



**OR:**

Isotopes are atoms of the same element with the same atomic number but different mass numbers.

### **ELECTRONIC STRUCTURE OF AN ATOM AND ATOMIC SPECTRUM.**

A spectrum is a bundle of different lines of different frequencies which may be visible or invisible when white light is passed through a glass prism or diffracting grating.

The study of interpretation of atomic spectrum when elements are heated explains how electrons in atoms of different elements are arranged in their atoms. Each element produces a unique set of spectral lines. Since no two elements emit the same spectral lines, elements can be identified by their line spectrum. Atomic Spectra are produced by emission or absorption of energy.

#### **Emission spectrum (atomic emission spectrum)**

When an element in the gaseous state is heated or subjected to electric sparks, it emits light of a certain wavelength. When this radiation is resolved by spectrometer, the observed spectrum consists of a number of discrete coloured lines on a black background.

#### **Absorption spectrum (atomic absorption spectrum)**

When white light composed of all visible wavelengths is passed through the cool vapour of an element, certain wavelengths may be absorbed. These absorbed wavelengths are thus found missing in the transmitted light. The spectrum formed this way is made up of a series of dark lines and is referred to as atomic absorption spectrum. The wavelengths of the dark lines are exactly the same as those of the bright lines in the emission spectrum. The absorption spectrum of an element is the reverse of the emission spectrum of the element. Atomic spectral lines are emitted or absorbed not only in the visible region but also in the infrared region or in ultraviolet region.

Since the atomic spectra are produced by emission or absorption of energy depending on the internal structure of the atom, each element has its own characteristic spectrum. Today, spectral analysis has become a powerful method for the detection of elements even though present in extremely small amounts. The most important consequence of the discovery of spectral lines of hydrogen and other elements was that it led to our present knowledge of the atomic structure.

### **THE HYDROGEN SPECTRUM**

This is a series (group) of lines, some in the visible region and others in the invisible region.

In each series, the spacing between the adjacent lines decreases as frequency of the waves giving the lines increases. (Or as the wavelength decreases) The decrease in the spacing is caused by decreased nuclear attraction in the electrons resulting into a continuum in each series.

In the visible part of the spectrum, this is observed as a number of lines, each of different colour. The four prominent colours being red, blue-green, blue and violet.

## Features of the spectrum

- The spectrum obtained consists of a number of definite lines.
- Each line corresponds to a definite wavelength of radiation.
- In each series, the interval between the sequences of lines becomes smaller and smaller towards the high frequency end of spectrum until the lines run together or converge to form a continuum of light. **Why do the lines get closer? They do because there is a decrease to the nuclear attraction of an electronic occupying a higher energy level as it is far away from the nucleus. Consequently the energy difference between the energy levels decreases.**

## Formation of hydrogen emission spectrum

This is formed when electricity (or electric discharge) is passed through a discharge tube containing hydrogen gas at low pressure. The hydrogen molecules break up into single hydrogen atoms. The single electrons of each hydrogen atom absorb energy and is promoted (or jumps) from the ground state (energy level  $n=1$ ) to higher energy level (excited state) where it is unstable.

When the electron of each hydrogen atom falls back to the ground state (lower energy level), it emits (gives) out light (or radiation) of a definite amount of energy giving rise to the emission spectrum recorded on the photographic plate.

## Formation of the absorption spectrum

This is formed when light is shone through hydrogen atoms and the electrons absorb energy of definite amount. The electron(s) jump to the excited state (higher energy levels) giving rise to the absorption spectrum which is recorded on a photographic plate.

## BOHR'S MODEL OF THE ATOM

Rutherford's nuclear model simply stated that an atom had a nucleus and the negative electrons were present outside the nucleus. It did not say anything as to how and where those electrons were arranged. It could not explain why electrons did not fall into the nucleus due to electrostatic attraction.

In 1913, Niels Bohr proposed a new model of atom which explained some of these things and also the emission spectrum of hydrogen. Bohr's theory was based on Planck's quantum theory and was built on the following postulates.

### **Postulates of Bohr's theory**

- Electrons revolve around the nucleus in circular paths which are known as orbits or energy levels and only certain orbits are allowed.
- No energy is radiated by the electron while it is rotating in permissible orbits. (Energy levels) The energy levels were designated using quantum numbers; 1,2,3...
- Under normal circumstances, the electron occupies the energy level nearest to nucleus ( $n=1$ ). It is then said to be in ground state. (most stable energy level)
- The return may occur in one step or in stages. To whatever level the electron returns, it emits some or all of its surplus energy in form of radiation.
- The frequency of the radiations depends on the energy differences between the two energy levels, calculated from Planck's equation,  $h\nu = E_2 - E_1$  where  $h$  is Planck's constant.  $\eta$  the frequency of a photon emitted or absorbed energy.

## Bohr's explanation of hydrogen spectrum

Hydrogen atom has only one electron occupying energy level,  $n=1$  where it is stable. When energy is supplied to hydrogen in the discharge tube, the electrons jump to higher energy level ( $n=2,3,4,5,6,\dots$ ) depending on the quantity of energy absorbed where it becomes unstable, then drops back to the ground level where it is stable due to nuclear attraction.

The process of returning to energy level  $n=1$  (ground state) may occur in steps and whichever energy level it returns to, it emits radiation of different wavelength which gives rise to different lines in the emission spectrum.

Since the discharge tube contains millions of hydrogen atoms, the atoms may be excited to different extents. Therefore electron transitions of many kinds may take place thus the different series of lines in the hydrogen spectrum. Lines in the same series correspond to energy transitions between higher energy level and common lower energy level. i.e. the Lyman series in the emission spectrum arises when the electrons move to the  $n=1$  level, the Balmer, Paschen, Brackett and Pfund series arise from transitions to  $n=2$ ,  $n=3$ ,  $n=4$  and  $n=5$  from the higher orbitals respectively.

Series	n	m	Region of the series
Lyman	1	2,3,4	Ultraviolet
Balmer	2	3,4,5	Visible
Paschen	3	4,5,6	Infrared
Brackett	4	5,6,7	Infrared
Pfund	5	6,7,8	Infrared

The wavelength of the lines and series to which they belong are related to the equation;

$$1/\lambda = R_H(1/n_1^2 - 1/n_2^2)$$

Where  $\lambda$  = wavelength of a particular line

$R_H$  = Rydberg's constant ( $10967800\text{m}^{-1}$ )

$n_1$  and  $n_2$  are the quantum numbers for the final and initial energy levels respectively.

### Worked example

Calculate the wavelength of radiation emitted when an electron falls from  $n=4$  to  $n=2$ .

**Solution**

**Note:** In each series, the lines become closer and eventually merge into one another as frequency increases. This means that the energy levels come closer with distance from the nucleus until when they merge into each other.

The formation of a continuum means the energy levels have merged and when an electron reaches this level, then it has been completely removed from an atom. i.e. ionisation has taken place. The frequency of the convergence limit is used to calculate the energy required for ionisation to occur.

### Evidence for the existence of energy levels in an atom

The hydrogen spectrum provides evidence for the existence of energy levels in an atom. This is because;

- Hydrogen has one electron yet it produces a spectrum containing many lines separated from each other.
- There are several series of lines. e.g. Lyman series, Balmer series, etc each series representing a particular energy level to which an electron returns.
- The spacing between adjacent lines in each series differs.
- There is a continuum in each series of lines.
- The light giving each line is of definite energy or frequency.
- Give out light of different colours.
- Each of the big lines comprises of two small lines.

### Using the spectrum to find ionisation energy of hydrogen

If enough energy is supplied to move the electron up to the infinity level, the atom will be ionised. The energy gap between the ground state and the point at which the electron leaves the atom can be determined by  $\Delta E = hf$  where  $f = c/\lambda$  where  $f$  is the frequency,  $c$  is speed of light,  $\lambda$  is the wavelength,  $h$  is Planck's constant.

### Significance or application of the line spectrum

- It shows that within an atom of elements, there are different energy levels (sub-energy or orbitals) within which the electrons are distributed around the nucleus.
- It also shows that the energy difference between these energy levels diminishes as the distance from the nucleus increases.
- Spectral lines are used in the determination of first ionisation energy of different elements.
- Spectral lines are also used in the identification of different metal ions. i.e. by the flame test.

### Information obtained from separate lines in the spectrum

- The lines give confirmation about the electronic structure of the hydrogen atom.
- The separate lines indicate that there are discrete or definite energy levels in the hydrogen atom.
- The energy possessed by an electron is quantized.
- Electrons can only exist in specific regions called orbits or energy levels.

### Worked example

a). Calculate the ionisation energy when an electron falls from  $n =$

to  $n=1$

### Solution

Energy given out when an electron falls to a lower energy level is given by;

### b).State any two characteristics of the emission spectrum of hydrogen.

- The spacing between the lines in each series decreases until they converge to a continuous spectrum (continuum)
- The lines in the visible spectrum have different colours.
- There are bright lines on a dark background.
- The hydrogen spectrum consists of a series of lines in both visible and invisible region of the electromagnetic spectrum.

### Example

Calculate the frequency of radiation emitted when electron falls from  $n=4$  to  $n=1$

### Note:

If energy is not enough to move an electron, no spectrum is emitted and the energy absorbed by an atom just increases its potential energy.

### Example

Find the wave length of the line formed in the Balmer series when an electron falls for third energy level.

### Solution

Explain why hydrogen has one electron yet produces a spectrum containing many lines

Solution

When light is passed through hydrogen atom get excited to lighter energy levels where it is unstable by absorption of energy as it moves from energy level to the next one in stages. Each amount of energy absorbed corresponds to a specific wave length. The energy absorbed in each stage gives rise to a clear line in the absorption spectrum.

Question

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The figure below shows part of the emission spectrum of hydrogen corresponding to the Balmer series

a) state any two characteristics of emission spectrum.

- The spacing between the lines in each series decreases until they converge into continuous spectrum.
- Lines in the visible spectrum have different colours.
- Bright lines on a dark background.
- Consists of a series of lines in both visible and the invisible region of the electromagnetic spectrum.

b). Calculate the quantum energy evolved in  $\text{KJmol}^{-1}$  corresponding to the green line in the above spectrum. (Planck's constant =  $6.625 \times 10^{-34} \text{Js}^{-1}$ , velocity of radiation =  $3.0 \times 10^8 \text{ms}^{-1}$ , Avogadro's number =  $6.02 \times 10^{23}$ )

### **No.6 JEB 2013 P1**

**a). State what is meant by principal quantum number.**

Principal quantum number,  $n$  represents a group of energy levels (orbits) indicating energy possessed by an element.

**b). The diagram below shows a series of lines in the ultraviolet region of the atomic spectrum of hydrogen.**

i). Indicate on the diagram the direction of increase in frequencies of spectral lines.

ii). Give two deductions that can be obtained from the separate lines in the spectrum

- Since each spectral line represents radiant energy of specific wavelength and frequency, then energy possessed by an electron is quantized.
- Electrons can only exist in specific regions called orbitals or energy levels.

iii). Explain why the emission lines get closer and eventually merge into a continuum.

The nuclear attractions of an electron occupying a higher energy level decreases as it is far away from the nucleus. Consequently, the energy difference between the energy levels decreases where formation of spectral lines that become closer and merge into a continuum. c). The frequency of the spectral lines at the start of the continuum is  $3.46 \times 10^{15} \text{ Hz}$ . Calculate the ionisation energy in kilojoules per mole. (Planck's constant =  $6.62 \times 10^{-34} \text{ Js}^{-1}$ )

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### ELECTRONIC DISTRIBUTION IN ATOMS



Within an atom, electrons occupy energy levels. Electrons occupying the same energy levels are said to belong to the same quantum shells denoted by their principal quantum numbers 1,2,3,4, etc or by the letters K,L,M and N, etc starting with the shell nearest to the nucleus. Principal quantum number is a quantum (energy) number that represents a group of energy levels (orbitals) indicating energy possessed by an element. When the lines in emission spectrum were examined with a spectroscope of high resolving power it was found that many of them consist not of a single line but of two or more lines close together. This implies that within a given energy level, there exist sub-energy levels in which the electrons differ slightly in energy. Thus similar transitions of two electrons in the same quantum shell produce radiations of slightly different wavelength if the electrons are in different sub-shells.

Theoretically in a given quantum shell, there are  $n$  possible sub-energy levels where  $n$  is the principal quantum number. Thus in the first main energy level, there is only one sub-energy level (sub shell) or orbitals. **An orbital** is the volume of space around the nucleus where there is a high probability of finding electrons. There are four orbitals (sub-energy levels) in which electrons are found. These include s,p,d and f.

**The s-orbital** is in the form

It carries a maximum of two electrons. In box form, it is represented as

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The second main energy level has two sub-energy levels (orbitals), the s and p orbitals. Thus electrons can be in 2s and 2p orbitals.

The third main energy level has three sub-energy levels (orbitals) which include s,p and d orbitals and electrons can be in 3s,3p or 3d-orbitals.

The fourth main energy level has four sub-energy levels (orbitals), s,p,d and f. So electrons can be in 4s,4p,4d or 4f orbitals.

Each type of energy level can hold a different number of electrons.

Sub-energy levels (orbitals)	Number of electrons
s	2
p	6
d	10
f	14

The table below shows the energy levels and sub-energy levels for the first four principal quantum numbers.

Energy n	Sub-energy levels	Total number of electrons
1	1S	2=2
2	2S2P	2+6=8
3	3S3P3d	2+6+10=18
4	4S4P4d4f	2+6+10+14=32

**Note:** The orbitals(sub-energy levels) differ in energy. Each orbital takes a maximum of two electrons.

The table below shows how electrons fill the orbitals in each sub-energy level.

Sub-energy level	Number of orbitals	Electrons
s	1	1×2=2
p	3	3×2=6
d	5	5×2=10
f	7	7×2=14

Chemist also often represent an orbital as a box that can hold up to 2 electrons. Each electron is shown as a half arrow indicating different spin. With an orbital, electrons must have opposite spins.

### **ELECTRONIC CONFIGURATION**

The electronic configuration of an atom is the distribution of the available electrons of an atom or ion in the various atomic extra nuclear region. The following rules are followed in writing electronic configuration.

- **Aufban's principle**

The energy level and sub-energy levels or orbitals of lower energy are filled first. ie. electrons always occupy the lowest empty levels first. For energy levels n=3, n=4 it was found out that 4s is filled before 3d and in the n=4, n=5, 5s is filled first before 4d. ie. After filling the second energy level, an overlap occurs between the third and fourth energy level such that the 4s is filled before 3d. Similar overlaps occur as the electronic configuration grows bigger as shown in the table below. The order in which electrons are filled in is arrived at as shown below.

- **Pauli exclusion principle**

Only two electrons can occupy an orbital and must have opposite spins.

So the maximum number of electrons in s-orbitals is  $2(S^2)$

The maximum number of electrons in p-orbitals is  $6(p^6)$

The maximum number of electrons in d-orbital is  $10(d^{10})$

The maximum number of electrons in f-orbital is  $14(f^{14})$

- **Hund's rule of degenerate orbitals (or maximum multiplicity)**

The rule states that if electrons are present in a number of degenerate (equal or same energy) orbitals electrons occupy all orbitals singly with parallel spins before any pairing occurs in any orbital.

Eg.

**The table below shows the electronic configuration of some elements**

**Questions**

**Write the electronic configuration of;**

**P**

**Ar**

**Fe**

**V**

**Ni**

**Cs**

a). What is the difference between the emission line spectrum and the absorption line spectrum.

b). What is meant by the term quantum number?

c). Explain;

- Hydrogen has one electron yet it produces a spectrum containing many lines.
- The spacing between adjacent lines in each series differ.
- There is a continuum in each series of lines.

d). What is the significance of the line spectrum?