little~~ the energy difference b/w the 3d and 4s electrons is less. For instance, the configuration of Mn is

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

Mn can lose the two electrons in the 4s - orbital to give Mn^{+2} in $MnCl_2$. Or it can lose the two electrons in s - orbital and also two electrons from the 3d-orbital to give +4 oxidation state( ) in MnO_2. Again it can lose the ~~two and five~~ $4s^2$ and $3d^5$ to give +7 oxidation state.

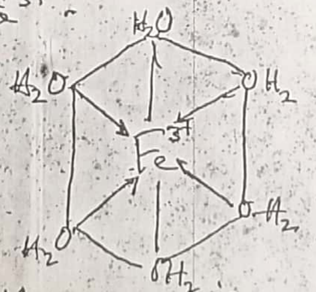
coloured ions formation.

The formation of coloured ions is as a result of the presence of unpaired electrons in the d-orbital. The ions of Sc and Zn are not coloured b/c they do not have partially filled d-orbitals in their ions. Sc^{3+} — $3d^0$ colourless and Zn^{2+} — $3d^{10}$ colourless.

When white light shines on a transition element ions, some of the energies of these coloured component are absorbed to excite the d-electron. ~~The remaining light~~ Those that do not absorbed cannot appear as white. The remaining light is transmitted as the colour of the metal ion.

3. ## Formation of complex ion

Transition elements have tendency to form complex ions. A complex ion has a central metal ion which is +ve and is linked to other atoms, ions or molecules called ligands by coordinate bond. The ligands are -vely charged ions. The ligands donate electron pairs to the vacant d-orbital of the metal ion. e.g. $[Fe(H_2O)_6]^{3+}$. Each water molecule uses a lone pair of electrons on the oxygen to form a co-ordinate bond with the Fe^{3+}.



They formed complexes b/c of the vacant d-orbital

4. Catalytic property

They are catalytic in nature b/c of their ability to f... bonds with reactant molecules b/c of the available number of 3d and 4S electrons. They are good catalyst b/c they change their oxidation states easily. They are particularly used in Industrial processes. For example:

Finely divided Fe is used in the Haber process for the manufacture of NH_3. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$.

Vanadium (V) oxide V_2O_5 is used in the contact process for the manufacture of H_2SO_4.

Nickel catalyst is used in the hydrogenation of alkenes to form alkanes and hardening of oil to form fat sold as margarine.

5. Paramagnetic property

Substances that are weakly attracted to a strong magnetic field are paramagnetic while those that are weakly repelled are diamagnetic in nature.

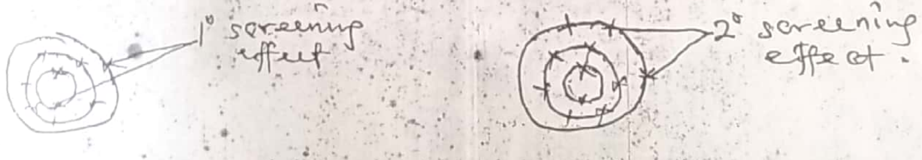
Paramagnetic property of transitional element is caused by unpaired electrons and the intensity is dependent on the no of unpaired electrons. The higher the intensity of paramagnetism or paramagnetic behaviour, the higher the no of unpaired electrons.

ATOMIC PROPERTIES OF ELEMENTS

Properties of element varies from one group to the other and across the periods. Some of these properties are:
1. Atomic radius 2. Ionic radius 3. Ionization energy.
4. Electron Affinity 5. Electronegativity.

1. Atomic radius: This is half the inter nuclei distance b/w two covalently bonded atoms of the same elements which is univalent.

The radius of an atom is determined by two forces and the forces are due to
(i) The strength of the nuclear charge
(ii). The screening effect: This is repulsion b/w electrons. It is divided into (a) primary screening (b) secondary screening effects. The primary screening effect is due to repulsion of the outermost electrons by the inner electrons while the secondary is due to repulsion b/w electrons in the same shell. eg.



Moving from left to right of a particular period, the radius of the atoms decreases. In this case all electrons are in the same shell but nuclear charge increases from left to right. The increase in nuclear charge results from the addition of proton which tends to draw all the electrons closer to the nucleus and hence decreases the size of the atom (i.e. radius decreases)

Moving down a group, the number of electrons in the out shell remain the same but there is additional shell which makes the outer electron far away from the nucleus, thereby increasing the radius of the atom.

2. Ionic radius

A positive ion is formed when an electron is removed from a neutral atom and ~~negative~~ when an electron is added to a neutral atom, a negative ion is formed. The size of a +ve ion is smaller than a ~~-ve ion~~ neutral atom. This is b/c when an electron is removed, the effective nuclear charge on the outer electron is increased, making the shell to be drawn closer to the nucleus and the size decreases.

The size of a -ve ion increases or bigger than that of its neutral atom b/c there is an increase in the repulsive force b/w the electrons and this makes the shell to expand and the size becomes bigger.

Moving from left to right of a particular period, the size of the ions decreases. Moving from top to bottom of a group, the size of the ions increases.

3. Ionization energy

This is the amount of energy needed to remove 1mole of a losely ~~bonded~~ bound electron from a neutral atom in the gaseous state. Ionization is endothermic process as it involves bond breaking b/w the electron and the +ve nucleus.

The energy needed to remove the 1st electron is called the 1st ionization energy

Assignment: Explain 2nd and 3rd ionization energy.

~~The ionization energy of the~~ 2nd Ionization energy differs in energy b/c the amount of energy needed to remove the 2nd electron is greater than the former. When the 1st electron is removed, the nuclear charge on the outer electron shell is increased. The shell is drawn closer to the nucleus and the size decreases. The outer electrons are now more firmly held to the nucleus thereby requiring more energy to remove.

* Moving from left to right, ionization energy increases. This is b/c the size of the atom decreases, the outer electrons are more firmly held to ~~the~~ nucleus due to increase nuclear charge, hence more energy needed to remove the electron.

The ionization ~~of~~ value energy of group II and III element and those of group V and VI greatly varies. The ionization energy of group II elements is greater than group III in the same period while element in group V is greater than group VI of the same period. This is b/c of completely filled orbital or half filled orbital that gives the atom extra stability.

* Moving from top to bottom of a group, ionization energy decreases b/c the size of the atom increases, and the outer-most electron is farther away from the nucleus, hence less firmly ~~held~~ held to the nucleus. Less amount of energy is required.

4. Electron affinity:

This is the amount of energy released when an electron is added to neutral atom in the gaseous state. This process is exothermic as it involves bond formation b/w the incoming electron and the +ve nucleus.

* Moving ~~at a cross~~ across a period, electron affinity increases. This is b/c the size of the atom decreases across the period and there is greater attraction for incoming electron by the +ve nucleus.

* Moving down a group, the electron affinity decreases. This is b/c the size of the atom is becoming bigger and there is less attraction of the +ve nucleus for incoming electron.

5. Electronegativity:

This is the ability of the an ~~in~~ atom in a molecule to attract electrons to itself.

* Moving across a period, electronegativities value increases. This is b/c the size of the atom is decreasing and there is an increase in nuclear charge and therefore, the attraction for electrons increases.

* Moving ~~this~~ down the group electronegativity decreases. This is b/c ~~of~~ the size of the atom increases and hence less the attractive effect of the nuclear charge on the electron.

Non metallic elements which attract electrons have high electronegativity value but metals which lose electrons easily have low electronegativity value. Fluorine is the most most electronegative element.