Infrared Spectroscopy for Pollution Monitoring
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Lecture-05
Atomic Structure II

So, greetings to you we are going to start our next session and just want to capture what we had discussed earlier regarding the atomic structure. Just in the in my last class I had mention to you that the Dalton's theory of atomic model we were consist only of the metals being indivisible.

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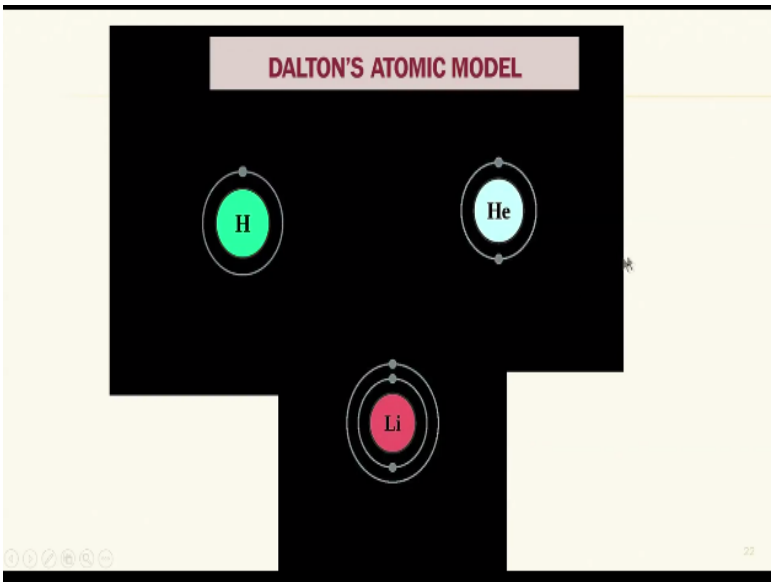

And then I had shown you this slide where hydrogen, helium and lithium etc., they are all supposed to be having independent existence.

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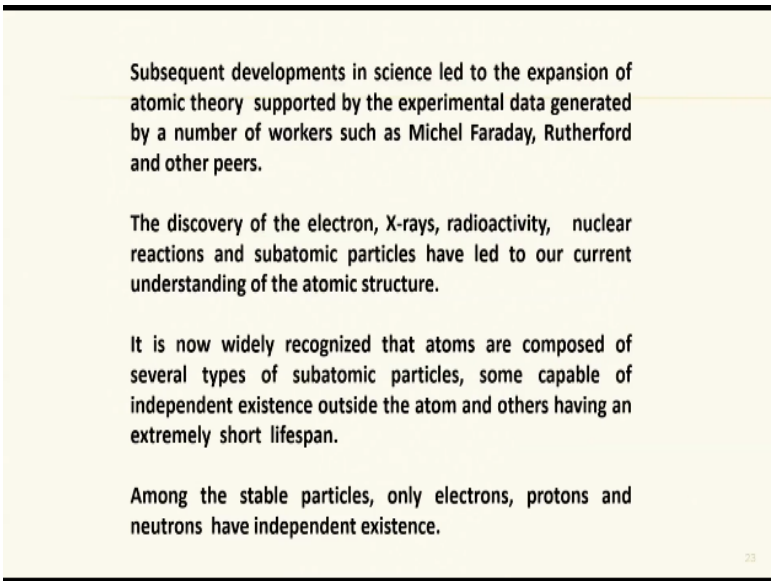

And then I had shown you that the how the development of our understanding of the atomic structure had occurred and then I had showed you the contributions of Michel Faradey, Rutherford and other people Pierce basically. And then I had we had discussed about the discovery of the electron, X-rays, radioactivity nuclear reactions and some atomic particles etc. These have led to the development of our understanding of the current atomic structure, so I had also shown you some results regarding the proton and electron, neutron, proton and electrons.

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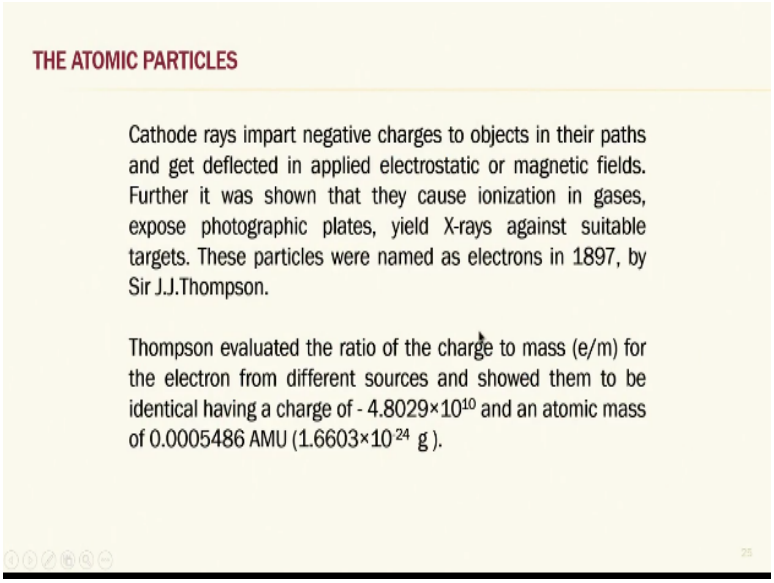

I had shown you that the electron is basically a negatively charged particle having a -4.8029*10 raise to 10 charge and then atomic mass of 0.0005486AMU that is the weight converted into grams would be approximately 1.6603*10 raise to -3.

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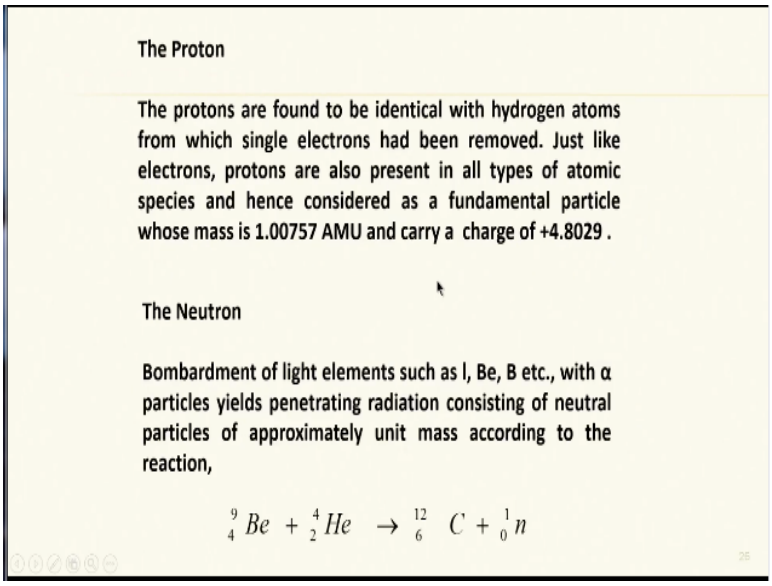

And then I had shown you about the protons in comparison with the electrons is it not. So, the proton charge and AMU I had shown you and I had shown you that the weight of an electron is about 16, 40 times smaller than that. And the neutron also existence of neutrons I had covered earlier.

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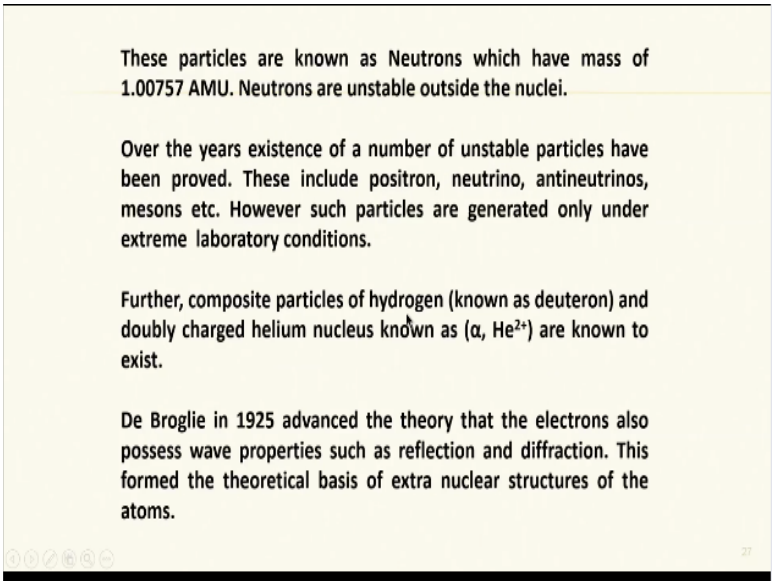

So, the particles known neutrons and other things.

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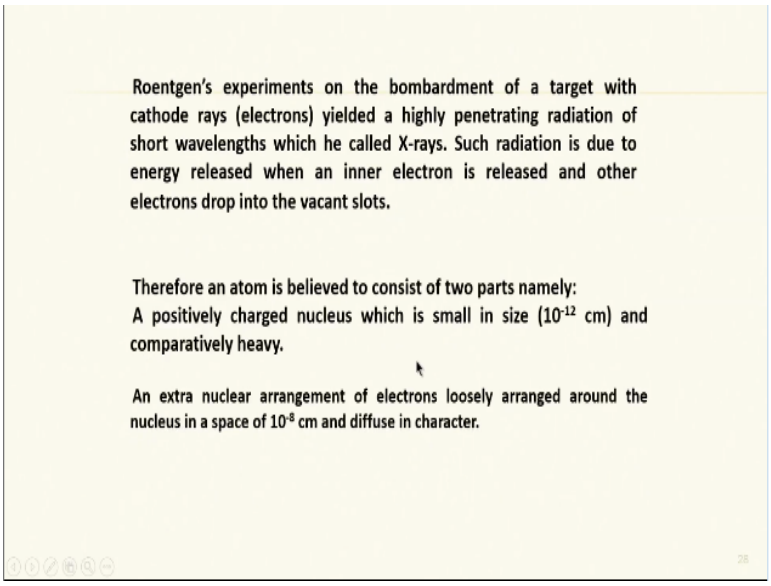

They have all been incorporated in our current understanding of the modern atomic theory.

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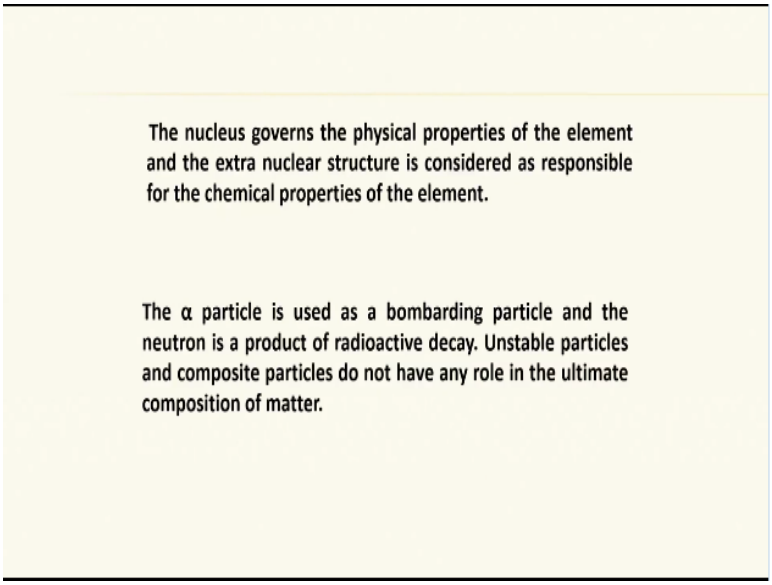

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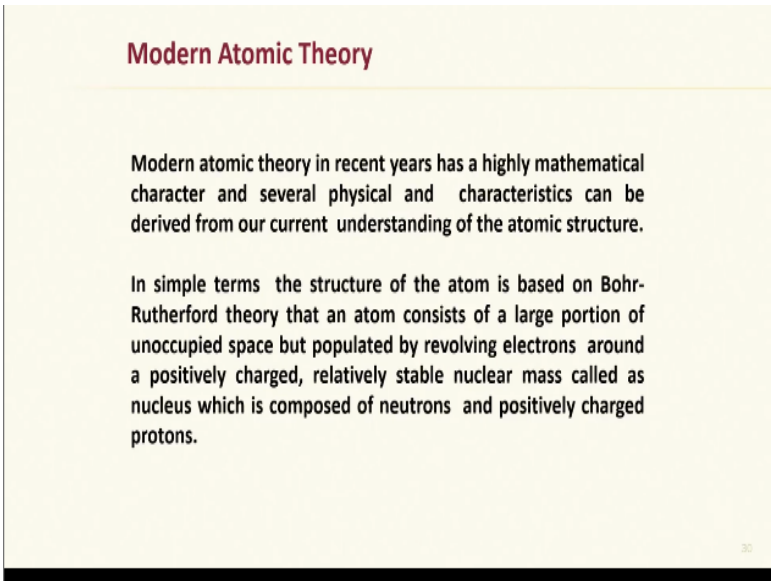

So, this is where we are starting our discussion today and what I want to emphasize now is that in modern atomic theory especially in recent years as a highly mathematical character. And several physical and other characteristics can be derived from our current understanding of the atomic structure. So, in simple terms the structure of the atom is based still on Bohr-Rutherford theory only that an atom consist of a large portion of the unoccupied space.

It that means an atom has large unoccupied space it is empty basically. So, the empty space is occupied at the center with a heavy proton and neutron collection followed electrons around the empty space going round and round which are sort of bound to the nucleus either not getting attracted into the nucleus or not going away from the nucleus. So, that is the space that is where the electrons will be moving around.

And these empty space is populated by revolving electrons surround the positively charged nucleus. So the negatively charged electrons are around the nucleus in the space above and they are not there at the exact place. Now our understanding usually involved that the electrons are going round and round in a fixed path. Now a days that possibility is being almost ruled out that the electrons can move anywhere else.

But the fixed path has been replaced by the probability theory where I can find the electron maximum. So, that again converts into fixed path only approximately but with a slight error with

a slight allowance of the distances where the electrons keep on moving around. So, this slide shows you that basically we have populate the electrons are populating the nucleus and the relatively stable nucleus nuclear mass is called as nucleus only. So, the nucleus consists of neutrons and positively charged protons, so neutrons are not charged and protons are charged.

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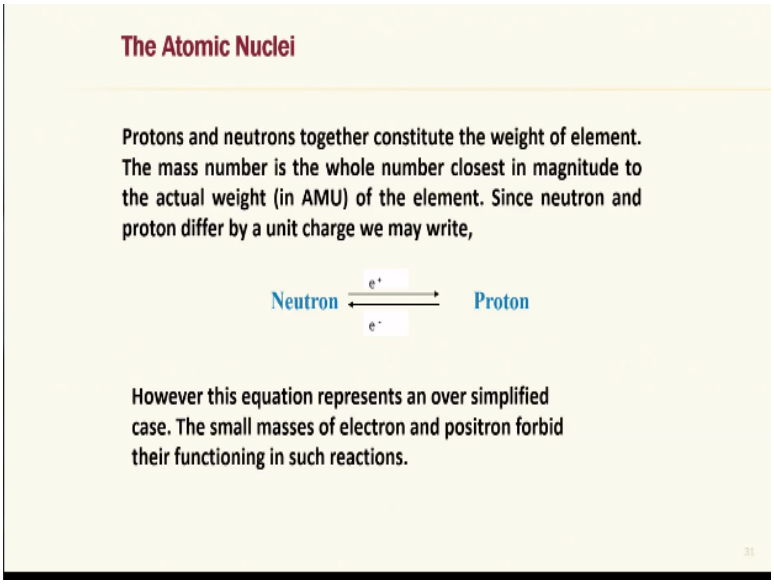

So, the atomic nuclei we are going to consider now there are 2 parts right, so in the atomic structure I said at the center there is heavy nucleus outside there are electrons. So, now we are going to consider the inner part that is heavier part that is atomic nuclei. So the actual weight of an element or an atom is the actual weight of the protons and neutrons, electrons being having the same atomic weight same atomic charge.

But of opposite sign do not in any way much contribute much to the atomic weight. So, the magnitude of an element is basically only due to the atomic mass of the neutrons and protons. So, the neutrons and protons differ only by the charge but not by the weight, so we can always say that there could be some certain amount of the charged transfer between the protons and neutrons we do not know but it is quite possible.

So, what we say is you take neutron add an electron and it goes to proton from the proton if you take out the positive take out the charge we get neutron. So, there is some sort of an equilibrium between the 2 and it could be there or it may be the particles maybe separate having separate

existence and entity even in the nucleus. We still do not know however this equation represents an over simplified picture as I told you.

So, the small masses of the electron and positrons forbid their functioning in such reactions. For example this e+ is something like positron, e- is an electron okay. So, that is also in simple terms only, it is not exact representation of the actual system that is prevailing.

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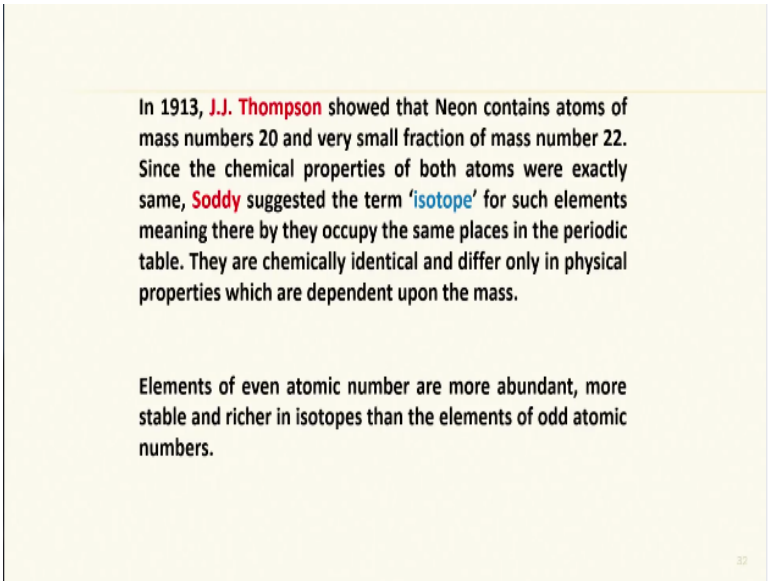

So, in this again a little bit of recapture that is 1937, he showed that the Neon contains atoms of mass numbers 20 and very small fraction of mass number 22. Then now you can consider that with J.J. Thompson's experiment the nucleus of an element maybe different for different atoms. Suppose you take 2 atoms of neon 1 is having mass 20 and another is having mass 22, every small fraction suppose you take a population of about 100.

And then out of 100 there will be 90 atoms with mass 20 and about 10 atoms with mass 22, that means the problem is how is it possible that they are also neutrons, they are also neon's, they are also protons and but the total mass number is different but the chemically all are same. So the chemical properties if both of them are exactly same then the scientific community started thinking that the only way is to think is the occupy the same places in the periodic table.

Because they occupy they have the same chemical properties but their mass numbers are different, atomic weights are different. So, but still they are similar in some fashion, even though they are actually different but they are similar in some fashion. So, Soddy suggested that the term isotope maybe used for this kind of description of such elements meaning thereby they occupy the same place in the periodic they are chemically uniform.

They are chemically identical and but they do differ only in physical properties because the actual weight of the atom is different one is 20 and another is 22. So, then people started looking for different kinds of isotopes for different elements why if this is the case, why it should be the case only with respective Neon's there may be other elements also having the same atomic mass or different atomic mass with the same chemical properties that is also quite possible.

Then people started looking for other elements find out how much of them contain the same number of neutrons and protons and different number of protons and neutrons. So a whole generation for data for isotopes got generated because of that study. But the pioneer again as was J.J. Thompson as shown earlier and the people understood that there are different kinds of elements which are chemically identical but they do differ only in physical properties.

And even elements of then they realized one more property that the elements of suppose there are isotopes or elements with odd number and even number of protons and neutrons. So if there are 20 atomic now weight is 20, if there are 10 and 10, 10 protons and 10 neutrons and the element is very stable and they are more abundant. Then in the same 20 suppose it contains 21, atomic weight. And then there will be chemically similar means 20 protons and 10 protons and 11 neutrons.

So it is an odd number but the same chemicals. So odd number of isotopes are less abundant and less stable and the quantity also will be less. So the atoms of even atomic number elements they are more abundant, more stable and richer in isotopes than the elements of odd atomic numbers. Another discovery that led to the understanding of the isotopes and nuclear structure etc. So except hydrogen, hydrogen has got 3 different kinds of isotopes, hydrogen, deuterium and tritium.

So, all of them carry the only one positive charge and 1 proton and 1 neutron but they have 2 neutrons and deuterium has got 2 neutrons and sorry deuterium has got 1 neutron and 1 proton.

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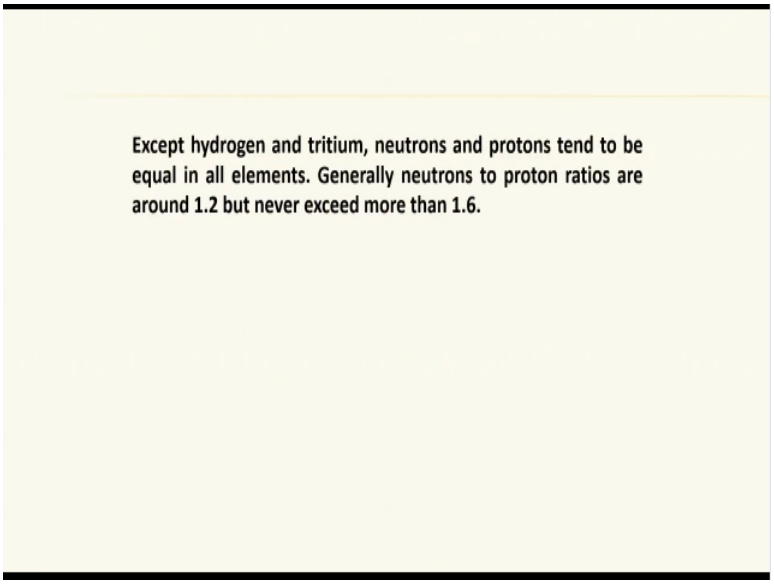

Hydrogen has got only 1 proton and tritium has got 2 neutrons+1 proton. So, atomic weight of tritium would be 3 instead of 1 but chemically they are all same. So, except hydrogen and tritium, neutrons and protons tend to be equal in all elements the tendency of the neutrons and protons seems to be they try to be abundant enough as far as in equal terms.

So generally neutron to proton ratios in all elements are approximately about 1.2 but they never exceed more than 1.6 also. So, our understanding of the nuclear structure got a little more broader when we started looking at the ratio of the protons and neutrons. That is how scientific discovery and development takes place, people look at different aspects of the same property but come up with new ideas regarding their stability, physical properties, chemical properties etc., etc.

That is the beauty and excitement of science with the same amount of information you get lot of things to say, to interpret, to understand, so many other possibility, now look at it. So, you can make postulate that nuclei with even number of neutrons are more abundant.

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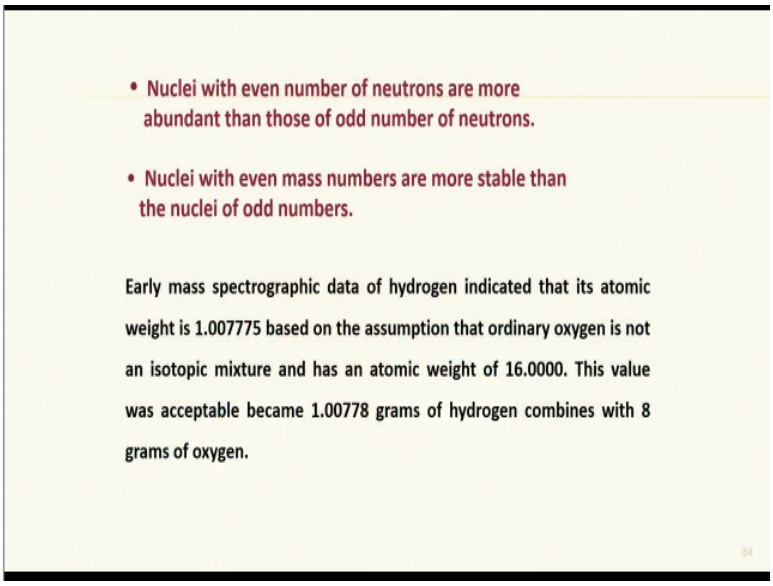

Then those of odd number of neutrons. So, 25, 264, 2, 4, 6, 10, 8 like that neutrons are more abundant than 1, 3, 5 etc., it is an odd number. Then we also have a property of stability that is nuclei with even mass numbers, even mass numbers means 2, 4, 10 etc., 2, 4, 6 you know about odd number odd and even numbers right.

So, with even mass numbers they are more stable than the nuclei of odd numbers that is also an important physical property that is discovered. So, early mass spectrographic data of hydrogen indicated that it is atomic weight is approximately 1.007775 that is atomic mass unit early. It is also it is weight atomic weight. So, this is based on the assumption that the ordinary oxygen is not an isotopic mixture.

But it has an atomic weight of 16, so what people thought this oxygen is very pure under any circumstances. So, the people thought okay we will take oxygen a standard measure the weight of all other elements because oxygen does not have isotope okay. So, this value was acceptable at that time and they rounded off this 1.007775 to 1.007778 last digit rounded off. So, the atomic weight of hydrogen is 1.00778.

And so many grams of hydrogen combined with 8 grams of oxygen to give you water 1gram mole of oxygen water. So, the discovery of again isotopes of oxygen 16, 17 isotopes you know

with 16, 17, 18 mass numbers throughout this theory. So, the people again started predicting that there are 2 types of mass numbers for oxygen also which one to take as standard.

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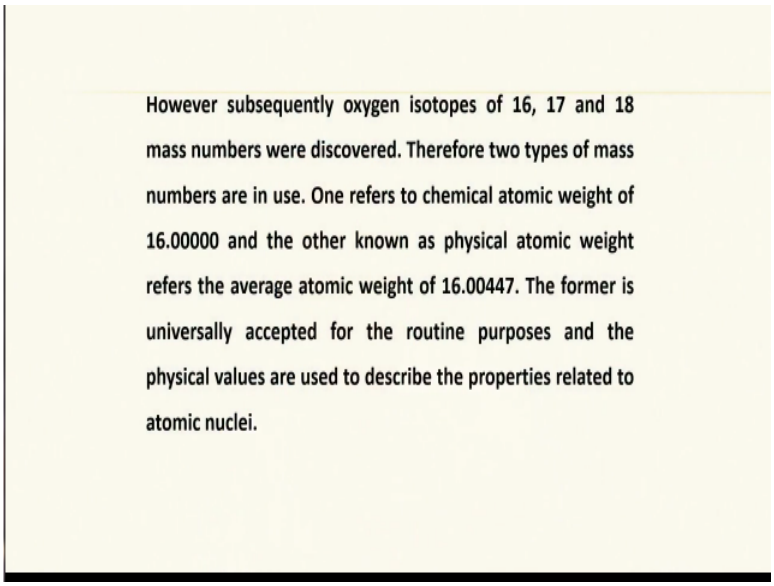

So, 1 refers to the atomic weight of 16.0000 that is 6 zeros and the other 1 is known as the physical atomic weight that refers to the average atomic weight of 16.00447 okay. So, the former is universally accepted for routine purposes, it is not the actual number nor is it is the correct number. So, correct number is obviously 16.00447 but people for all practical purposes when I do not need such a high decimal number to talk to or to take into calculation.

We normally go for 16 but actual atomic weight with respect to the available abundance of the different isotopes of oxygen 16, 17 and 18 works out to 16.00447. So the former is mutually accepted for routine purpose and the physical values are use to describe the properties related to atomic nuclei. So then the nuclear stability as I was telling you that the presence of stable elements, it means the neutrons and protons are held together by attractive forces.

Remember neutrons and protons at the center of the atom they also must be held together otherwise there will be not there at all why a charged particle like proton should hold a neutron which does not have a charge. But the facts look otherwise that both neutrons and protons are together, so there must be some sort of attractive force between the protons and neutrons in any element.

Because every element contains protons and neutrons except hydrogen right. So, once hydrogen is discounted we have deuteron, tritium, deuterium, tritium etc., and then lithium they all of them have got neutrons along with the protons at the nucleus. So there must be some sort of attractive forces between the protons and neutrons.

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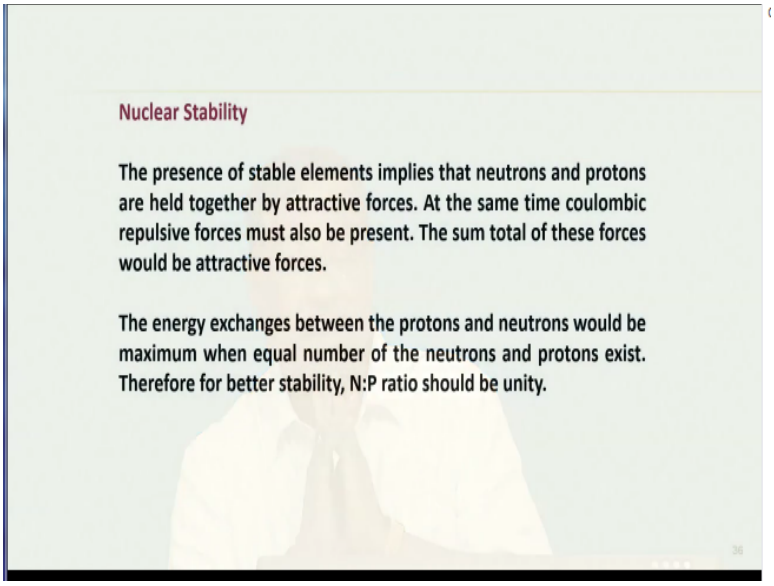

So, the at the same time the coulombic forces must also be present for repulsion, so the sum of the sum total of these coulombic forces as well as attractive forces would be more attractive than the repulsive forces otherwise they would not be together as simple as that okay. So just imagine the protons are there, neutrons are there, protons are positively, neutrons are not charged, still they are together with due to some reason.

And there must be some sort of binding forces, if there are binding forces between the positive charge and 0 charge of the neutrons there must also be repulsive forces between the 2, it is just logical. So, the idea is when both positive attractive charges and repulsive charges are there in between the protons and neutrons of an element the sum total must be positive or attractive if they are to be held together, so that is the logic.

So the energy there must be some sort of energy exchange between the protons and neutrons otherwise it is not possible to for them to be together. So, it would be maximum, when protons

and neutrons existing equal numbers. So, the possibility of an isotope having an even number being more abundant automatically explains itself. Therefore for better stability the N/P ratio that is look the slide now, the N/P ratio should be unity only that is for better stability. There cannot be any other way of interpreting such nuclear forces.

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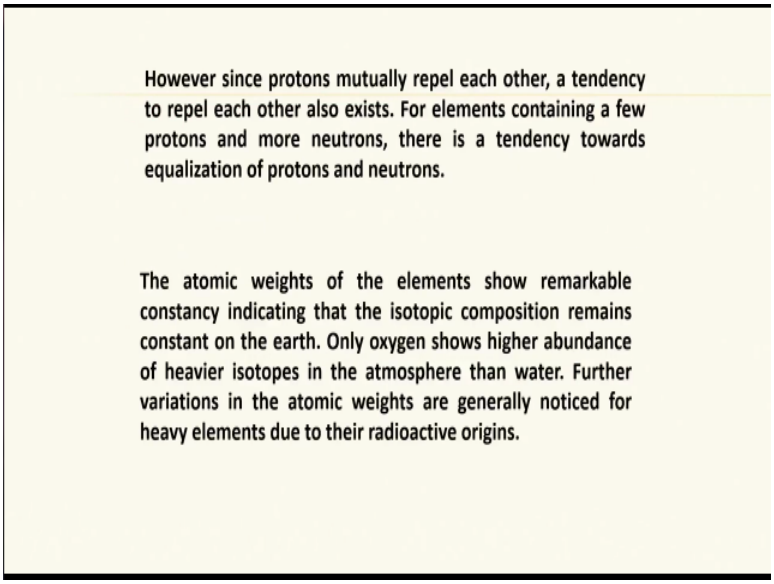

So, we can again say consider another possibility what is that possibility, so here we consider a proton is having a positive charge. Now there are number of protons in a given nucleus, so but there are the positively charged proton and negatively charged neutrons are held together by some forces that is understood. But there must be very big repulsive force between 2 positively charged protons, that is understood know.

So, if protons are still held together there must also be a repulsive between the 2 protons of the same element right. So, otherwise they need not be together at all, so there must be a tendency to repel each other existing. So, for elements containing few protons and more neutrons this tendency towards, there is a tendency towards equalization of protons and neutrons.

So, the atomic weight of an element show remarkable constancy indicating that the isotopic composition remains constant on the earth. Only oxygen shows higher abundance of heavier isotopes in the atmosphere than water, so this you should understand why water has got hydrogen and oxygen, hydrogen has got hydrogen, deuterium and tritium. So, the water must be

having very high abundance of isotopes of water okay compare to just water with hydrogen, water with deuterium and water with tritium.

But oxygen also has an isotopes, so all the molecules all the water molecules in a given water body would be containing the all the isotopes of hydrogen, deuterium, tritium and oxygen 16, 17 and 18. So only oxygen among these only oxygen shows higher abundance of heavier isotopes in the atmosphere also than water. So, it makes lot of difference in understanding why such a thing should happen because water also evaporates along with all the isotopes at room temperature.

We all know that humidity is there, relative humidity is there and everywhere there is water in the air. So the oxygen with higher isotopes should also be there in the environment with different isotopes. Further variations in atomic weight are also seen for heavy elements that due to radioactive origin. We will not go much into detail about that but it is better to understand that just like oxygen, just like water.

There must be other elements in the showing variation in the atomic weight for other element but they could be of radioactive origin some of them could be radioactive, some of them need not be radioactive that means the radioactive elements will keep on contributing to the isotopes population of isotopes.

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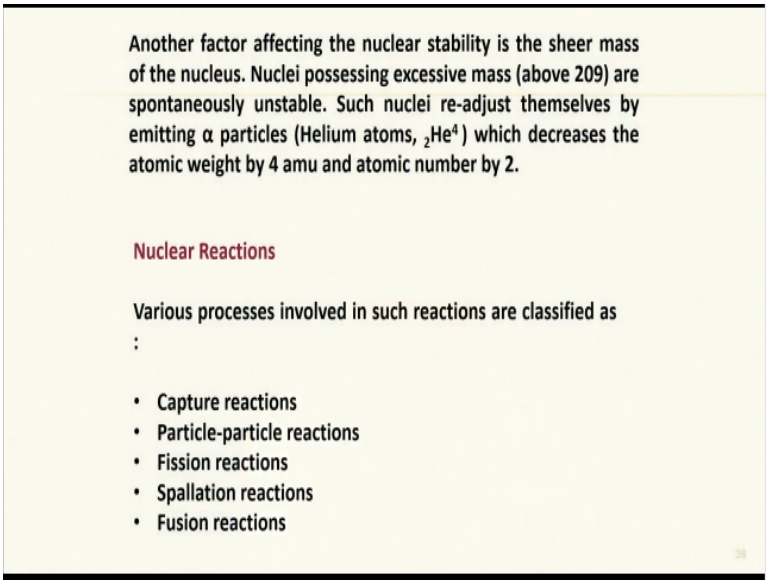

So, another factor that affects the sheer mass of the nucleus, so nuclei possessing excessive mass are spontaneously unstable okay. Now the beauty of chemistry look at it, if the element small is beautiful you know every poet says small is beautiful, small is hand level, small is manageable and all those things we know. The same as true with respective elements also, the elements in the periodic table there are about 109 elements in the periodic table is it not know starting from hydrogen, helium, lithium, Beryllium, boron, carbon, nitrogen etc. etc.

And then copper, nickel, platinum, palladium, actinides, lanthanides, actinides, radioactive elements, lawrencium and all newly discovered elements. Among all these the 1 property that is very evident is the atomic weight and then suddenly we find at as the element becomes bigger and bigger. That means as the number of protons and neutrons keep on increasing there comes a certain time when higher elements are not so stable.

It is just like putting a heap of cards one above another and there will be certain amount of stability but the moment you cross certain stage the stability it is starts wobbling you know pack of cards you make them stand one above another like a pyramid you keep on building one above another at some state it will start wobbling and falling. Exactly same thing happens even here because element we know that elements with excessive mass that is more than 209.

That is assume that half of them are atom protons and half of them are neutrons about 108 is the element maximum. So, above that all the elements are spontaneously unstable it is not possible to for the elements stable in the environment. So, what happens to such elements when they are synthesized in the environment or in some conditions, we all know that lot of elements are discovered in the radioactive reactors, nuclear reactors.

So, assume that such an element with higher atomic weight is formed and we keep on reading that lot of scientist keep on working on combining neutrons and protons etc. to produce higher elements. So, such nuclei even if they are formed they will have a very short lifetime that means they must disintegrate by themselves. So, such nuclei re-adjust themselves by emitting alpha particles.

That is what are alpha particles, alpha particles are 2 Helium atoms, Helium atom with 2 atomic number and 4 atomic weight. So, they start emitting alpha particles which decreases the atomic weight by 2 atomic weight by 4 AMU and atomic number by 2. So, now we know that the nuclear stability is also a function of the neutrons and protons okay your show you keep on building them they start disintegrating I just now said that the elements with higher atomic number more than 209 will start emitting helium atoms.

And then they undergo disintegration to produce lower atoms which are more stable that is understood, that means we are talking about nuclear reactions right. So, what kind of nuclear reactions normally we expect in the building of the atoms, so look at the slide now. We have number of chemical reactions which will show you that how to build up nuclear new elements or the nuclear reactions themselves can be classified into different systems.

That is 1 is capture, another is particle-particle reactions and then fission reactions, spallation reactions and fusion reactions. So these are all different classes of nuclear reactions that we can expect them to go around.

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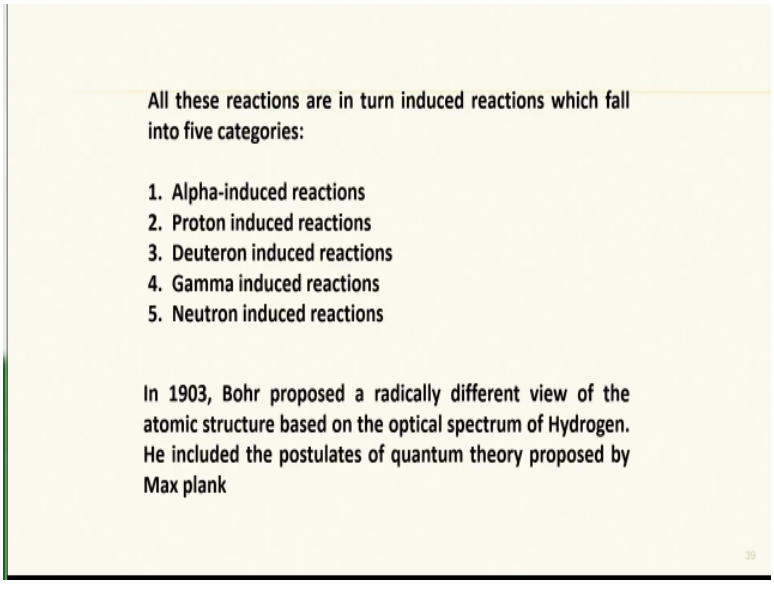

And then there are other reactions in turn induce reactions which will fall into 5 categories, that is alpha induced reaction. So, that is alpha particle 2 Helium atoms with 4 atomic mass and then proton induced reactions you take an atomic element. And then bombard them with protons such

reactions are known as proton induced reactions. So, sometimes you protons means hydrogen okay, hydrogen atoms keep on bombarding them you will get certain amount of reactions.

Then there are deuteron induced reactions and then you can take the elements and they make them react with gamma rays. And then gamma these are known as gamma induced reactions and then or you can simply bombard them with neutrons. So, neutron induced reactions are also there in the nuclear reaction region. So, in so far about the nuclear this thing I do not want to go more into detail.

Because in this course we are not going to deal much with atomic nuclei, the whole system of this electro infrared spectroscopy does not deal specifically with the nuclear reactions or with the nucleus also. It mostly deals with the electrons in the circulating around the nucleus, so now our discussion will having known the nature of the nucleus our discussion will move towards the electrons.

Now in 1903 Bohr proposed a radically different view of the atomic structure based on the optical spectrum of hydrogen. So, this was probably the first time the spectrum was used spectrum of hydrogen was used to interpret to correlated to the atomic structure, that is electronic structure. So, the earlier foundations of physics had been laid quite somewhere or even around 1700 and then there was quantum mechanical theory also was there, quantum mechanics theory was around since quite long time.

And then the blackbody radiations etc., where studied earlier there was Wien's law and then Stephen's law and many other laws had contributed to our understanding of the quantum mechanical theory also a little bit. And for the first time Bohr try to correlate the quantum mechanics and quantum theory and electronic structure or spectral structure of hydrogen. So, the first time look at the slide now that is what I have written actually he included the postulates of quantum theory by proposed by the proposed by Max Plank.

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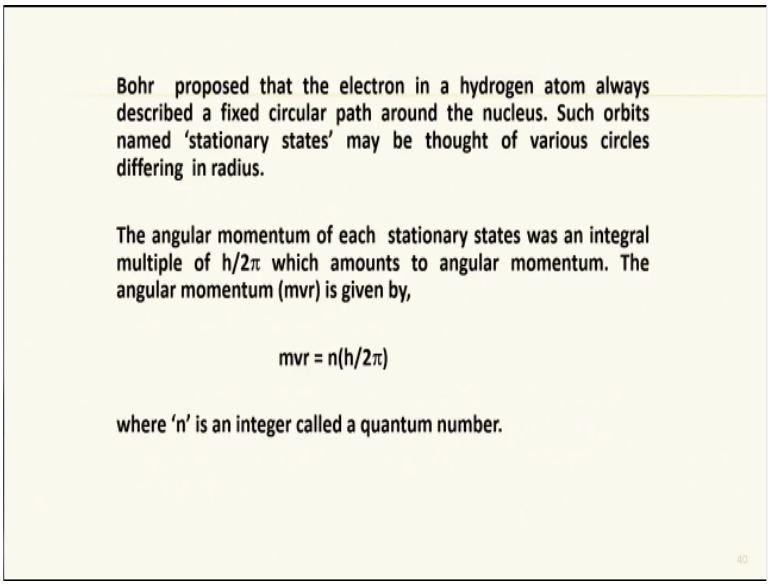

And what did he actually propose, he propose that the electron in hydrogen atom always described say prefix say circular path. This figure we have seen earlier that in the Dalton's when I was explaining to you about the Dalton's theory, I will show you electrons going round and round with this small red orbits. So, that is Bohr's theory and he had described a fixed circular path around the nucleus for the electrons to move around.

So, such orbits are called stationary states and they may be thought of various circles differing in radius. So, the angular momentum of each stationary state was such this is Bohr's theory. That is the angular momentum he described for each stationary state was an integral multiple of h/2 pi where h is Plank's constant Pi and now what it is 3.14 to etc. etc. it the number goes on infinitely. So, they are all multiples of h/2 Pi which amounts to angular momentum.

So the angular momentum is given by a very simple equation that is mvr mass*velocity*radius. These is that multiple of nh/2 Pi. I have written it in the slide you can take a look but the point here is mvr=nh/2 Pi is there now. There is n, n is an integer called as quantum number, he did not say n is a variable number, it is not contain as variable but it is it assumes n=1. And then n=2, n=3 etc., but not n=1.1 or 1.01 or 1.2, 1.7, 2.7 like that it cannot be a fractional number.

So, he postulated that as long as the electron remained in a stationary orbit going round and round it neither radiates energy nor absorbs energy. So the fundamental principle of spectroscopy

is that the transition there must be some amount of transition in the energy level for the electron to go is not violated.

That means on it is own if you do not subject any element to any external force the electrons will remains stationary in the same orbit going round and round, that is their business. So, the going round and round in an electronic orbit is described by the mechanical forces of attraction and repulsion and angular momentum and etc. etc. centrifugal force and center fugal forces.

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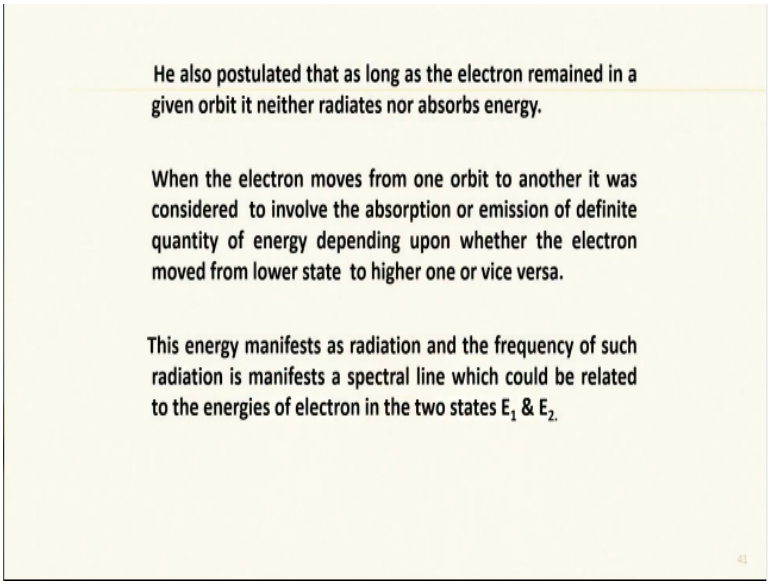

So, that the electron does not fall into the nucleus, so when the electron moves from 1 orbit to another it was consider to involve the absorption or emission of definite quantity of energy depending upon whether the electron moved from lower state to higher state or higher state to lower state. So lower state to higher state means energy becomes less because it is distance from the nucleus becomes larger or from higher state to lower state means it comes nearer the nucleus and it is energy increases.

So the electron moves from lower state to higher state or vice versa depending upon the conditions. So, the energy manifest itself as radiation and the frequency of such radiation is a manifest spectral line which could be related to the energies of the electron in both the states that is E1 and E2. This E1 and E2 are simply arbitrary numbers that do not mean much except to

signify the 1 is E1 is maybe lower, E2 may be higher, arbitrary could be rather way around also okay.

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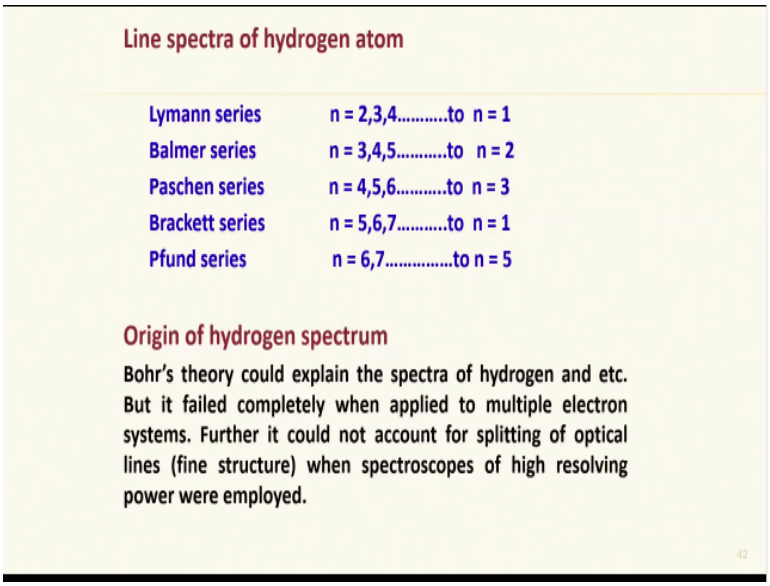

So, we assume now that the spectrum of an electron of 1 electron can be of 2 types, 1 is going to higher energy another is going to lower energy. But there are number of electrons okay, so all these electrons move could be moving from 1 energy level to another energy level, all electrons. Then another possibility exist that the electrons from second energy level may fall to the first, electrons from third energy level may fall to the first or second.

Electron from third level may fall to first, second or third right, so the possibilities of electrons moving from 1 energy state to any other state is quite large it is that means the more number of possibilities means more number of spectral lines okay. So, what this line spectra of hydrogen what was observed and they know most of these where recorded even somewhere around the year 1700s okay late 1700s.

But people did not know how to interpret them it was first time introduced somewhere around 1800s and so, when people try to understand what is happening in this spectrum. So, we knew a series of dark lines seeing. But and correlate them to wavelength and spectrum also. So, according to this Bohr's law n is n varies from 1 to any number, 1 to n or 1 to infinity also okay.

So, the n is when n is 1 all electrons from orbit number 2, orbit number 3 and orbit number 4 all of them can fall to n=1 it is first electronic level. And then instead of when from 3, 4, 5 electrons in orbits 3, 4, 5 may fall to second orbit, 2, 3, 4 by fall in 1 fall up to 1 and 3, 4, 5 may fall up to 2 and 4, 5, 6 may fall up to 3 and 5, 6, 7 should fall up to 1 and electrons in orbit 6 and 7 may fall up to 5.

So, there could be higher numbers but they do not much significance in the interpretation of line spectra of hydrogen. So, if this is the case n=2, 3, 4 and n= if the all of them fall to the same energy level that means the region of spectrum is these are all these spectral lines follow a particular transaction transition. And for n is 2 to 1 there is 1 line, 3 to 1 there is 1 line, 4 to 1 there is another line.

So, it is describes all the possibilities describe a series of lines, spectral lines as for as hydrogen ion is hydrogen spectrum is considered. So, we have different series 1 is Lymann series when n=1 final resting place for the electron and then this is in the ultraviolet region. And second is Balmer series that is in the visible region. And then Paschen series near ion Brackett series, Pfund series etc.

These are all in microwave and radio wave regions etc., so the origin of hydrogen spectrum Bohr's theory could explain the spectra of hydrogen. But it failed completely to when apply to multiple electron systems see in this case in the case of hydrogen there is only 1 electron that could that 1 electron could be in n=1, n=2, n=3 etc., but suppose I have an element with 10 electrons.

So, all the 10 maybe in n=1, n=2, n=3 like that the possibilities of the electrons being in different orbits could become enormous and the spectrum could become very complicated. So, Bohr's theory failed to account for the multiple electron systems further it could not account for splitting of optical that we will study when we go up in and understanding of our electronic structure but basically it is regarding the fine structure and spectroscope of high resolving powers were employed.

This again required a technical advancement of manufacturing very high level spectroscopes. So, we will study further about the electronic structure and electronic transitions and their relation with the spectrum in our next class, thank you.