

Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 03

Atomic structure II

Greetings to you, we will start off where we left in the last class.

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The electronic excited energy levels involve large amounts of energy ranging from 35.71 k cal in the visible to several hundreds in the far uv. Each electronic level is associated with several vibrational modes but maximum population is at $v = 0$ level. Consequently the absorption arising out of this transition will be most intense. This tendency is enhanced in the liquid state where the vibrations are further dampened by intermolecular inter actions. Thus a broad absorption band results.

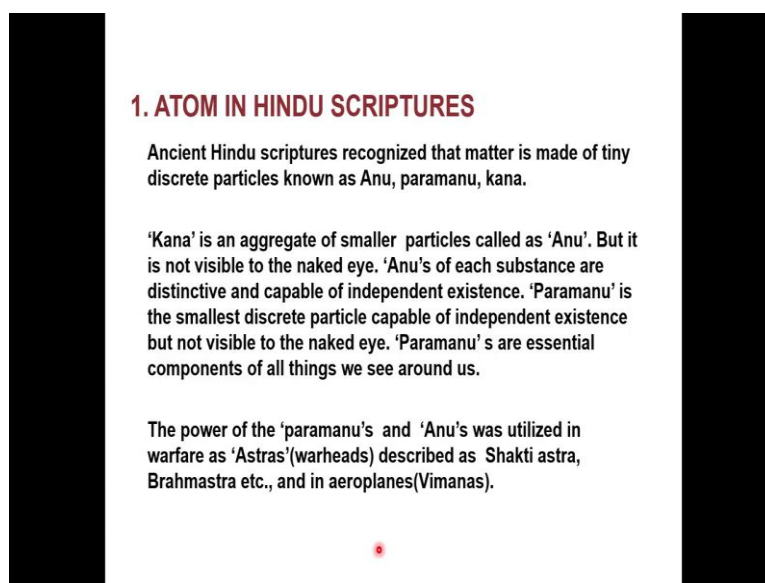
The σ to σ^* transitions are very energetic and are found only below 200nm i.e in the vacuum ultraviolet region. Compounds in which all the valence electrons are

I think I had shown you this slide where the electronic excited energy levels involve large amounts of energy from 35 to 35.7 kilo calories in the visible range to several hundreds in the far ultra violet range. Each electronic level we have to understand that it is associated with several vibrational modes. That means other energy levels which are associated with which are in smaller size, but maximum population is always that vibrational level 0. Consequently the absorption arising out of this transition will be maximum, so it will be most intense. So, this tendency is normally enhanced in the liquid state where the vibrations are further dampened by intermolecular interactions.

Usually, what happens is a broad absorption band results, suppose we take the electronic spectra from vapor state in that case what happens the electronic transitions will become much more sharper compare to liquids state and compare to liquid state solid state electronic transitions if you take the spectra they will be still broader the interactions will be weaker.

So, coming back to these transitions we say sigma to sigma star transitions are very energetic; that means transition of electrons from single bond to excited single bond structure. So, such energetic things energetic transitions are found only below 200 nanometers that is in the vacuum ultra violet region consequently compounds are elements which have absorptions bands below 200 are very difficult to measure in ultra violet are a atomic absorption spectrometer also compounds in which all the electronic term valence electrons all the valence electrons are most intense now.

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1. ATOM IN HINDU SCRIPTURES

Ancient Hindu scriptures recognized that matter is made of tiny discrete particles known as Anu, paramanu, kana.

'Kana' is an aggregate of smaller particles called as 'Anu'. But it is not visible to the naked eye. 'Anu's of each substance are distinctive and capable of independent existence. 'Paramanu' is the smallest discrete particle capable of independent existence but not visible to the naked eye. 'Paramanu' s are essential components of all things we see around us.

The power of the 'paramanu's and 'Anu's was utilized in warfare as 'Astras'(warheads) described as Shakti astra, Brahmastra etc., and in aeroplanes(Vimanas).

Let us look at atoms in the Hindu scriptures, this I had also mentioned in the last class that we called them Anu, paramanu and kana. Kana is an aggregate of smaller particles Anu called as Anu, but it is not visible to the naked eye, Anu of each substances are distinctive and capable of independent existence, paramanu is the smallest pa discrete particle capable of independent existence, but not visible to the naked eye

So, paramanu is are essentially essential components of all the things we see around us the power of the paramanu and Anu was utilized in the warfare even in puranas which are known as astras in modern the terms you can call them warheads and then these astras in puranas they are described as Shakti, astra, Brahmastra, etcetera and in aeroplanes also they used to carry these things they use to be known as Vimanas, but coming back to the modern times.

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2 .DALTONS THEORY(1802)

Matter is composed of tiny real particles called atoms which are indivisible and cannot be created or destroyed.

Atoms of all substances are identical in nature, weight, size and other properties. Atoms of pure substance and others differ in weight and other characteristics from other substances.

Atoms combine in definite proportions resulting in chemical compounds.

We have Dalton's theory which was propounded in 1802. So, what he said is matter is composed of tiny real particles called as atoms which are kana's or paramanu's are Anus whichever way you feel describing corresponding equivalents which are these atoms are indivisible this was in 1802 by Dalton and he said they can be created nor destroyed. That means, every atom in every element is capable of independent existence you cannot cut it down further in to smaller particles which we know is not true nowadays.

So, but what he said at that time must have been relevant and what he also said is atoms of all substances are identical in nature this is also in consonance with Indian philosophy that every human being individually is alike and except may be final details, but they are made of the same 5 elements that is pancha buthas; akasha, vayu, neeru, water and then fire and sound; these are pancha buthas. So, atoms of pure substances and others differ in weight and other substances. So, if there are more substan more atoms in a particular element it looks different if there are less atoms it looks different, but each of them have having separate characteristics owing to the number of atoms present in a element in an element. So, at we also said atoms combining definite proportions resulting in chemical compounds so that is also a very important concept. That means all compounds are having member of elements that mixed in definite proportions for example.

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3.FUNDAMENTAL COMPONENTS OF ELEMENTARY PARTICLES

Particle	Notation	Mass* (AMU)	Charge* esu $\times 10^{18}$	Relative charge
Electron	e	0.0005486	-4.8029	-e
Proton	p,	1.00757	+4.8029	+e
Neutron	n,	1.00893	0	0
Positron		0.0005486	+4.8029	+e
Neutrino	ν	0	0
Antineutrino	0	0
Meson	π	0.156	± 4.8029	$\pm e$
	μ	0.118	± 4.8029	$\pm e$
Deuteron	d,	2.01416	+ 4.8029	+e
Alpha	$\alpha,$	4.00279	+9.6058	+2e

*AMU - Atomic mass unit, equivalent to
+esu is the fundamental unit of electrical charges

If we take water it will be having hydrogen and oxygen mixed in 1 is to 2 proportion one is one of hydrogen and 2 of oxygen atomic weight will be 2 of hydrogen and 1 of oxygen.

So, then the line many of these atoms are also found to be divisible, but Dalton's theory can be again extended to a number of divisible components for example, now we that an atom contains an electron; electron can now we can extend Dalton's theory that electrons are not divisible, but subsequently we also know that electrons can be divisible and they may or may not have independent existence, but right now what I am showing you is a fundamental list of components called as elementary particles the may or may not have independent existence. But the particles which I am showing you in this slide are the once which we recognize from our scientific vocabulary atomic vocabulary and these include electron it ca it is denoted by e and mass is atomic in atomic mass units it raise approximately 0.0005486 and its charge is 4 point minus 4.8029 ESUs in to 10 raise to 10 and relative charge is o f that is.

What we use in day to day application is we denote it by minus e because electronic carries a negative charge corresponding proton which carries a positive electrical charge it is mass is approximately 1.00757. So, it is charge is exactly same as an electron and denoted by p then we have what is known as neutron this is also Dalton's according to Dalton's theory and modern atomic theory denoted by n weight is approximately

equivalent to a proton 1.008 and charge is neutral and relative charge is also neutral then we know what is known as positron there is no symbol as such, but it is exactly same as an electron and, but it as positive charge compare to electron. Now electron carries negative charge whereas, positron will carry positive charge this does not have independent existence similarly we have other particles known as neutrinos which does not have any mass.

But charge is also 0 and relative charge is also 0 then we have what is known as antineutrinos again no charge mesons are there which carry which could be positive or negative charge and it can be plus denoted by plus or minus e similarly mu mesons positive or negative deuterons deuteron is a is nothing, but 2 hydrogen atoms. So, the mass should be 2 if we take hydrogen is one or proton as one proton and hydrogen are essentially same. So, ma deuteron is to hydrogen atoms used in to one. So, the mass charge will be same because it is it contains 1 proton and 1 neutron, so positive electron similarly alpha particles that is helium atom having 2 positive charges. So, these are the basic fundamental particles of atomic mass as modified by the Dalton's theory Dalton's theory has been modified to include all these fundamental (Refer Time: 10:49).

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4. MODERN ATOMIC THEORY

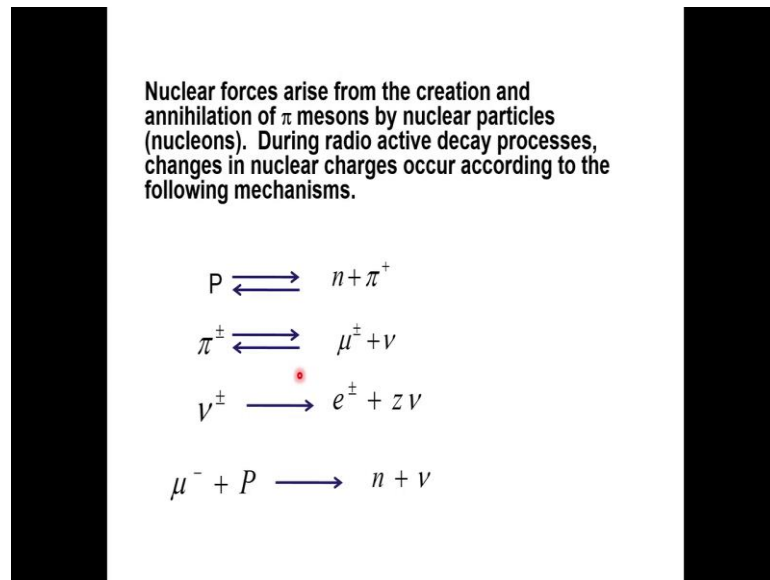
- An atom consists of a positively charged nucleus of about and comparatively heavy.
- An extra nuclear arrangement of electrons which is comparatively large and diffuse in character.
- Nucleus consists of a number of protons and neutrons. They are formally related as:

Neutron Proton

So, now we can summarize modern atomic theory as an atom consists of a positive charge and nucleus it can that is nucleus comparatively heavy because a proton is heavier than electron and it has an extra nuclear arrangement of electrons which is comparatively

large and diffuse in character. That means electrons are hanging around a space circular spa spherical space around the nucleus. So, nucleus consists of number of protons and neutrons and they are formally related.

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So protons are related to neutrons as proton convert gets converted to neutron and a charge and this mesons by mesons can be converted in to mu mesons plus some frequency discharge radiation discharge and the mesons also can be converted in to different particles fundamental particles and all these things can happen during radioactive decay processes not in normal circumstances. So, changes in nuclear charge are occurring according to the following mechanisms.

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Nuclei with 2,8,20,28,50,82 or 126 neutrons or protons are especially stable. These so called magic numbers represent closed shells of nucleons.

For a given element with Z protons a number of species may exist with the same number of protons but varying in the number of neutrons. Such elements exhibit the same chemical properties but differ in atomic weight and are called isotopes.

Nuclei of same mass number but differing in charge also exist which are called as isobars. But they do differ in their chemical properties. (e.g Ca & Ar)

So, now we tell that the basic element atom consist of protons neutrons pi mesons these that etcetera, but for are all practical purposes if I want to describe a stable electronic stable electronic structure I should imagine a nucleus with neutrons and protons with electrons around it in this spherical space. Now, when an element becomes stable there is a rule of 8 and nuclei now I am talking about nuclei not the electrons nuclei which 2, 8, 20, 28, 50, 82 or 126 neutrons or protons are especially stable; that means, any element having 20 atomic mass is stable.

It may be; it may consist of neutrons or protons it may be having 50 or 82 or 126, these are called as magic number, they represent closed shells of nucleons for a given element Z with Z protons a number of species may exist with these same number of protons, but varying in the number of neutrons what we are saying is the protons in a given for a given element it has to contain its nuclear should contain neutrons and protons. So, protons and neutrons which 2, 8, 20, 28, etcetera, they are all stable.

So, the stable will stable elements may have different combinations of protons and neutrons, but still correspond to 50, 82 and 126 or 2, 8, 20 like that. So, such elements exhibit the same chemical properties, but differ in atomic weight. So, these are called as isotopes what are isotopes, isotopes are substances which carry the same number of protons, but varying number of neutrons. So, neutrons do not carry any charge.

So, long as the element remains the same neutrons may vary a little bit on a 2 extra this side that side, but then they are the exhibit same chemical properties. So, this properties and elements having such nuclear structure are called as isotopes it may also happen that nuclear with the same mass number, but differing in charge; that means, we are talking about different elements, but weight is same. So, these things have exhibit atomic different chemical properties, because they are different elements, but their weight is same. So, such elements are called as isobars, but they do differ in their properties for example, calcium and organ they have different atomic number different number of protons, but their total atomic weight is almost same.

So, how do these neutrons are and protons normally exist because protons carry high positive charge neutrons do not carry any positive charge. So, how do they hold each other is a question? So, normally what we say is attractive force exist between neutrons and protons they are very weak forces, so by weak forces.

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Attractive forces exists between neutrons and protons. Energy exchanges occur via mesons among them. The actual neutron to proton ratio is due to the balance between the tendency towards neutron-proton equalisation and proton reduction. All the radio active decay processes are therefore aimed at attaining stable nuclei. This is achieved by :

(i) B-Emission neutron/proton ratios	}	For high
(ii) Neutron Emission		
(iii) Positron Emission	}	For low neutron/proton ratios
(iv) Orbital Electron Capture		
(v) Proton Emission		

They are all held together. So, energy exchange is occur between protons and neutrons via mesons among them. So, the actual neutron to proton ratio is due to the balance between the tendency towards neutron proton equalization and proton reduction. So, all the radioactive decay processes are therefore, aimed at obtaining stable nuclei. So, if you look at some of the electronic structures of radioactive elements they keep on radiating alpha radiations beta radiations gamma radiations and all these things by emitting the

radiations their mass and charge will keep on changing, but decreasing also. So, when they keep on decreasing they move towards periodic table where the atomic weight and atomic number keeps on reducing and we know many elements in the periodic table which are having very low atomic weights and atomic numbers and most of the elements what we see iron cobalt nickel.

And all these things including calcium, magnesium, etcetera, etcetera, led all these things end up having lower atomic weight so that they do not become radioactive materials. So, any radioactive material which is having a higher number of neutrons and protons in the nucleus under goes radiation to give you a stable, but stable element which is having lower atomic number. So, that is where most of the radioactive decay processes proceed.

So, the actual neutron to proton ratio is due to the balance between the tendency towards neutron proton equalization and proton reduction. So, this can be achieved by beta emission this I have already explain to you the neutron proton ratio will change neutron emission also will reduce the atomic weight positron emission will not reduce the atomic weight orbital electronic capture quite possible. But and proton emission definitely will lead to lower nuclear weight or lower atomic weight.

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An unstable nucleus (having AMU > 83) arising out of radio active decay or nuclear reaction, readjusts itself to a stable nucleus by the emission of an α particle . In the process mass is lost by 4 AMU and charge is lost by 2 units until it reaches a stable configuration.

Nuclear stability is also attained by the absorption or release of energy. The energetics of nuclear reactions are of course associated with mass changes according to Einstein's equation,

$$E = mc^2$$

So, an unstable nucleus arising out of radioactive decay or nuclear attraction readjust itself to a stable nucleus by the emission of a particle if the process mass is lost by alpha particle if an alpha particle is lost the mass will mass loss will be four atomic units and

charge loss will be 2 units, so because an alpha particle corresponds to a helium atom. So, it keeps losing alpha particles from the nucleus until it reaches a stable configuration that of for example, that of lead. So, nuclear stability is also attained by the absorption and release of energy.

So, the energetics of nuclear reactions are of course, associated with mass changes according to Einstein's equation which is a very famous equation I have written it here which says that E is equal to mc^2 ; that means, the amount of an energy release is a multiple of its mass and velocity of light squared.

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The release of energy takes place either in the form of heat or as radiations. The mass change corresponding to the conversion of hydrogen into helium,

$$2\,{}^1_1\text{H} + 2\,{}^1_0\text{n} \rightarrow {}^4_2\text{He} + Q$$

is 0.0302 AMU. This is equivalent to 28.12 MeV of energy per helium atom or 6.45×10^8 kcal per gram atom of helium. This is equivalent to the temperatures prevailing on sun. Hence nuclear reactions are of interest as a source of energy.

So, the release of energy takes place either in the form of heat or radiations if it is heat it will be enormous like in an atom bomb and if it is radiation you can still feel the heat because most of the neutrons when they pass through actual materials they generate heat, but not as much as in a nuclear bomb. So, the mass change corresponding to different conversion of hydrogen into helium for example, if we take a look I want to convert hydrogen into helium. So, hydrogen is having one proton helium is having 2 protons; that means, I have to take 2 hydrogen atoms or 1 hydrogen and 1 neutron and then convert it into some sort of a combination of elements with the amount of heat released to convert the essential difference in the mass of hydrogen and helium.

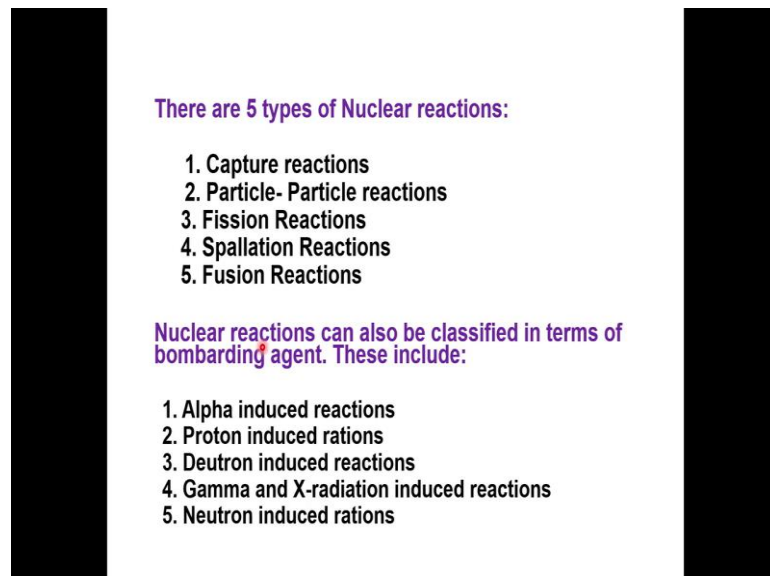
So, if I write that equation you can see here on the slide that I have written here 2 hydrogen atoms of one mass plus 2 neutrons of one mass and no charge will give

raise to 10^{22} and 2×10^8 atomic mass and it gives you 2×10^8 atomic number plus some amount of heat Q and the difference is 0.0302 , atomic mass units the energy difference Q corresponds to this much; that means so much of energy is to be released when we form a helium atoms starting from one 2×10^8 hydrogen atoms and 2×10^8 neutrons this is equivalent to 28.12 mega electronic bolts of energy per helium atom or 6.45×10^8 kilo calories per gram atom of helium I just convert per atom in to grams.

So, this is equivalent to the temperature prevalent in the sun on the sun. So, 6.45×10^8 kilo calories is the amount of energy that corresponds to the mass change when a helium is formed and this kind of energy corresponds to the temperature prevailing in the sun. Therefore, we assume that the sun is having almost all the elements that are present on the earth, but they are being formed and being destroyed in the atmosphere of the sun in suns atmosphere. So, nuclear reactions are of interest to us as a source of energy.

Because if I can combine 2×10^8 hydrogens and 2×10^8 nitrogens and form helium I should be able to generate so much amount of heat I can do lot of things with the amount of heat that is generated by such a reaction.

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There are 5 types of Nuclear reactions:

1. Capture reactions
2. Particle- Particle reactions
3. Fission Reactions
4. Spallation Reactions
5. Fusion Reactions

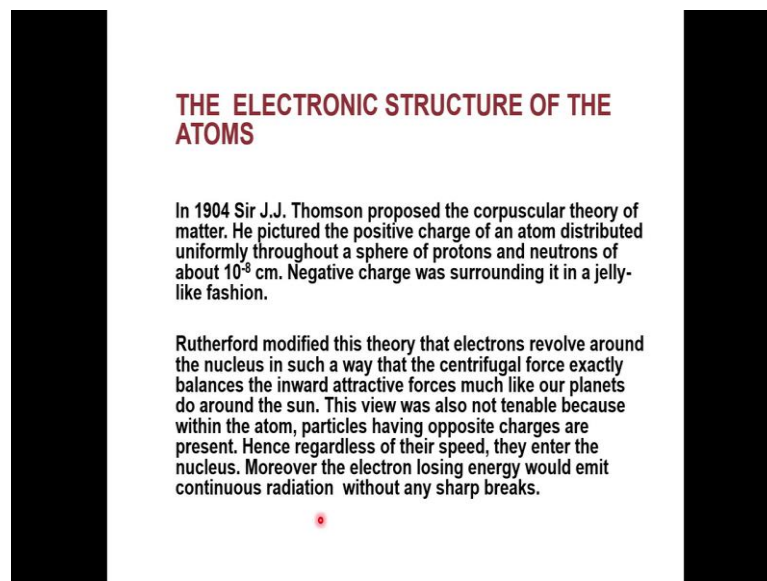
Nuclear reactions can also be classified in terms of bombarding agent. These include:

1. Alpha induced reactions
2. Proton induced rations
3. Deuteron induced reactions
4. Gamma and X-radiation induced reactions
5. Neutron induced rations

So, there are 5 types of nuclear reactions one capture reaction I can capture the electrons and protons and neutrons I can have particle interactions and then I can have fission reactions a big element can be converted into smaller elements and then spallation

reactions and then fusion reactions I can take 2 elements and fuse them together. So, oath another way of classification for these things are in terms bombarding agent I can take alpha particles to bombard and carry out chemical reactions proton induced reactions I can take protons deuteron induced gamma and x radiation induced and neutron induced reactions all these are such reactions can be carried out in atomic reactors with adequate precautions they cannot be carried out in normal a laboratories prevailing in the sun.

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THE ELECTRONIC STRUCTURE OF THE ATOMS

In 1904 Sir J.J. Thomson proposed the corpuscular theory of matter. He pictured the positive charge of an atom distributed uniformly throughout a sphere of protons and neutrons of about 10^{-8} cm. Negative charge was surrounding it in a jelly-like fashion.

Rutherford modified this theory that electrons revolve around the nucleus in such a way that the centrifugal force exactly balances the inward attractive forces much like our planets do around the sun. This view was also not tenable because within the atom, particles having opposite charges are present. Hence regardless of their speed, they enter the nucleus. Moreover the electron losing energy would emit continuous radiation without any sharp breaks.

Now, that is about the about the nucleus you remember that we have being discussing the atomic structure basically because we have to know how an atom looks how at an atom works how an atom can be utilized in the chemical analysis. So, now, we know that there are atoms all elements are made up of atoms and the atom consist of a nuclear part as well as an electronic part. So, far we have discussed about the nuclear part now we will discuss about the electronic part.

So, I have said that electrons are there in this spherical atmosphere around the nucleus now how do we know that the spherical structure contains electrons they must have been found by somebody they must have been deducted and determine by somebody and it was a J J Thomson in to 1904 who proposed the corpuscular theory of matter he pictured positive charge of an atom distributed uniformly throughout its sphere of protons and neutrons of about 10^{-8} cm. Negative charge was surrounding it in a jelly like fashion he that his imagination.

So, Rutherford modified this theory that electrons revolve around the nucleus in such a way that the centrifugal force electrons are revolving and the centrifugal force generated by the electrons is exactly balancing the inward attractive forces of the electrons just like our planet go around the sun now there is a fast similarity between sun and planets and nucleus and electrons. So, the electrons are going around the nucleus round and round and round and the electrons they are attracted towards the proton, but they do not fall in to the proton; that means, it generates centripetal force centripetal centrifugal forces that of attraction and repulsion are exactly matched in a stable nucleus. So, this view was also not enable, because if they do not match the electrons will fall in to the nucleus generating nuclear reactions.

So, regardless of their speed they enter the nucleus some time or the other more over the electron losing energy would admit emit continuous radiation now imagine an electron is going round and round it is attracting the nucleus is attracting it was very heavy 1840 times heavier than the electron. So, it keeps on attracting and some time it falls, but if it is falling to a in to the nucleus it would be slowly losing its energy its own energy and it must be emitting radiation this does not happen; that means, the electrons around the nucleus are moving around in such a way that they do not fall in to the nucleus that is the catch.

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In 1903, Bohr proposed a radically different view of the atomic structure based on the optical spectrum of Hydrogen. He included the postulates of quantum theory proposed by Max plank.

Bohr proposed that the electron in a hydrogen atom always described a fixed circular path around the nucleus. Such orbits named 'stationary states' may be thought of various circles differing in radius. The angular momentum of each stationary states was an integral multiple of $n \cdot h/2\pi$ which amounts to angular momentum. The angular momentum mvr is given by

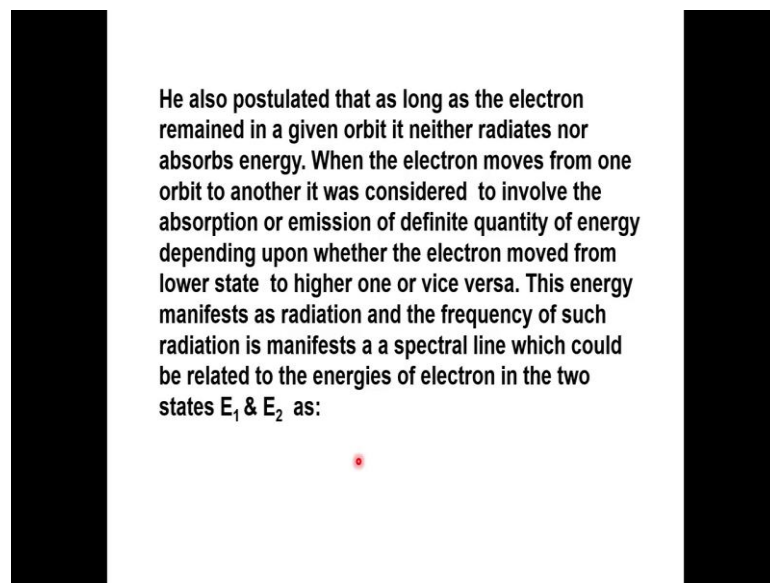
$$mvr = n(h/2\pi)$$

where n is an integer called a quantum number

So, Bohr proposed a radically different view of the atomic structure based on the optical spectrum of hydrogen he included that 2 postulates of quantum theory proposed by max plank what do the max plank say and Bohr proposed that the electron in a hydrogen atom.

Always moved in a fixed circular path; that means, it will never fall in to the nucleus, it describes a circular path around the nucleus such a circular path is named as stationary state where the electron is moving around the angular movement on each stationary state was an integral multiple of $n h$ by 2π n is number o number of electrons h is planks constant π is you know what it is 2 point; 3.142. So, this describes n in a the number of stationary state. So, this amount to angular momentum this angular momentum is given by $m v r$ is equal to $n h$ by 2π where n is called as a quantum number.

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He also postulated that as long as the electron remains in a given orbit it neither radiates energy nor absorbs energy. So, when the electron moves from one orbit to another it was considered to involve the absorption or emission of in a definite quantity of energy corresponding to the difference between these stationary energy levels. So, this energy manifests.

Whenever it electron moves from one energy level to another energy level the energy is dissipated and the frequency the it is dissipated as radiation and also because energy is fixed the frequency of such radiation manifests as a spectral line which could be related

to the energies of electron in the 2 states that is higher energy state and lower energy state that I designate as E 1 and E 2.

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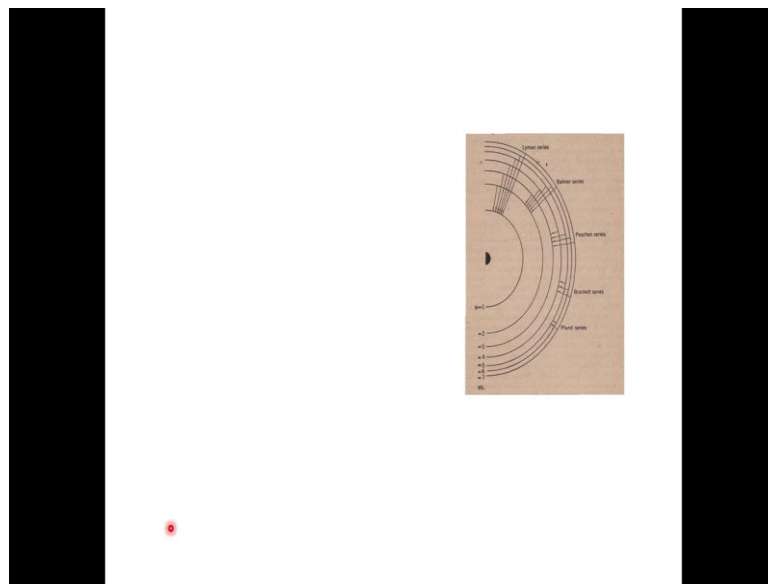
Line spectra of hydrogen atom	
Lyman series	n = 2,3,4.....to n = 1
Balmer series	n = 3,4,5.....to n = 2
Paschen series	n = 4,5,6.....to n = 3
Brackett series	n = 5,6,7.....to n = 1
Pfund series	n = 6,7.....to n = 5
Origin of hydrogen spectrum scann pp 83, Morrison Bohr's theory could explain the spectra of hydrogen and etc. But it failed completely when applied to multiple electron systems. Further it could not account for splitting of optical lines (fine structure) when spectroscopes of high resolving power were employed.	

The difference between E 2 minus E 1 use the energy difference that is radiated heat or a spectral line. So, a when the elements are when the electrons are moving to one state to another it may fall from fifth energy level to first energy level or it may from fall from third to second energy level fifth to forth; forth to third all of them 5 4 2 3 4 can all fall into 1 3 2 5 can fall into energy level 2 4 5 6 can fall into energy level 3. So, the energy levels corresponding to each state is different. So, a single element containing a single electron can generate number of spectral lines when the stationary energy levels are involved and transition occurs.

So, a single hydrogen atom can give rise to number of energy and states and they can be deducted spectrally because the energy difference corresponds to the wavelength and that can be related to frequency. So, all these things can be shown as different lines in his spectra. So, the line spectra of hydrogen contains Lyman series a number of spectral lines corresponding to energy electrons moving from 2 3 3 etcetera to 1 and then this is in ultraviolet range vacuum ultraviolet and then it is a Balmer series another series which where the electrons will fall from three four 5 etcetera to n is equal to 2 that is second electronic level.

Similarly we have Paschen this is in visible range Balmer series paschen series is where 4 5 6 will fall to three bracket series will fall to one and pfund series will fall to n is equal to 5. So, the Bohr's theory could explain the spectra of hydrogen, but it failed completely when it are apply to multiple electronic systems further it could not account for splitting of optical lines when spectroscopes of high resolving power sometimes we will see 2 frequency lines. So, Bohr's theory could not explain.

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So, this is the picture of an electron electronic transition where the Lyman's this these are the Lyman series where all the electrons are falling in to the state one this is Balmer series this is Paschen series and this is bracket series and this is pfund series. So, a single hydrogen atom can give rise to number of spectral lines.