

# CHM 121 FOUNDATION CHEMISTRY

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**INTRODUCTION :** Chemistry is the study of matter, its properties and the principles governing the changes which matter can undergo. Also chemistry involves carrying out analysis / experiments, making careful and thorough observations and drawing conclusion from the observations.

### ATOMIC THEORY OF MATTER

Atomic theory was first put forward in 1808 by an English scientist, John Dalton. According to Dalton's atomic theory, atom is defined as the basic unit of an element that can enter into chemical combination. This theory forms the basis of theory of the atom. The postulates of Dalton's atomic theory of matter are

1. Elements are made up of small, invisible particles called atoms.
2. Atoms can neither be created nor destroyed.
3. Atoms of the same element are alike in every respect and differ from atoms of all other elements.
4. When atoms combine, they do so in simple ratio.
5. All chemical changes result from the combination or separation of atoms.

Note: Atomic theory of matter was partially

Supported by experimental evidences deduced from Law of conservation of mass law of definite proportion & law of multiple proportion.

With more research work, modifications were made on Dalton's atomic theory of matter. These are :-

1. Matter is composed of more fundamental particles, some which are electrically neutral, some carry positive charge and some negative charge. This implies that atom is divisible.
2. Atoms can neither be created nor destroyed. This holds for ordinary chemical reaction and supports law of conservation of mass but not in nuclear reaction.
3. Atoms of the same element are alike in all respect and differ from atoms of all other elements. The discovery of Isotope makes the above statement unacceptable.
4. When atoms combine, they do so in simple ratios or small whole numbers. This holds true for inorganic compds which contain few atoms per molecule and does not hold for organic compds such as proteins, fats, starch and polymers.

### Assignment

- \* Highlight the postulates of Dalton's atomic theory of matter and discuss the modifications.
- \* Read up about the following laws of chemical combination.
  - ⇒ Law of conservation of mass.
  - ⇒ Law of definite proportion.
  - ⇒ Law of multiple proportion.

### DISCOVERY OF THE SUB-ATOMIC PARTICLES

Based on Dalton's atomic theory, Atom can be defined as the basic unit of an element that can enter into chemical combination. Dalton imagined an atom that was both extremely small & indivisible. However, a series of investigations that began in the 1850's & extended into the twentieth century clearly demonstrated that atoms actually possessed internal structure, that is they are made up of even smaller particles which are called sub-atomic particles. This research lead to the discovery of three such particles - Electrons, Protons & Neutrons.

### THE ELECTRON

The discovery of electron and the study of their behaviours came about with the

invention of the cathode ray. Experiment showed that when an electric current from a high voltage source was passed through a glass discharge tube containing gas at a low pressure, the tube glows. The glow was due to some kind of ray called CATHODE RAYS. It was argued that since these rays travel in a straight line from the cathode (-ve terminal) to the anode (+ve terminal), the ray must be negative in nature.

J. J. Thompson, in 1897, settled the issue by proving that cathode rays are negatively charged particles. He built an apparatus (see below) in which deflection of a beam of cathode rays caused by magnetic field was countered by an opposing deflection caused by an electric field.

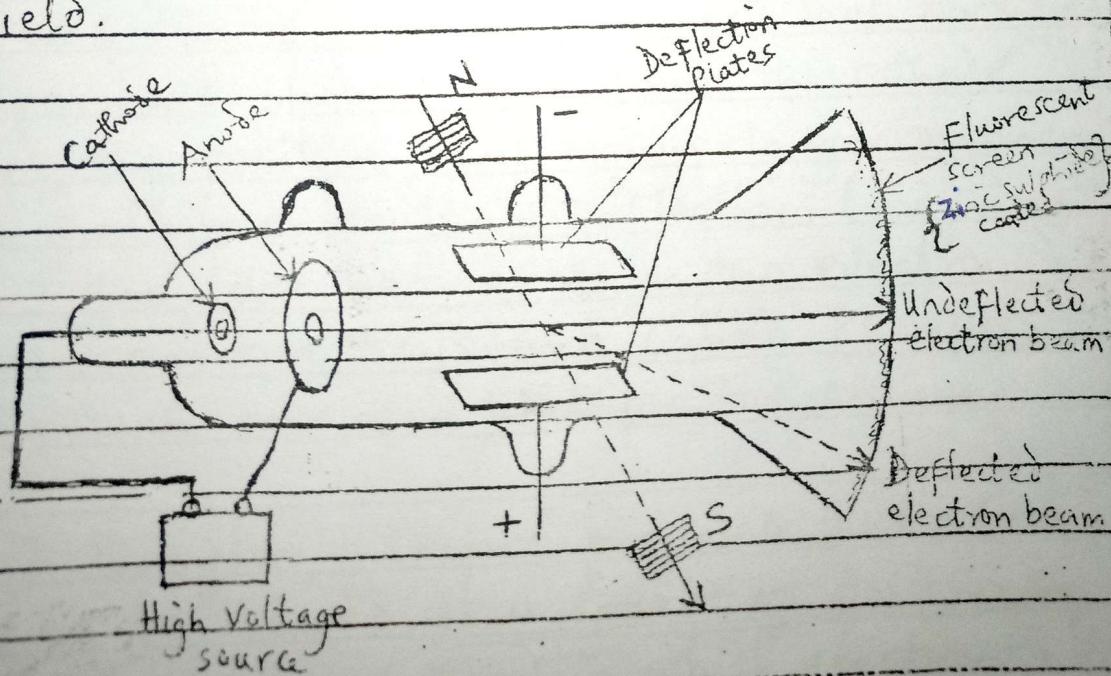


Fig 1 : Thompson's apparatus

Cathode rays leave the cathode and accelerates toward the anode. Many pass through the hole in the anode and stream across the tube from left to right. The electric field alone deflects this beam down, and the magnetic field alone deflects it up. In careful experiments, Thompson varied the fields so as to balance exactly the opposing deflections. From the conditions of balance, he demonstrates that cathode "rays" have mass and are truly particles. These particles characterised by Thompson were recognised to be fundamental units of electricity called ELECTRONS.

He went further and measured the ratio of electric charge to mass of an electron to be  $-1.76 \times 10^8 \text{ C/g}$ .

Where  $C$  = Coulomb, unit of electric charge.

→ Thereafter, in a series of experiments carried out between 1908 & 1917, an American scientist Robert Millikan, in his famous OIL DROP experiment founded the charge on the electron to be  $-1.602 \times 10^{-19} \text{ C}$ , from there he calculated the mass of the electron to be  $\frac{1}{e}$

$$\text{Mass of an electron} = \frac{\text{Charge}}{\frac{\text{Charge}}{\text{Mass}}}$$

$$= -1.602 \times 10^{-19} \text{ C}$$

$$= -1.76 \times 10^8 \text{ C/g}$$

$$= 9.10 \times 10^{-28} \text{ g}$$

Exceedingly a small mass

\* Read about the Millikan's oil drop experiment.

### THE PROTON

Since atom as a whole is electrically neutral, there must exist inside the atom enough positively charged components to balance the negative charge of the electrons. J.J. Thompson repeated his earlier experiment but this time used a perforated central cathode. He noticed rays in opposite directions to the anode and proved it was due to positively charged ions. Further experiments showed that unlike the cathode rays, the positive rays require larger magnetic field to cause them deflections (indicating that they are heavier than the electrons).

These positive rays are called PROTONS and each carries a unit positive charge.

⇒ J.J. Thompson, therefore proposed that atom could be viewed as a sphere of positively charged matter (atom) in which electrons are uniformly distributed (or embedded).

to make it neutral at every point.

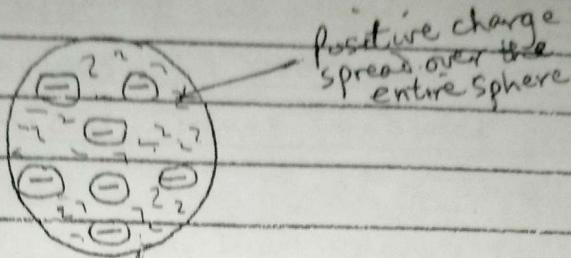


Fig 2 : Thompson's model of the atom.

This view was dropped because of findings of Ernest Rutherford and two other scientists, Wilhelm Geiger and Ernest Marsden.

atomic model)

### ✓ RUTHERFORD MODEL OF ATOM

In 1910, Rutherford together with his associate Geiger and an undergraduate (his student) Marsden, bombarded a thin gold foil with fast moving alpha particles. They found that most of the  $\alpha$ -particles pass through the foil undeflected. Some were deflected as large angles while very few were sent back on their paths.

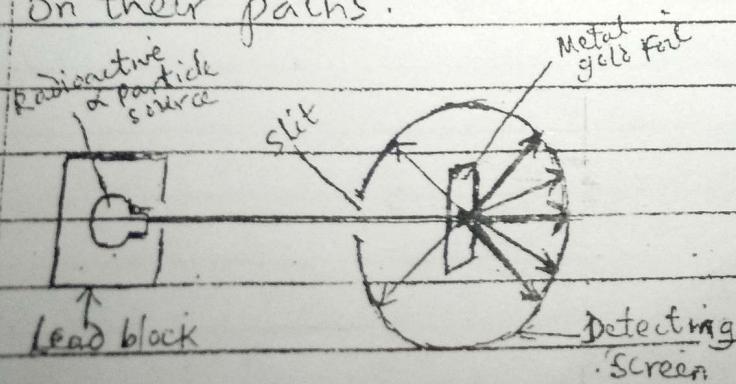
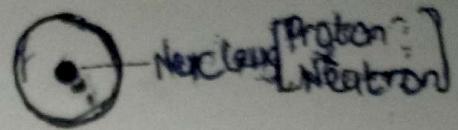


Fig 3(A) Scattering of  $\alpha$  particle by a metal foil (Thin gold foil)



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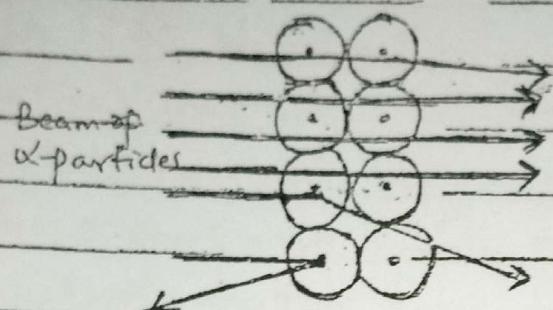


Fig 3(B)

Magnified view of  $\alpha$ -particle being deflected by atomic nuclei.

- Alpha particles are positively charged and many of them passing through the foil undeflected suggested that most of the ~~gold~~ <sup>atoms</sup> ~~foil~~ was empty. Rutherford, using the findings in the above experiment proposed a model for atom.
- He proposed that the atom consisted of a tiny positively charged nucleus.
- The nucleus is centrally placed in the atom and the electrons surround it.
- The very small number of deflections of  $\alpha$ -particles suggests that the nucleus is a centre of heavy mass and positive charge.
- The protons and neutrons occupy the nucleus while the electron move in orbits around it.

In a separate experiment, it was found that each proton carries the same quantity of charge as an electron & has a mass of  $1.672 \times 10^{-24}$  g about 1840 times the mass of the charged electron.

NB Neutrons have no charge tho they have high electrical radiation

QUESTION 10

Paper 1B

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## THE NEUTRON

Rutherford & his team postulated that there must be another type of sub atomic particle in the atomic nucleus. The prove was provided by an English Physicist James Chadwick in 1932. He bombarded a thin sheet of Beryllium with  $\alpha$ -particles, a very high energy radiation was emitted. Later experiments showed that the rays actually consisted of electrically neutral particles having a mass slightly greater than that of protons but carries no charge. Chadwick named these particles

### \* NEUTRONS

The table below shows the properties of sub-atomic particles.

PARTICLES	MASS (g)	COULOMB (C)	ELECTRON CHARGE
Proton	$1.67 \times 10^{-24}$	$+1.602 \times 10^{-19}$	+
Neutron	$1.67 \times 10^{-24}$	0	0
Electron	$9.10 \times 10^{-28}$	$-1.602 \times 10^{-19}$	-

In 1895, Wilhelm Rontgen (German scientist) noticed that when cathode rays struck glass and metals, new and very unusual rays were emitted.

These rays were highly energetic and could penetrate matter, darkened covered photographic plates & caused a variety of substances to fluoresce, but could not be deflected by a magnet. They did not consist of charged particles as did cathode rays. Rontgen called them X-RAYS.

In 1914, Moseley found that he could assign numbers called atomic number to an element based on the frequency of the X-rays the element emits when it is used as the anode of an X-ray tube. Further experiments enabled him to conclude that the atomic numbers represented the number of protons in the nucleus.

### ATOMIC NUMBER / MASS NUMBER / ISOTOPES

⇒ Atomic number - Is the no of protons in the nucleus of an atom of an element. Note - In neutral atom, the no of protons is equal the no of electrons.

⇒ Mass number - Is the sum total of neutrons & protons present in the nucleus of an atom of an element.

Mass no.  $\rightarrow A$ Eg. Atomic no.  $\rightarrow Z$  X

No of Neutron = Mass no minus Atomic no

$$A - Z$$

Example : Fluorine mass no = 19

$$\text{Atomic no.} = 9$$

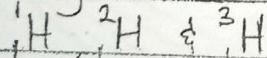
$$\text{No of neutron} = 19 - 9 = 10$$

⇒ Isotope - Atoms of the same element having the same atomic number but different mass number. The occurrence or existence of isotopes is called ISOTOPY. Isotopy arises due to the difference in the number of neutrons in the nucleus of an atom of a particular element.

Isotopes of an element have same chemical properties.

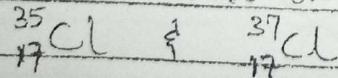
Examples :-

⇒ Hydrogen has three isotopes

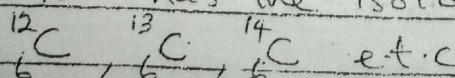


(i.e. Protium, deuterium & tritium respectively)

⇒ Chlorine has two isotopes



⇒ Carbon has the isotopes

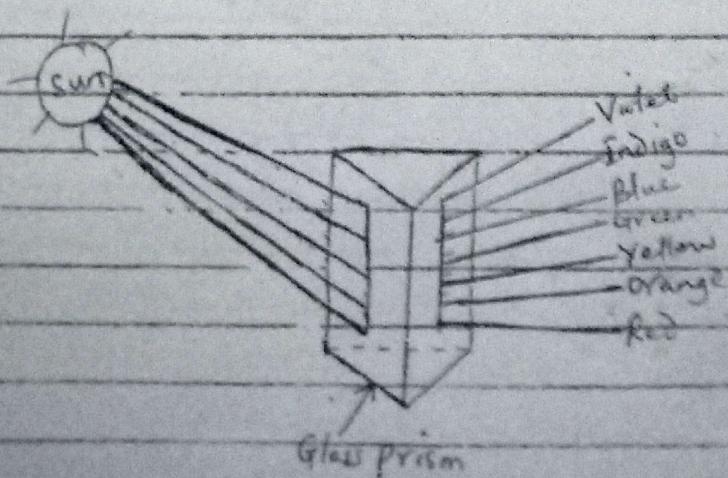


\* Mention other elements that exhibit isotopy & their isotopes.

## EMISSION SPECTRA

When any element is heated to a very high temperature or when an electric discharge is passed through a gaseous element at low pressure, it emits radiation of certain definite wavelengths which are characteristics of that particular element. The radiations are called SPECTRA and can be observed using a suitable instrument SPECTROSCOPE.

Sir Isaac Newton in the mid 1600s passed a beam of Sunlight through a glass prism. The prism separated the light into series of different colours like a rainbow. This series of different colours is called the VISIBLE SPECTRUM.



Each colour of light is associated with specific amount of energy. This means that light is a form of energy.

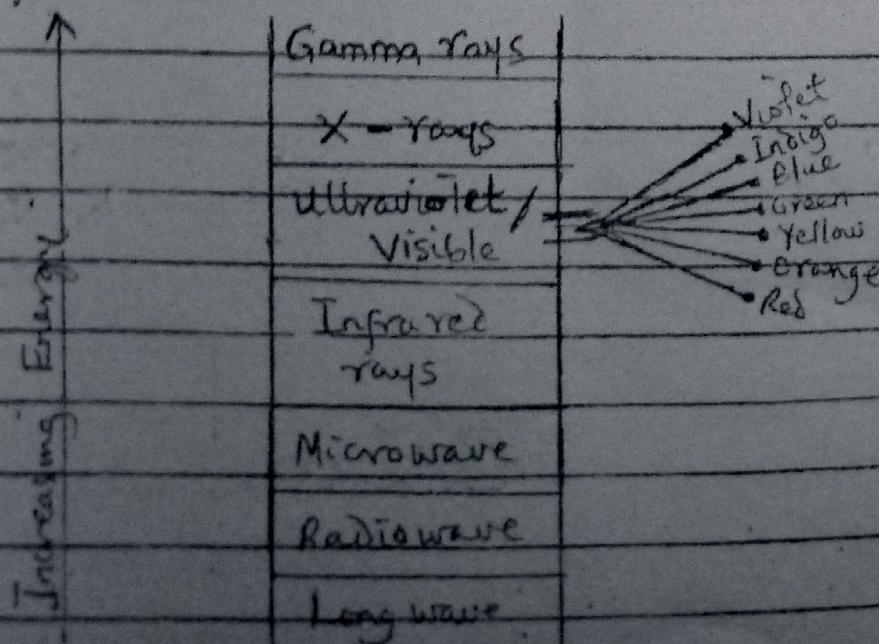
Also, this type of spectrum consists of

different constituent colours merging into each other is called CONTINUOUS SPECTRUM.

Continuous spectrum is produced by Sunlight or light from any hot body. The visible spectrum produced by Sunlight is a small part of the electromagnetic Spectrum.

The spectrum produced by an element consists of a series of bright lines separated by dark bands. This spectrum is called LINE SPECTRUM. i.e. Line spectra consist of series of sharply defined lines each corresponding to a definite wavelength. Each element produces its own unique line spectrum. The line spectra have been found to be very useful in identifying elements in unknown samples.

- \* Draw and label fully the electromagnetic spectrum.



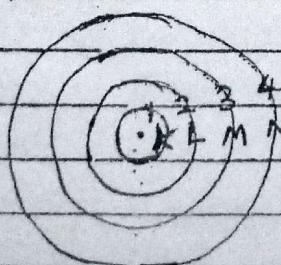
Sketch of the electromagnetic spectrum.

## THE BOHR ATOMIC MODEL

In 1913, Neil Bohr suggested that electrons are responsible for line spectra. He <sup>proposed</sup> suggested the existence of certain circular orbits/shells at definite distance from the nucleus in which the electron rotates (this Bohr's theory has some limitations eg., it cannot be used for more complex atoms).

Bohr's work and much subsequent work led to the following conclusions :-

- Several groups of electrons may occur in an atom and each group is known as an electron shell or orbit.
- Shells/orbits are numbered 1, 2, 3, 4 etc or K, L, M, N etc outward from the nucleus



Jump from 1 shell to another,  
it does that when in a  
excited state

- All electrons in a given shell have approximately equal energy. This energy increases in successive shells outward from the nucleus.
- Electrons can jump from one shell to another.

In a normal state of an atom, the most stable arrangement of electron is that which gives a minimum energy, ie the electron is in

its lowest energy level and the atom is said to be in its ground state. When an electron is at an energy level above its lowest level, the atom is said to be in an excited state.

The movement of electrons from one energy level to another involves the emission and absorption of radiation (energy). The fact that an element can only emit/absorb light at certain frequencies suggests that electrons in an element exist only at certain energy levels.

The energy emitted/absorbed by element is not continuous but in "PACKETS", specific amounts which are called QUANTA (Quantum)

The quantum energy is given by

$$E = h\nu$$

$$\text{But } \nu = c/\lambda$$

D/4

$$E = \frac{hc}{\lambda}$$

Where,

$$h = \text{Planck's Constant} = 6.625 \times 10^{-34} \text{ JS}$$

$\nu$  = Frequency of radiation in Hertz (Hz)

c = Velocity of light ( $3 \times 10^8 \text{ m/s}$ )

$\lambda$  = Wavelength

The quantum theory was used to further explain the structure of an atom. Bohr interpreted spectra in terms of the quantum theory and made the following assumptions about the Bohr's atom :-

1. The electrons move in an orbit around the nucleus and only certain orbits are allowed.
2. The electron does not radiate energy when in these orbits but has associated with it a definite amount of energy in each orbit.
3. Radiation is emitted when an electron undergoes a transition from one orbit to another of lower energy, and radiation is absorbed when electron undergoes a transition from one orbit to another of higher energy.
4. The frequency of radiation is given by  $\Delta E = h\nu$   
 $\Delta E$  = difference in energies of electron in the two levels;  
 $h$  = Planck's constant  
 $\nu$  = Frequency of radiation.

Exercise (a) : Calculate the ionization energy of an element ionized by radiation having wavelength of 242 nm.

$$(1 \text{ nm} = 10^{-9} \text{ m})$$

$$\Rightarrow E = \frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ s}^{-1}}{242 \times 10^{-9} \text{ m}}$$

$$J - KJ \approx 1000 \text{ or } 10^3$$

$$KJ - J \times 1000 \text{ or } 10^3$$

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$$= \frac{19.875 \times 10^{-34+8+9}}{242} = 0.082 \times 10^{-17} \text{ J/m}^2$$

$$S.F = \frac{8.2 \times 10^{-19}}{1000 \times 10^3} = 8.21 \times 10^{-22} \text{ KJ/m}^2.$$

→ **Exercise(b)**: The ionization energy of a given atom is  $8.21 \times 10^{-21} \text{ J}$ . Calculate the wavelength of the electromagnetic radiation which is just enough to ionise the outermost electron of the given atom (express your answer in nm)  
( $1\text{nm} = 10^{-9} \text{ m}$ )

$$\Rightarrow E = \frac{hc}{\lambda}$$

$$8.21 \times 10^{-21} \text{ J} = \frac{6.625 \times 10^{-34} \text{ Js}}{\lambda} \times 3 \times 10^8 \text{ ms}^{-1}$$

$$\lambda = \frac{6.625 \times 10^{-34} \text{ Js}}{8.21 \times 10^{-21} \text{ J}} \times 3 \times 10^8 \text{ ms}^{-1}$$

$$= \frac{19.875 \times 10^{-34+8-(-21)}}{8.21} = 0.0242 \times 10^{-5} \text{ m}$$

$$m - nm = \frac{0.0242 \times 10^{-5}}{10^{-9}} = 242 \times 10^{-9} \text{ nm}$$

$$= 242 \text{ nm}$$

$$0.0242 \times 10^{-5-(-9)}$$

$$0.0242 \times 10^{-5+9}$$

$$④ 0.0242 \times 10^4 = 242 \text{ nm}$$

$$m - nm \neq by 10^{-9} \text{ nm}$$

$$m - nm \neq by 10^{-9} \text{ nm}$$

## ATOMIC SPECTRUM OF HYDROGEN

When an electric discharge is passed through hydrogen gas at a very low pressure, line spectrum of hydrogen is obtained. An intensive study on the hydrogen spectrum has established that it consists of a number of series of spectral lines which are related to each other and are named after their discoverers. These lines are of different wavelengths and frequencies and are related to the various energy levels in the hydrogen atom which could be occupied by electrons.

These series of lines are :

Series	Regions/Location in electromagnetic spectrum
Lyman	Ultraviolet
Balmer	Visible
Paschen	Infra Red
Brackett	Far Infrared
Pfund	Far Infrared.

The wave numbers of the atomic spectra of hydrogen are given by :-

$$\text{Lyman}, \gamma = \frac{1}{\lambda} = R \left( \frac{1}{n^2} - \frac{1}{m^2} \right), \quad n = 1 \\ m = 2, 3, 4, \text{etc}$$

Wave number ( $m$ ) is the invers of wave length ( $\text{cm}^{-1}$ )

$$v = \gamma \lambda$$

Note: All  $n$  &  $m$  are integers  
 $m$  is always greater than  $n$ .

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Balmer,  $\nu = \frac{1}{\lambda} = R \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$ ,  $n=2$   
 $m=3, 4, 5, \text{etc.}$

Paschen,  $\nu = \frac{1}{\lambda} = R \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$ ,  $n=3$   
 $m=4, 5, 6, \text{etc.}$

Brackett,  $\nu = \frac{1}{\lambda} = R \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$ ,  $n=4$   
 $m=5, 6, 7, \text{etc.}$

Pfund,  $\nu = \frac{1}{\lambda} = R \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$ ,  $n=5$   
 $m=6, 7, 8, \text{etc.}$

Where  $R$  = Rydberg Constant

$\lambda$  = Wavelength of radiation.

Bohr interpreted these line spectra in terms of the quantum theory and from the Planck's hypothesis it follows that if the energy levels which an electron can occupy are defined, then the frequencies of the radiation emitted or absorbed are also defined; ie Hydrogen atom can only emit or absorb electromagnetic radiation of certain frequencies (Reason why line spectrum of H-atoms are observed).

## QUANTUM THEORY OF ATOMIC ORBITALS

The quantum theory attempts to understand how electrons are arranged in the atom based on wave and quantum mechanics treatment. The space or region, around the nucleus, in which an electron in a given energy level is most likely to be found is defined as orbital; so rather than describing a fixed Bohr orbit in which electrons are located, the modern theory gives a probability description of atomic orbitals. The result of the quantum mechanical treatment of atom is summarised below :

⇒ PRINCIPAL QUANTUM NUMBER ( $n$ )— Recall that in Bohr's model, each orbit is denoted by a principal quantum no. This designation is retained in the quantum model but to represent distinct ENERGY LEVELS. Each principal quantum no ( $n$ ) corresponds to a particular energy level and has integral values of 1, 2, 3, 4 or K, L, M, N etc. The Principal quantum no,  $n=1$  represents the lowest energy level that an electron can occupy. Electron with the largest ("n") value has the most energy and occupies the highest level and therefore the most easily removable or ionizable electron.

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The maximum possible number of electron in an energy level is given  $2n^2$ . ( $n \geq 1$ )

### AZIMUTHAL OR SUBSIDIARY QUANTUM NUMBER ( $l$ )

It is also referred to as Angular quantum no because it tells us the "SHAPE" of the orbitals. It shows how many energy SUB-LEVELS are present in each electronic energy level.

The value of " $l$ " is dependent on the value of the principal quantum no ( $n$ ). For any given value of " $n$ ",  $l$  has possible integral values ranging from  $0 \dots (n-1)$

#### Example:

If  $n=1$ , there is only one possible value of  $l$ . That is,  $l=(n-1)=1-1=0$

If  $n=2$ , there are two possible values of  $l$ . i.e,  $l=(n-1)=2-1=1$ . Hence,  $0 \pm 1$

If  $n=3$ , there are three possible values of  $l$ . That is,  $l=(n-1)=3-1=2$ . Hence,  $0, 1 \pm 2$

The sub-levels with  $l=0, 1, 2, \pm 3$  are usually referred to S-, P-, d- & F- sub-levels respectively.

Note: The letters S, P, d, f have their different meanings as thus:

S - sharp, P - Principal, d - diffuse &

f - fundamental.

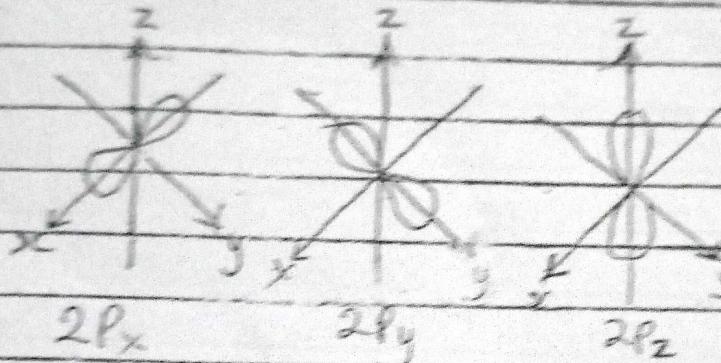
### SHAPES OF ORBITALS

- \* When  $l = 0$ , the shape of the orbital is spherical and it is called S-orbital.



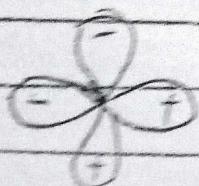
Spherical S-orbital.

- \* When  $l = 1$ , the shape of the orbital is dumb-bell and it is called P-orbital.



The three P orbitals are vertical in shape & energy but their orientation are different.

- \* When  $l = 2$ , the shape of the orbital is double dumb-bell and it is called d-orbital.



double dumb-bell d-orbital

- \* When  $l = 3$ , a more complicated orbital shape is formed which is called f-orbital.

Note : The plus (+) and minus (-) signs are symmetries and not charges.

⇒ MAGNETIC QUANTUM NUMBER (M) - This gives the number of ORBITALS present in

each sublevel. Within a subshell, the value of 'm' depends on the value of the angular quantum no (l). For a certain value of l, there are  $(2l+1)$  integral values of m ranging from  $-l \dots 0 \dots +l$ .

### Example

If  $l=0$ , then  $M = (2l+1) = (2 \times 0 + 1) = 1$  (value is 0)

If  $l=1$ , then there are  $[(2 \times 1) + 1]$  or three values of M namely  $+1, 0$  and  $+1$

If  $l=2$ , there are  $[(2 \times 2) + 1]$  or five values of M, namely  $-2, -1, 0, +1$  and  $+2$ .

If  $l=3$ , there are  $[(2 \times 3) + 1]$  or seven values of M, namely  $-3, -2, -1, 0, +1, +2$  and  $+3$ .

### Note:

The number of "m" values indicate the no of orbitals in a subshell within a particular sublevel.

SPIN QUANTUM NUMBER (S) : This explains the magnetic properties of an electron, since electrons have electrical & magnetic properties. They become like magnet due to spin when placed in a magnetic field. The spin quantum no has values of  $+1/2$  and  $-1/2$ . This means that the spinning can be applied to a magnetic field that is parallel or opposite to the direction of the applied magnetic field that is antiparallel, eg [1b]

## ELECTRONIC CONFIGURATION OF ATOM

The quantum treatment essentially deals with the arrangement of electrons in atom. The use of quantum numbers to express electronic configuration of atoms depends on the following rules :-

- (A) PAULI'S EXCLUSION PRINCIPLE - States that no two electrons in an atom can have the same four quantum numbers.

OR

Two electrons in the same atom cannot behave in identical manner. This implies that the a particular orbital cannot hold more than two electrons and the electron pair in the orbital must have opposite spin [1b].

- (B) HUND'S RULE - States that in filling of orbitals, electrons occupy each energy level singly before pairing takes place. OR  
Electrons in the same subshell will occupy different orbitals with the same spin as far as possible before electron pairing takes place.

Eg. Nitrogen with atomic no 7.

Electronic Configuration  $1S^2, 2S^2, 2P^3$

$n=1$ 

1L	1S <sup>2</sup>
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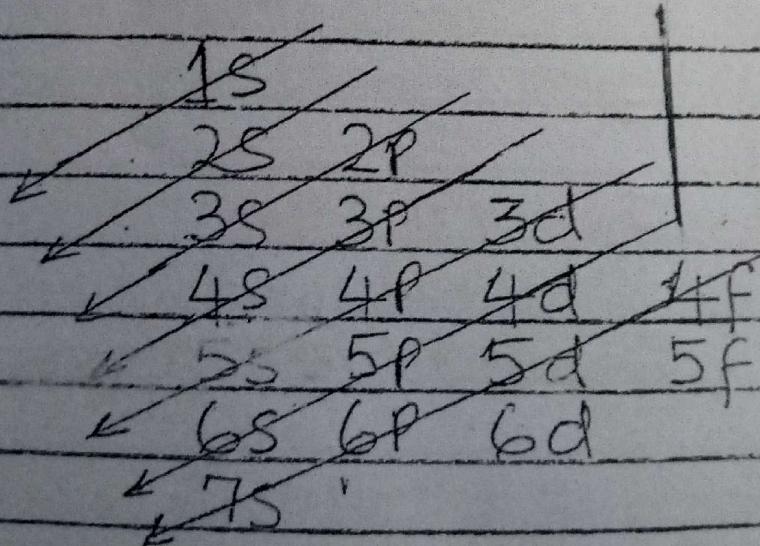
$n=2$ 

1L	2S <sup>2</sup>	2P <sup>3</sup>
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P<sub>x</sub> P<sub>y</sub> P<sub>z</sub>

Q) AUFBAU PRINCIPLE - States that electrons occupy the lowest energy level (ground state) first before electrons occupy the next available orbital or energy level (Higher one)

Note : The sequence of energy levels of orbitals.



# THE PERIODIC TABLE

The word PERIODIC means - Recur at regular intervals.

Many Scientists contributed to the development of the periodic table, but the most important step was taken in 1869 by a Russian scientist Dmitri Mendeleev, who made a thorough study of the relation between atomic size of the elements and their physical and chemical properties.

PERIODIC TABLE :- Is a tabular arrangement of elements in Rows & columns highlighting the regular repetition of properties of the elements.

Periodic Law states that the properties of the elements are the periodic function of their atomic number.

OR

Periodic Law states that when elements are arranged by atomic number, their physical and chemical properties vary periodically.

PERIODIC TABLE SHOWING THE 1ST TWENTY ELEMENTS

Group	IA	IIA	IIIA	IVA	VIA	VIIA	O
1	<sup>1</sup> H						<sup>1</sup> H <sup>2</sup> He
2	<sup>3</sup> Li <sup>4</sup> Be	<sup>11B</sup> <sup>12C</sup> <sup>13N</sup> <sup>14O</sup>	<sup>14B</sup> <sup>15C</sup> <sup>16N</sup> <sup>17O</sup>	<sup>15B</sup> <sup>16C</sup> <sup>17N</sup> <sup>18O</sup>	<sup>16B</sup> <sup>17C</sup> <sup>18N</sup> <sup>19O</sup>	<sup>17B</sup> <sup>18C</sup> <sup>19N</sup> <sup>20O</sup>	
3	<sup>11</sup> Na <sup>12</sup> Mg						<sup>9</sup> F <sup>10</sup> Ne
4	<sup>14</sup> K <sup>20</sup> Ca						<sup>17</sup> Cl <sup>18</sup> Ar
5							
6							
7							

## Description of the periodic table:

The periodic table is divided into seven horizontal rows known as PERIODS and eight vertical columns known as GROUPS. Elements are arranged in the periodic table based on their atomic numbers.

GROUPS :- The vertical columns of elements (group) are numbered 0 - 7 (roman numerals). Elements in the same group usually have the same number of valence electron which corresponds to the group number. Eg Elements of group I have Valency of 1, Elements of group II have Valency of 2. Elements of groups IIIA, IVA, VA, VIA & VIIA exhibit valencies of 3, 4, 5, 6 and 7 respectively. Also, elements in the same group display similar physical and chemical properties and they form similar compounds.

PERIODS :- The periods or the horizontal rows of elements, are numbered from 1 - 7. Elements in the same period have the same number of electron shell, ie elements of period 2 have two electron shells (K, L), those in period 3 have (K, L, M) etc. The number of valence electrons of the elements in the same period increases progressively by one across the period from left to right. Among the elements in period 6 and 7 are elements of the lanthanide and actinide series respectively. They are also called the inner-transition elements.

Besides the eight main groups, there are also the transition group of elements. They lie between group II A and IIIA in the periodic table.

The periodic table also shows a diagonal division of the elements into metals & non-metals. The metals are found on the left side of the table and the non-metals on the right. Groups I A and II A make up the S-block. Elements in this block are the reactive alkali and alkaline earth metals.

Groups III A - VII A and O form the P-block. Electrons are added progressively to the p-orbitals as we move across from groups III A - VII A and O.

In group O, we have the unreactive noble gases. The transition elements occur between groups II A and III A in the periodic table. They form the d-block because they contain d-electrons in addition to the S and P electrons.

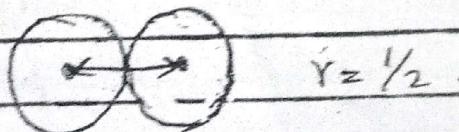
The lanthanide and actinides also occur between groups II A and III A in periods 6 and 7 respectively. They form f-block because they contain f-electrons in addition S, P, d electrons.

### The Periodic Table and Atomic Properties

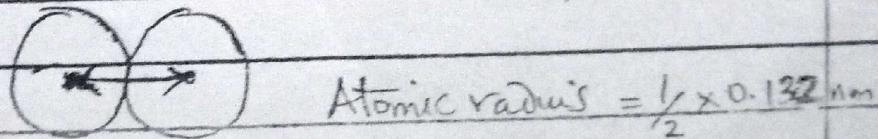
Having learnt that physical and chemical properties of the elements vary periodically with the atomic number. There are also variations in atomic properties of elements on the periodic table. Some of these properties are atomic and ionic sizes, ionization energy, electron affinity, electronegativity, electropositivity, boiling point and melting point, conductivity, atomic volume, density etc.

\* A. **Atomic size (Atomic radius):** The atom is a very small entity and so it is difficult to determine its size i.e. distance from the centre of the nucleus to the outermost orbit. However, with the help of modern techniques such as X-rays and electron diffraction, it is possible to determine atomic radius of covalently bonded atoms.

**ATOMIC RADIUS** or size of any atom is taken to be one half the distance between the nuclei of two adjacent bonded atoms.



For example, the distance between the nuclei of oxygen atoms in an oxygen molecule is 0.132 nm. So the atomic radius of an oxygen atom is 0.066 nm.



$$\text{Atomic radius of oxygen} = 0.066 \text{ nm}$$

**Atomic Size across the period :** Size of atom in the same period decreases steadily from left to right as the atomic number increases. [Recall that as we move across the period, one electron is added increasingly from one element to the next and electrons are being added to the same shell]

about the same distance from the nucleus. Simultaneously, protons are also being added to the nucleus. Two forces are acting on these electrons (attractive & repulsive). Increase in the number of protons increases the nuclear charge which progressively exert a stronger attraction upon the electrons around it and would pull them towards the nucleus. There will also be forces of repulsion amongst the electrons as more electrons are added. Evidence shows that nuclear attraction increases more rapidly across a period than the repulsive forces between the electrons. As a result, atomic size/radius decreases with increasing atomic number.

Atomic size down the group — Atomic size/radius increases as atomic number increases down a given group. Here the increase in the attractive force exerted by the nucleus (ie increased nuclear charge effect) is outweighed by the effect of the extra shells of electrons being added.

B. IONIC RADIUS/SIZE — N.B Ions are formed when atoms lose or gain electrons.

The ionic radius of a given element is the distance between the centre of an ion and the centre of its nearest neighbour of opposite charge.

(a) A positive ion (cation) is formed by removing one or more electron from an atom. The ionic

Size of a positive ion is smaller than the corresponding atom and the more electron are removed, (that is, the greater the charge on the ion) the smaller it becomes. This is because, the number of positive nuclear charge is more than the number of negative electronic charge, hence the electrons are pulled in.

Example :-

$$\text{Atomic radius Na} = 0.186 \text{ nm}$$

$$\text{Ionic radius } \text{Na}^+ = 0.116 \text{ nm}$$

(b) A negative ion (anion) is formed by addition of one or more electrons to an atom. The ionic sizes of negative ions are greater than their corresponding atomic radii. This is because, the number of positive nuclear charge is now less than the number of negative electronic charge hence the pull on the electron is reduced.

[There is also increase in repulsion between the electrons resulting in larger electron cloud]

therefore the size of the negative ion (anion) is increased.

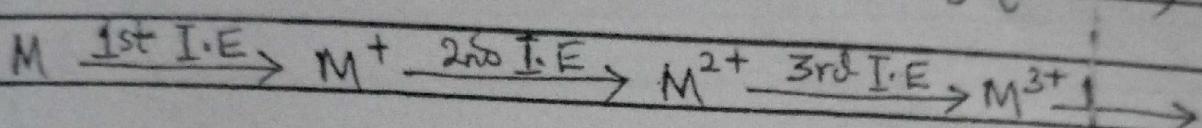
$$\text{Atomic radius Cl} = 0.099 \text{ nm}$$

$$\text{Ionic radius } \text{Cl}^- = 0.128 \text{ nm.}$$

C → IONIZATION ENERGY :- If energy is supplied to an atom, electrons may be promoted to a higher energy level. If sufficient energy is supplied, the electron may be completely removed giving a positive ion.

What is ionization energy ??

The energy required to remove completely the most loosely bound electron from an isolated gaseous atom is called IONIZATION ENERGY. Since it is possible to remove one, two or three electrons from most atoms there is a first, second or third --- ionization energy (I.E.)



Generally, there is decrease in ionization energy down a group of the periodic table and increase across the period (left to right).

The ionization energy is affected by the following factors : Atomic radius, charge on the nucleus, screening or shielding effect of inner electron shells.

→ Atomic radius (distance of the outermost electron from the nucleus) - Across the period, the ionization energy increases as atomic <sup>number</sup> increases since atomic size decreases. As the atomic size decreases, the attraction of the positive nucleus for the electron increases. More energy will be needed to remove the outermost electron, thus the ionization energy will increase. (Vice Versa)

→ Charge on the nucleus (Nuclear charge) - As the nuclear charge increases, its attraction for the

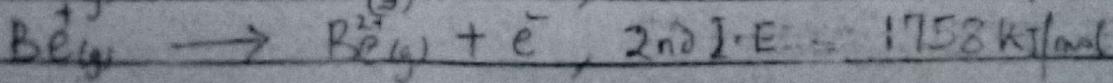
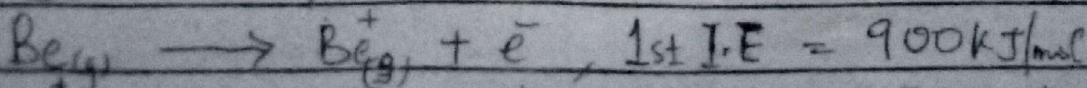
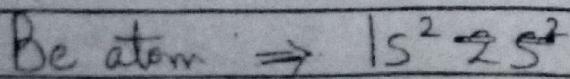
Outermost electron increases, so more energy is needed to remove the outermost electron. Implying that the ionization energy will increase.

→ Screening/shielding effect of the inner electron shells : Ionization energy decreases down the group. This is because of extra electron shells added which screens the outer electrons from the nucleus. The outermost electrons are repelled by all the other electrons and prevented from experiencing the full attraction of the positively charged nucleus. The outermost electron is screened (shielded) from the nucleus by the repelling effect of the inner electrons.

The screening effect by inner electrons is more effective the closer these atoms are to the nucleus. (Note : The electrons in the same shell also exert a screening effect on one another but the effect is so small.)

The ionization energies are determined from the spectra and are usually measured in KJ/mol.

Example : Beryllium atom has 1st I.E of 900KJ/mol and 2nd IE = 1758KJ/mol; Why is the 2nd IE higher..



Reason:

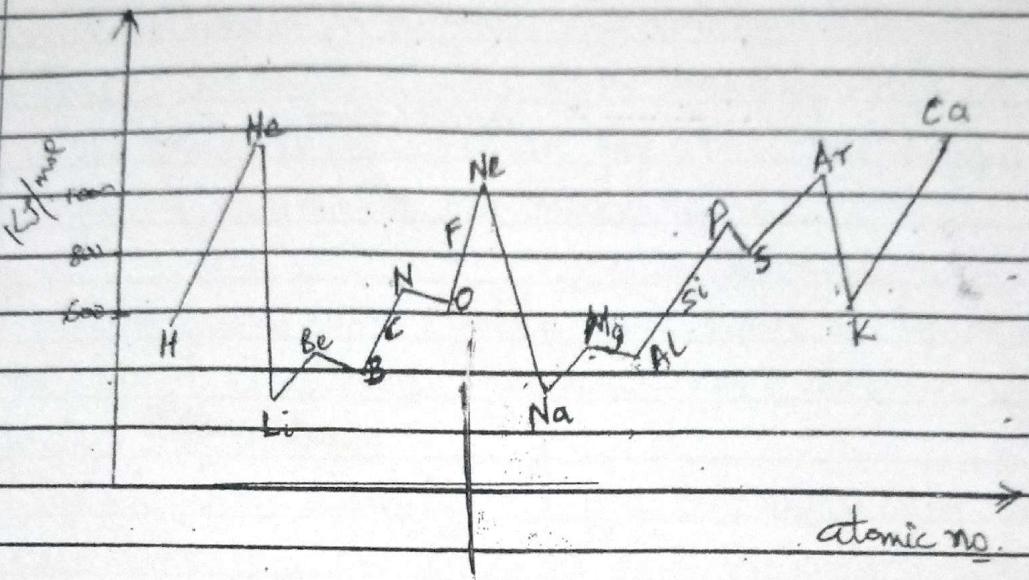
1st I.E is energy needed to remove one of the 2S electron in Be atom. The 2nd I.E is the energy needed to remove the 2nd 2S electron from the positive ion ( $\text{Be}^+$ ). Its value is higher because the electron is being removed from the +ve ion which strongly attracts the electron.

Note: The electronic structure of atoms can be predicted by studying the ionization energies. For example, the following are ionization energies for Be in KJ/mol.

1st	2nd	3rd	4th
900 KJ/mol	1758 KJ/mol	14,905 KJ/mol	21,060 KJ/mol

From the ionization energies, it can be concluded that Be has four electrons, two of the electrons in a higher energy level and are easy to remove (ie from the low values of their ionization energies). The other two electrons are in a low energy level and very difficult to remove. (ie From the very high values of the Ionization energy).

A sketch of 1st Ionization energy of the 1st 20 Elements.



Looking at some variations in ionization energy with atomic no. Example, Ionization energies of

Beryllium - 900 KJ/mol  $\rightarrow 1s^2 2s^2$  (All subshells are filled)

Boron - 800 KJ/mol  $\rightarrow 1s^2 2s^2 2p^1$  (P subshell contains only one electron)

#### Note :

Since filled electron shells are associated with extra stability e.g. (He, Ne, Ar). There is also some energetic stability associated with completely filled subshells. This means that the electronic configuration of beryllium is more stable than that of boron and hence has a higher ionization energy.

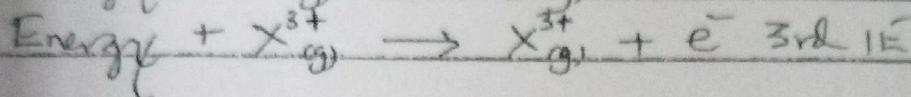
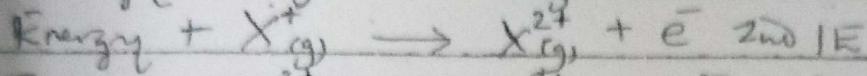
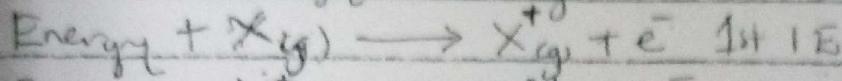
Also,

N -  $1s^2 2s^2 2p^3$  (more stable, has half-filled 2p subshell)

O -  $1s^2 2s^2 2p^4$  (Contains one electron more than nitrogen).

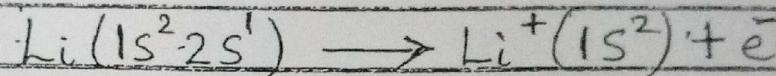
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Ionization energy is always an endothermic reaction



$$\Delta H / 4 \quad I_1 < I_2 < I_3 < I_4$$

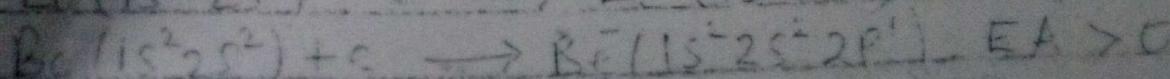
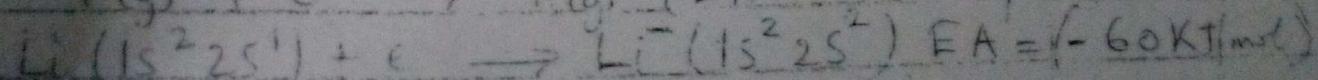
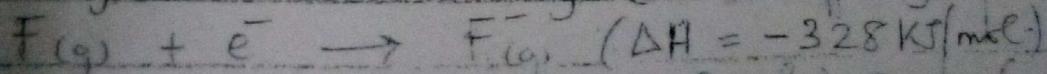
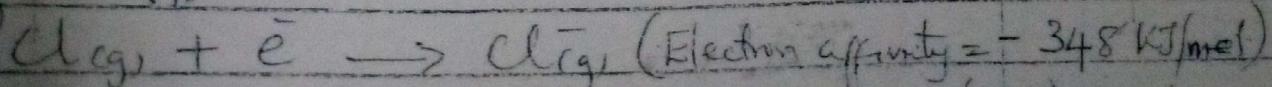
Example



Note

~~Reason for decrease in IE down the group.~~ Reason for decrease in IE down the group. As you move down the group, atomic no. increases (Elements in same group has similar electronic configuration). Shell number increases down the group. A greater separation between the nucleus and the electron means a weaker attraction, so it becomes increasingly easier to remove the 1st electron from an atom, as we go down the group.

ELECTRON AFFINITY - Electron affinity is the energy liberated when an electron is added to a neutral gaseous atom to form a negative ion. That is, the energy released when an extra electron is added to a neutral gaseous atom forming anion.



Note: Electronegativity measurement involves  $1/E_A$

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Electron affinity increases with decrease in atomic radii across the period and decreases with increase in atomic radii down the group. This is because atoms with smaller atomic radii tend to <sup>have stronger</sup> attraction for electrons and so form negative ion more easily.

N.B ① Noble gases have stable <sup>electronic configuration</sup> and have no tendency to accept electrons. They have zero electron affinity.

② The electron affinity is affected by size of atom, effective nuclear charge and screening effect.

ELECTRONEGATIVITY - Electronegativity is the ability/tendency of an atom in a molecule to attract electrons to itself. That is the measure of the power of an ~~electron~~ atom to attract electrons when combined in a compound. Electronegativity of elements increase across a period and decrease down a group of the periodic table. Electronegativity is affected by the atomic radius, effective nuclear charge, screening/shielding effect as well as the electronic configurations of the atoms.

→ Small atoms attract electrons more than large atoms i.e. atoms with smaller sizes are more electronegative than atoms with large size. This is due to closerness to the nucleus.

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Increase in effective nuclear charge results in an increase in electron attracting power thereby increasing the electronegativity. Also atoms with nearly filled shells of electrons will tend to have higher electronegativity than those with sparsely ~~filled~~ occupied shell. (Why?) Because of the desire to have a stable filled shell.

N.B The most electronegative elements are the reactive non metals (eg. Fluorine) at the top right hand corner of the periodic table. While the least electronegative elements are the reactive metals (eg. Caesium) at the bottom left-hand corner of the periodic table.

Atomic size increase down the group and effective nuclear charge decreases resulting in electron attracting power (electronegativity) of atom decreasing.

shell. They are non-metals. The inert or noble element He (2), Ne (2,8), Ar (2,8,8) all have complete shell arrangement of electrons. The electron arrangement in stable ions of metals and non-metals also show that complete shell of electrons is a stable configuration e.g.  $\text{Na}^+(2,8)$ ,  $\text{F}^-(2,8)$  and  $\text{O}^{2-}(2,8)$ .

In chemical bonding therefore elements tend to attain the noble or inert gas configuration. There are many types of bonds.

We shall however focus on three types: (i) Electrovalent (ii) Covalent (iii) Coordinate Covalent.

## ELECTROVALENT (IONIC) BONDING

When atoms interact for bond formation only the outermost parts of the atoms are in contact and so only the outer electrons in the outermost shell (valence electrons) are involved. The outermost shell electrons arrangement is therefore very important in determining the type of bond. Electrovalent bonding involves electron transfer from the valence shell of one atom to the valence shell of the other.

One atom loses electrons to become positively charged and the other gains electrons to become negatively charged. The positively and negatively charged ions are called cations

①

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## THE CHEMICAL BONDS /

When elements combine, compounds are formed. The forces that hold atoms together in compounds are called chemical bonds. The combination of chemical elements to give a compound is a chemical reaction. Some elements are very reactive and exist in nature only in combined states, e.g. sodium in sodium chloride (common salt) and calcium in calcium trioxocarbonate (marble). Few elements are relatively unreactive and exist rarely as free elements.

They are called noble or rare elements, e.g. no compound of helium, argon and neon exists.

Most elements have intermediate reactivity and exist as free elements as well as in chemical compounds e.g. carbon occurs as graphite and diamonds as well as in petroleum and many organic compounds. There are some non metallic elements that exist only as diatomic molecules in the free state. These elements also occur in combined states.

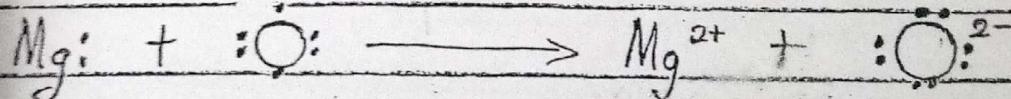
Arrangement of electrons in atoms showed some correlation between electron arrangement and properties.

$\text{Li} (2,1)$ ,  $\text{Na} (2,8,1)$ ,  $\text{K} (2,8,8,1)$  all have similar configuration with one electron each in their outermost shell. They are metals. The inert or noble  $\text{F} (2,7)$  and  $\text{Cl} (2,8,7)$  all need one electron to complete their outermost electrons.

protons in the nucleus of fluorine.

The giving up of electrons is not restricted to atoms with only one valence electron. Elements in groups  $\text{IIA}$  and  $\text{IIIA}$ , as well as many of the transition elements, will do the same thing. Neither is the acceptance of electrons limited to those atoms that need one valence electron to satisfy the octet rule.

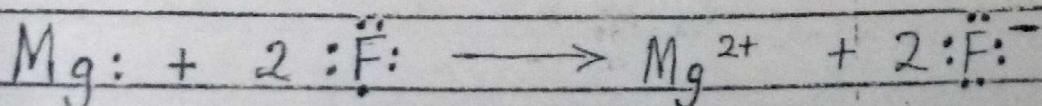
Those that need two, three, or more can also participate. See the examples below for illustration of such cases.



Two electrons were transferred.

	Before	After
Mg	$1s^2 2s^2 2p^6 3s^2$	$1s^2 2s^2 2p^6 (\text{Mg}^{2+})$
O	$1s^2 2s^2 2p^4$	$1s^2 2s^2 2p^6 (\text{O}^{2-})$

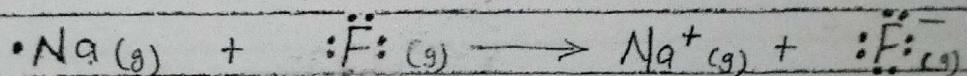
Observe that both product ions have attained the favoured octet.



Again, two electrons were transferred. This time two fluorine atoms took one electron each.

and anions respectively. The ionic bond results from the attraction between these oppositely charged ions. This type of bonding is usually between metals and non-metals.

For example, if a fluorine atom, which is one short of eight valence electrons, collides with a sodium atom, Sodium will give up and transfer its valence electron to the fluorine atom under the correct conditions. The products are a sodium ion and a fluoride ion, both of which now meet the octet requirement. This reaction is represented in an equation as follows:



Following the change, using electron configuration is informative:

	Before	After
Na	$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6 (\text{Na}^+)$
F	$1s^2 2s^2 2p^5$	$1s^2 2s^2 2p^6 (\text{F}^-)$

It is apparent that both atoms have attained a noble gas configuration (octet rule) by transferring to the fluorine the electron in the sodium's 3s level. The positive charge on the sodium ion can be traced to the unbalanced proton-electron count in sodium, leaving it with a net of +1. Similarly, the one negative charge on the fluoride ion is due to 10 electrons not balancing the nine

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The electrostatic attractive force between two unlike charges, such as a positive ion and a negative ion, is often strong enough to hold the two ions together. In the gas phase, for example,  $\text{Na}^+\text{Cl}^-$  units have been observed. When this happens we say that an ionic bond or electrovalent bond has been formed.

Note that the participating particles are ions, not atoms.

### Structure of Electrovalent Compounds

It is incorrect to speak of a molecule of an ionic compound like NaCl or LiF. Ionic compounds are usually solid consisting of regular arrangement of equal number of positive and negative charges.

Most ionic compounds are crystalline at room temperature. A study of these crystals shows that they are composed of alternating positive and negative ions in a three-dimensional lattice.

This regular arrangement of cations and anions in the solid crystal is called the lattice. When the crystals melt, the liquid is an excellent conductor of electricity. This is evidence for the presence of ions in the parent crystals. The force that holds the ions together in these crystals is the ionic bond. A positive ion can be surrounded, within certain limits, by negative ions, and they in turn attract positive ions. This gives the alternating array of ions.

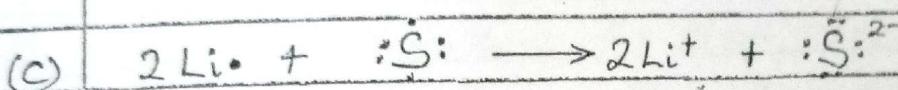
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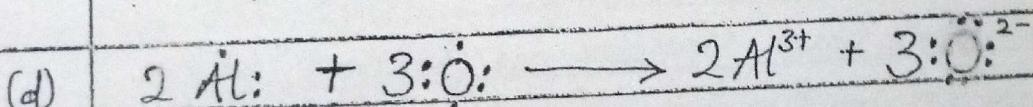
	Before	After	
Mg	$1s^2 2s^2 2p^6 3s^2$	$1s^2 2s^2 2p^6$	$(Mg^{2+})$
F	$1s^2 2s^2 2p^5$	$1s^2 2s^2 2p^6$	$(F^-)$
F	$1s^2 2s^2 2p^5 e^-$	$1s^2 2s^2 2p^6$	$(F^-)$



This time two lithium atoms were required per sulphur atom.

	Before	After	
Li	$1s^2 2s^1$	$1s^2$	$(Li^+)$
Li	$1s^2 2s^1$	$1s^2$	$(Li^+)$
S	$[Ne] 3s^2 3p^4$	$[Ne] 3s^2 3p^6$	$(S^{2-})$

Sulphur obeys the octet rule, whereas Li followed the duplet rule.



Two aluminium atoms will provide six electrons, which exactly satisfies the needs of three oxygen atoms.

	Before	After	
Al	$[Ne] 3s^2 3p^1$	$[Ne]$	$(Al^{3+})$
Al	$[Ne] 3s^2 3p^1$	$[Ne]$	$(Al^{3+})$
O	$[Ne] 3s^2 3p^4$	$[Ne] 3s^2 3p^6$	$(O^{2-})$
O	$[Ne] 3s^2 3p^4$	$[Ne] 3s^2 3p^6$	$(O^{2-})$
O	$[Ne] 3s^2 3p^4$	$[Ne] 3s^2 3p^6$	$(O^{2-})$

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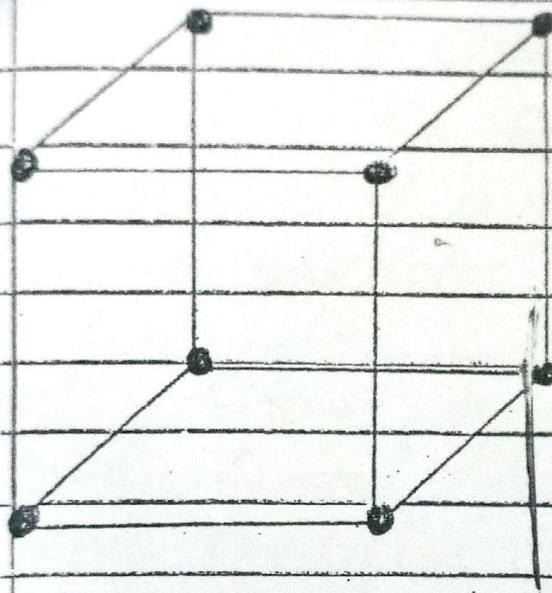
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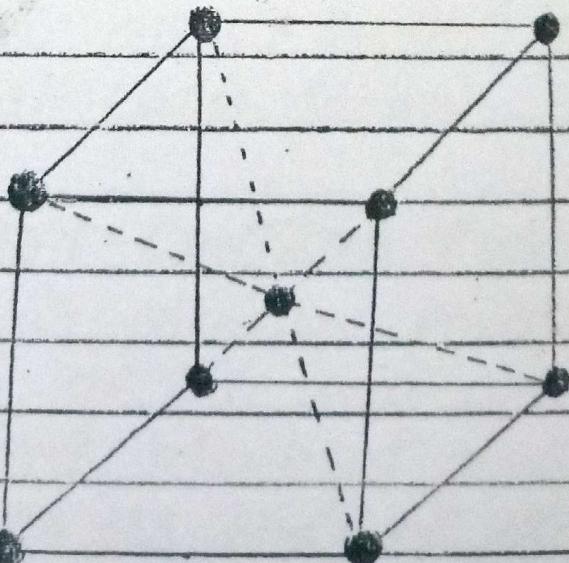
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Simple cubic, body-centred cubic, and  
face-centred cubic - shown below.



Simple Cubic Unit Cell



Body-centred cubic unit cell

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When we want to describe the structure of an ionic compound, we draw a picture of the simplest repeating unit or **UNIT CELL**, in the three-dimensional network of its ions. By describing the size, shape and contents of the unit cell - and the way the repeating units stack to form a three-dimensional solid - we can unambiguously describe the structure of the compound. Because a unit cell is a part of a larger three-dimensional structure, ions at the corners, edges, and faces are shared by neighbouring unit cells. Only when this is taken into consideration does the ionic formula match the ratio of ions in the unit cell.

In 1850 Auguste Bravais showed that every crystal, no matter how complex its structure, could be classified as one of 14 unit cells that meet the following criteria.

- (i) The unit cell is the simplest repeating unit in the crystal.
- (ii) Opposite faces of a unit cell are parallel.
- (iii) The edge of the unit cell connects equivalent points.

We shall focus on only one classification of unit cell, the cubic unit cell. There are three types of cubic unit cells -

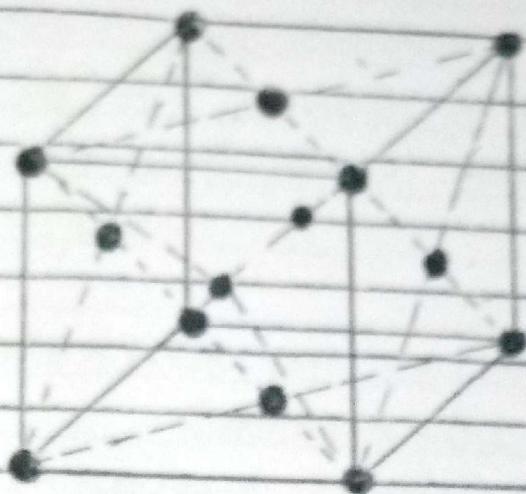
unit cell of NaCl, for example, contains an equivalent  $\text{Cl}^-$  ion at each of the eight corners of the unit cell.

1. The SIMPLE CUBIC unit cell, as its name implies, is the simplest of all unit cells. It consists of a minimum of eight equivalent particles at the eight corners of a cube.

Other types of cubic unit cells are derived from the simple cubic cell. Particles can be present on the edges or faces of the unit cell, or within the body of the unit cell. But the unit cell must contain equivalent particles at each corner.

2. The BODY-CENTRED CUBIC unit cell also has eight identical particles on the eight corners of the unit cell. However, there is a ninth identical particle in the centre of the body of the unit cell. If the particle at the centre of the unit cell differs from the ones that define the eight corners, the crystal is classified as simple cubic.

3. The FACE-CENTRED CUBIC unit cell starts with identical particles on the



### Face-Centred Cubic Unit cell

Cubic unit cells are important for two reasons. First, a number of metals, ionic solids and intermetallic compounds crystallize in cubic unit cells. Second, these unit cells are relatively easy to visualize because for a particular substance the cell-edge lengths are all the same and the cell angles are all  $90^\circ$ .

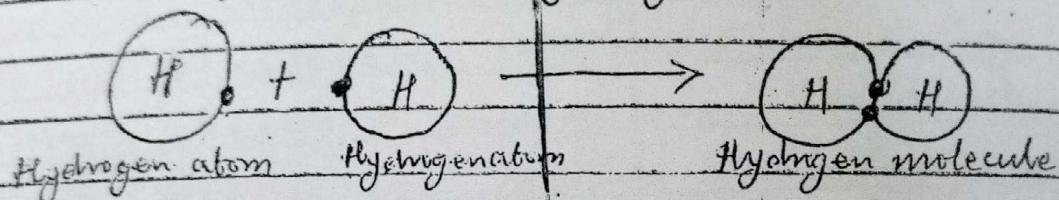
Each unit cell contains a number of LATTICE POINTS. A particle can be found at each lattice point in the crystal. This particle can be an atom, an ion or a molecule.

By convention, unit cells are defined so that the cell edges always connect equivalent points. Therefore, an identical particle must be found at each of the eight corners of a cubic unit cell. The

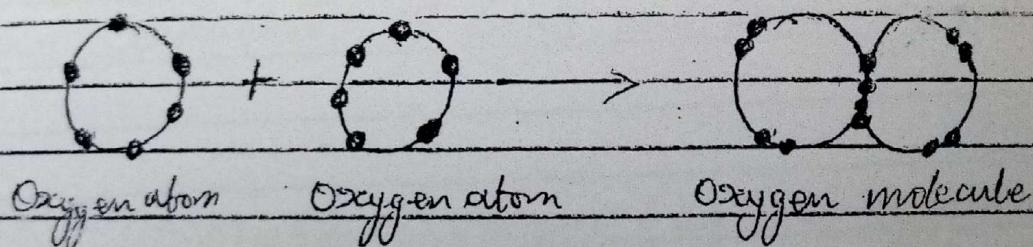
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Power(s) is/are contributed by the two atoms involved in the bonding. The bonding force results from the attractions of the shared electron pairs by the nuclei of the atoms involved in the bonding. This type of bonding is between non metals. Consider the following examples.

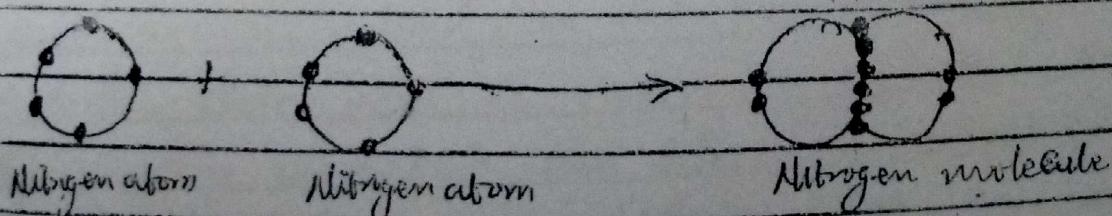
### 1. Formation of Covalent Hydrogen molecule



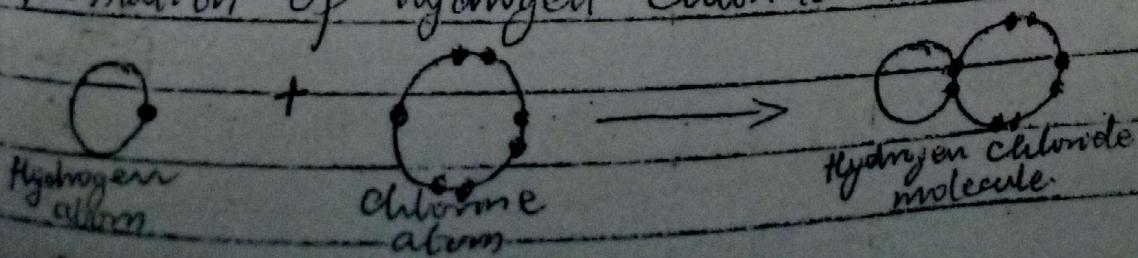
### 2. Formation of covalent oxygen molecule



### 3. Formation of Covalent nitrogen molecule



### 4. Formation of hydrogen chloride molecule



atom must share to attain an inert gas configuration. Covalent compounds form molecules and depending on the intermolecular forces between the molecules they may be gases ( $\text{O}_2, \text{H}_2, \text{HCl}$ ) or liquids ( $\text{Br}_2, \text{H}_2\text{O}$ ) or low melting solids (candle wax).

## Properties of Covalent Compounds

Covalent compounds are:

- (i) made up of discrete molecules hence they are mostly liquids or gases at room temperature,
- (ii) generally having low melting and boiling points
- (iii) generally not [very] soluble in water but soluble in organic solvents.
- (iv) non conductors of heat and electricity.

## COORDINATE COVALENT (NATIVE) BONDING

In a covalent bond the shared electrons are donated and controlled by both atoms that are involved in the bonding. This is not the case with co-ordinate covalent bond.

One atom donates the electron pairs but atoms control the donated pair(s).

Once a coordinate covalent bond is formed it is not different from ordinary covalent bond. The electron pair is attracted by both nuclei of the bonded atoms. For this type of bond to be formed, one atom

In example 1, the pair of electrons shown between the nuclei represents the covalent bond (it is common to replace them with a single line, H-H). Each hydrogen atom contributes its electron to the pair and both atoms, in sharing the pair, attain the favoured helium configuration. The electrons are spread over, ~~and~~ between and around both nuclei. When counting the number of electrons surrounding a given nucleus, the shared pair is treated as if it belongs exclusively to each nucleus.

When two atoms share four electrons (two pairs), they are said to form a DOUBLE BOND. A case in point is oxygen molecule. One oxygen atom is double-bonded to another as shown in example 2.

Atoms that share six electrons (three pairs) have a triple TRIPLE BOND. Nitrogen gas,  $N_2$ , has a triple bond.

Two unlike atoms can share electrons as exemplified by the formation of HCl from the atoms (example 4). In this situation the hydrogen atom follows the rule of two (duplet) and the chlorine atom follows the octet rule.

An electron pair constitute a bond and two pairs constitute a double bond as in oxygen molecule. The number of electron pairs shared depend on the number of electrons each

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State the presence of a dative bond in the molecule we indicate with arrow the direction of electron donation ( $\rightarrow$ ) The arrow points towards the acceptor atom. Coordinate covalent bonding is common with metal complexes.

The molecules donating the electron pairs are called ligands and the metal ion the central atom.

## METALLIC BONDING

Metal atoms don't have enough valence electrons to reach a filled-shell configuration by sharing electrons with their neighbours. The valence electrons on a metal atom are therefore shared with many neighbouring atoms, not just one. In effect, these valence electrons are delocalized over a number of metal atoms.

In order for electrons to be delocalized it is necessary that the valence subshell levels not be separated by a large energy gap. Because the delocalized valence electrons are not tightly bound to individual atoms, they are free to move through the metal. A useful picture of the structure of metals therefore envisions the metal atoms as positive ions locked in a crystal lattice surrounded by a sea of

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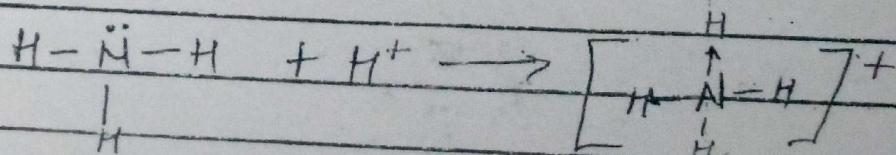
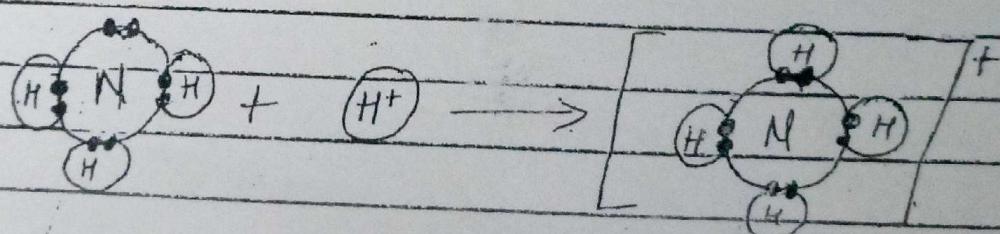
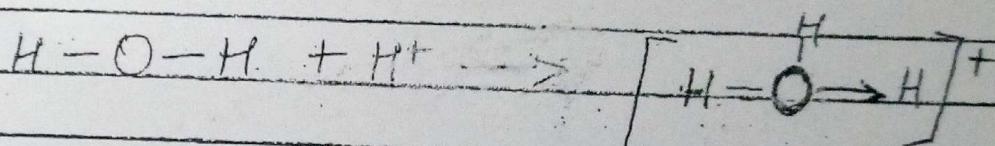
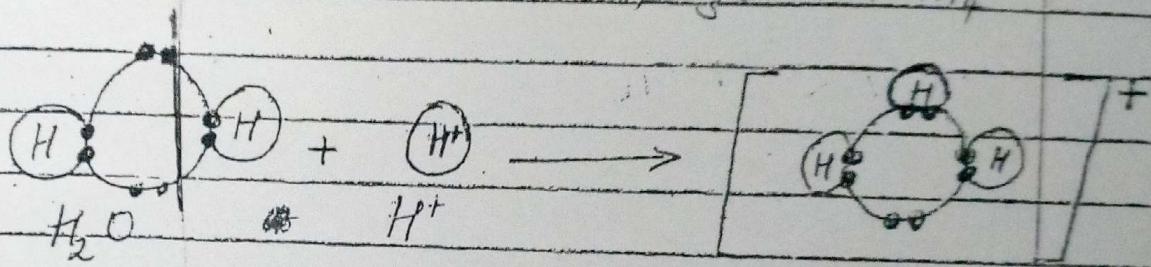
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must have a lone pair of electrons. (Lone pairs are electron pairs that are not used in bonding to other atoms). The other atom must have a vacancy in its valence shell to accept the lone pair. The bond formation also results in inert gas configurations for both atoms.

Consider the formation of hydroxonium ion and the ammonium ion,  $H_3O^+$  and  $NH_4^+$



Note that the positive charge is now controlled by the entire molecule. The dative bond can not be differentiated once formed from other covalent bonds but sometime to indi-