

**Atomic and Molecular Absorption Spectrometry
for Pollution Monitoring**

Dr. J R Mudakavi

**Department of Chemical Engineering
Indian Institute of Science, Bangalore**

**Lecture – 02
Atomic structure**

So, this is the second part we are starting our discussion earnestly with the atomic and molecular structure. Now many of you know what I am going to teach because it is a part of your studies right from your high school days and college days.

(Refer Slide Time: 00:45)

ATOMIC AND MOLECULAR STRUCTURE

The concept that the matter is built up of tiny discrete particles traces its origin to ancient Hindu scriptures such as Vedas. The description of atom and electrons and molecules known as paramanus, anu and kana has permeated the Indian social milieu since 2000 B.C. However it was John Dalton 'the father of modern atomic theory' who provided the first scientific hypothesis of the structure of the atom in 1802. He suggested that the matter is composed of tiny real particles called atoms which are indivisible, cannot be created or destroyed. Atoms of each pure substance are identical in nature, weight, size and other properties. Atoms of one pure substance differ in weight and other characteristics from those of other substances. Further he suggested that union of atoms in definite numerical proportion results in chemical combinations.

But nevertheless it is important to recapture the atomic and molecular structure, because that has got fundamentally something to do with spectroscopy; because spectroscopy is a science that deals with the interaction of matter with electromagnetic radiation. Therefore, the components of the matter are the ones which are going to be affected by the properties, interaction of electromagnetic radiation normally involves the interaction of with electrons, protons, nucleus and all those things therefore, it is important for us to know about the atomic and molecular structure of a compound.

So, what I am going to teach you in this aspect. So, we can see on the slide in front of you that the concept that the matter is built up of tiny discrete particles traces its origin to ancient Hindu culture scripture such as Vedas. The description of atoms and electrons in

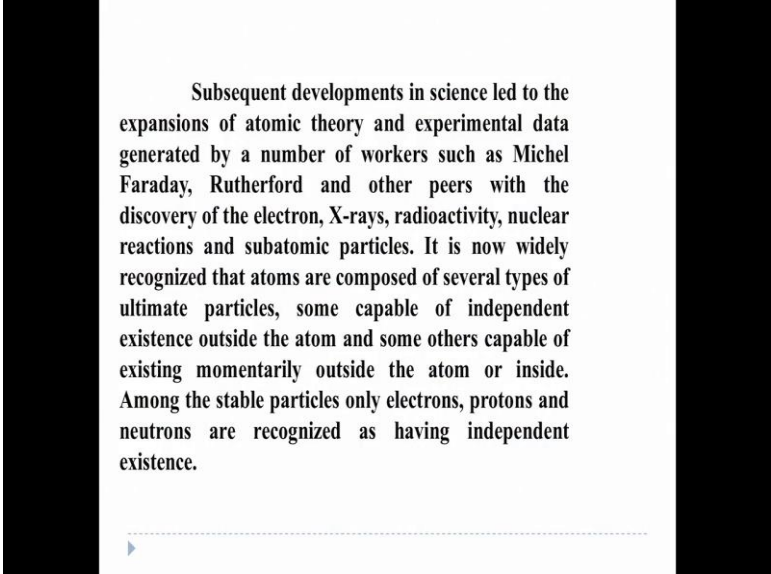
molecules are known as paramanus, anu and kana and all these terminology has permitted the Indian social milieu since 2000 B.C; however, it is the much of the information about the atomic structure etcetera paramanu and other things, has when you in Indian culture has been lost, but it was John Dalton in ah 1802 he provided as the first glimpse into the structure of atoms, and rightly he is called the father of modern atomic theory, he provided the first scientific hypothesis of the structure of the atom in 1802 he suggested that the matter is composed of tiny real particles called as atoms, which are indivisible and which cannot be created nor destroyed.

Atoms of each pure substance are identical irrespective of the nature of the material; what he said essentially is the atom in gold, metal all atoms are uniform and identical. Similarly atoms in steel iron there all uniform and identical to each other, and similarly for copper this metal and other metals etcetera. So, atoms of each pure substances are also identical in nature weight, size and other physical properties. Therefore, atoms of one substance pure substance differ in weight and other characteristics from other substances then the same substance; further what he suggested is that the union of atoms occurs in definite numerical proportions, which results in chemical combination which we normally recognize nowadays has compound formation ok.

So, the this much knowledge has not changed because over the years you have learnt quite a lot about what is a nucleus, what is a proton, what is a electron and all those things, but the fundamental principles what he thought has somewhere around 1802 is that the chemicals are formed by the combination of several elements, which will produce compounds in definite proportions this does this has not changed.

So, the principles evolved several 100 years ago they are all still applicable for our day to day life in some form or the other our. (Refer Time: 05:13) might have changed our method of dealing might have been changed, our method of discovery and other things have changed, but the fundamentals remain essentially same for example, even the atoms we know that they are composed of electrons, protons, neutrons, meson and several pi mesons etcetera, but the fundamental being fundamental particles they remain identical to each other that is what Dalton has suggested; that that is why and the greatness of Dalton lies.

(Refer Slide Time: 05:49)



Subsequent developments in science led to the expansions of atomic theory and experimental data generated by a number of workers such as Michel Faraday, Rutherford and other peers with the discovery of the electron, X-rays, radioactivity, nuclear reactions and subatomic particles. It is now widely recognized that atoms are composed of several types of ultimate particles, some capable of independent existence outside the atom and some others capable of existing momentarily outside the atom or inside. Among the stable particles only electrons, protons and neutrons are recognized as having independent existence.

So, but I will continue our discussion like this that subsequent developments in science have led to the expansion of atomic theory, and experimental data generated by a number of workers such as Michel Faraday, Rutherford and other peers in the discovery of electrons, X-rays, radio activity, nuclear reactions and subatomic particles; it is now widely recognized that atoms are composed of several types of ultimate particles which I just now told you that they are all too small for even independent existence, but nevertheless they are all ultimate particles the same. So, some of them are capable of independent existence outside the atom and some others are capable of existing only momentarily; outside the atom or inside an atom. Among this stable particle what we normally recognize in our day to day chemical life scientific life is electrons, protons, and neutrons as having the independent existence for our day to day science requirements also.

So, we invoke their structure and we invoke their properties at each and every aspect of a chemical reaction.

(Refer Slide Time: 07:14)

Among the atomic components only three particles namely electrons, protons and neutrons are recognized as stable particles.

The stable particles : Electrons, protons and neutrons

Electrons are made up of small but energetic negatively charged particles whose existence was proved by Sir J.J Thompson. Electrons are fundamental particles of all substances.

So, among the atomic components in the stable particles therefore, are electrons, protons and neutrons. Electrons are made of this is a very simple system if I want to teach about electrons etcetera you will be laughing at me, but at the same time it is important for us to recognize that electrons are made up of small, but energetic negatively charged particle, whose existence was approved by sir J J Thomson and electrons are fundamental particles of all substances that we come across in our day to day life.

(Refer Slide Time: 07:50)

incandescence, impart negative charges to objects in their paths and get deflected in applied electrostatic or magnetic fields. Further it was shown that they cause ionization in gases, expose photographic plates, yield X-rays against suitable targets. These particles were named as electrons in 1897, by Sir J.J.Thompson. Thompson evaluated the ratio of the charge to mass (e/m) for the electron from different sources and showed them to be identical having a charge of -4.8029×10^{10} and an atomic mass of 0.0005486 AMU ($1.6603 \times 10^{-24}g$).

De Broglie in 1925 advanced the theory that the electrons also possess wave properties such as reflection and diffraction. This formed the theoretical basis of extra nuclear structures of the atoms.

Then incandescence the impart negative charge electrons in general, when they strike the strike a TV screen or something like that cathode radio, they impart negative charges to their objects to their paths and get deflected in applied electromagnetic or electro static fields.

So, if there are if the there is a positive article if there is a positive electrode, and if there is a negative electrode electrons will always move towards the positive electrode right. So, these are all fundamental laws which nobody can change, further they had also shown that they could cause ionization in gases. So, electrons do cause ionization gases they whenever we expose photographic plates, the cause the photographic plates to burn off and then yield the yield X-rays and again (Refer Time: 09:00) suppose you take the electrons and heat them on a metal plate this thing and then you will get other raise which are not electrons, but electromagnetic radiation having a different wave length.

So, electrons are also being smaller particles they can be treated as waves or they can also be treated as particles. So, all these waves and particles will move in a wave form and whenever these electrons are bombarding the metals, the movement of the amplitude and frequency of the out coming rays will change, and they are known as x rays some of them could be hard X-rays. Some of them could be soft x rays soft X-rays people use it for X-ray medical purposes etcetera to photograph the bones and bone structure etcetera and hard X-rays are used for some other purposes such as the identification as the metals in a high energy fields.

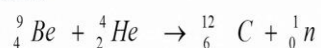
So, Thomson it was sir J J Thomson evaluated the ratio of the charge to mass, this is a very important property charge to mass for a electron from different sources what he said is the it has a charge of minus 4.9029×10^{-10} , and an atomic mass would be approximately 0.0005486 atomic mass units because we do will do not use atomic mass units when we convert it into actual number, what it means is an electron ways 1.6603×10^{-24} grams. Now the another advance with respect to electro electrons was de Broglie's theory that they also posses wave of properties such as reflection and diffraction, this formed the theoretical basis of extra nuclear structure of the atoms.

(Refer Slide Time: 11:05)

The protons are found to be identical with hydrogen atoms from which single electrons had been removed. Just like electrons, protons are also present in all types of atomic species and hence considered as a fundamental particle whose mass is 1.00757 AMU and charge is +4.8029.

The Neutron

Bombardment of light elements such as Li , B , B etc., with α particles yields penetrating radiation consisting of neutral particles of approximately unit mass according to the reaction, These particles are known as neutrons.



So, I think this much information should be more than enough for you for our at least for our purpose. If you are studying slightly higher degree or something like that, then it would be spending sometime on how the electrons are discovered, how the experimentally set up etcetera etcetera, but essentially what we should know about electrons in our course is what I have thought you so far. We may not use a electronic charge or atomic mass units directly in our day to day requirement, but that much information is helpful.

Now, you may also say that the what about the other particles protons; protons are the exact opposite of electrons. So, if a substance is made up of protons and electrons, the charge should match the is not it. The protons are found to be identical with hydrogen atoms because that is the lowest element smallest element we know. So, let us the having independent existence. So, the proton it is suppose to be having one proton, and that is known as proton; you can also call hydrogen atom as proton from which single electron has been removed, if you take hydrogen atom to make the hydrogen atom neutral you need to have one proton and one neutron.

Now, proton is their electron has been removed. So, it must be having a positive charge. So, the protons are also present in all types of atomic species, and hence considered as fundamental partial whose mass is 1.00757 atomic mass units and its charge is 1 plus 4.8029 then the other particle that we know of having independent existence is the

neutron, the bombardment of light elements such as lithium, beryllium, boron etcetera with alpha particles yields penetrating radiation consisting of neutral particles of approximately unit mass according to the reaction what I have that I have written here, that is $9\text{Be} + 4\text{He} \rightarrow 12\text{C} + 1\text{n}$, and 4 atomic mass with helium with two protons and if you bombard them with helium atoms, what you will be getting is a neutron particle with one atomic mass and zero charge that is important is zero charge.

So, the property of the neutrons is very well utilized in our day to day life, because many of these substances because they contain more neutrons apart from protons and electrons they lend stability to the metals, stability to the elements stability to the compounds etcetera.

(Refer Slide Time: 14:20)

The atomic mass of a neutron is 1.00757 AMU.
Outside nuclei neutrons are unstable.

Over the years a number of unstable particles have been proved such as positron, neutrino, antineutrinos, mesons (particles incapable of independent existence). However such particles are generated only under certain conditions.

Further composite particles of hydrogen (known as deuteron) and doubly charged helium nucleus known as (α , He) are known to exist

(Refer Slide Time: 14:23)

The former is used as a bombarding particle and the latter is a product of radioactive decay. Unstable particles and composite particles do not have any role in the ultimate composition of matter.

1.3 Modern Atomic Theory

Modern atomic theory in recent years has a highly mathematical character and several physical and chemical characteristics can be derived from our current understanding of the atomic structure. In simple terms the structure of the atom is based on Rutherford's theory that an atom consists of a large portion of unoccupied space but populated by revolving electrons around a positively charged, relatively stable nuclear mass called as nucleus which is composed of neutrons and positively charged protons.

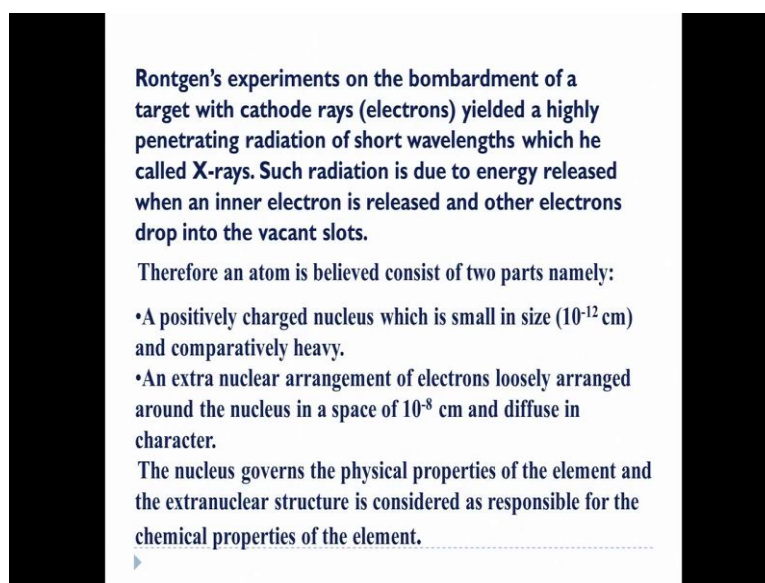
So, that is a very important aspect. So, the former is used as an alpha particle is used as a bombarding particle in the previous example what is have previous slide, and the latter is the product of radioactivity decay. Now neutrons that means, neutrons have been discovered in radioactive decays. So, unstable particles and composite particles do not have any role in the ultimate composition of the matter this is what I have been trying to tell you. So, sort of a fundamental truth what it is, basically unstable particles and composite particles do not have any role in the ultimate composition of the matters, they do not take part in the chemical reaction or even if they do their effect is so minimal, but we can safely ignore the presence of sub atomic particles in our day to day life.

Now, the modern atomic theory what we have been discussing is in recent years has a highly mathematical character; we can write several equations for the particle movement, and for the nuclear movement, and all those things, and several physical and chemical characteristics can be derived from our current understanding of the atomic structure. In simple terms what I want to tell you is that the structure of the atom as we understand today is based on Rutherford's theory, that an atom consist of a basic protons and neutrons along which there are several electrons going round and round, the charge on the protons is balanced by the revolving electrons and the a revolving electron around a nucleus presents a very stable picture, because of this centric fetal and centric fusel forces, and an atom remains in space that is it does not the electron does not fall into the protons. Because normally you should remember that electron as no mass almost nil, so

it may if there is moment term is not balanced, the electron may fall into the proton and several things can happen which are not imaginable in on day to day life.

So, in simple terms what we have is an atom what we should understand is an atom should consist of a large number of unoccupied space, but populated by revolving electrons around a positively charged, relatively stable nuclear mass called as nucleus which is composed of neutrons and positively charged protons.

(Refer Slide Time: 17:20)



Rontgen's experiments on the bombardment of a target with cathode rays (electrons) yielded a highly penetrating radiation of short wavelengths which he called X-rays. Such radiation is due to energy released when an inner electron is released and other electrons drop into the vacant slots.

Therefore an atom is believed consist of two parts namely:

- A positively charged nucleus which is small in size (10^{-12} cm) and comparatively heavy.
- An extra nuclear arrangement of electrons loosely arranged around the nucleus in a space of 10^{-8} cm and diffuse in character.

The nucleus governs the physical properties of the element and the extranuclear structure is considered as responsible for the chemical properties of the element.

So, they were also have also been explaining to you about the X-rays. So, (Refer Time: 17:26) experiments on the bombardment of a target with cathode rays, that is electrons has yielded a highly penetrating radiation of short wavelength, and which he calls X-rays. So, search radiation is also due to the energy released when an inner electron is release because when you take the electrons bombardment them on a piece of metal, the metal will knock off some of the electrons and search radiation is due to be released also when an inner electron is released other electrons drop into we can we can what.

Now, you should understand the atomic structure in such a way that there are electrons round and round, there will be grown there will s shell, k shell, l shell, m shell etcetera. So, when an electron from l shell goes off the one with m shell will fall into that, and the to maintain the electrical neutrality. So, such radiation is due to the energy released when an electron is release therefore, an atom is believed to consist of two parts namely, a positively charged nucleus which is small in size the what is a size, the size is

approximately 10^{-12} centimeter, it is comparatively heavy with respect to all the electrons put together in the same system. So, it is also an extra nuclear arrangement of electrons loosely arranged around the nucleus in a space of about 10^{-8} centimeter, now you should recognize here when I say that the electronic the nuclear size is 10^{-12} centimeter and electrons are arranged in a space of about 10^{-8} centimeter, the space around it is of the order of about 10^{-4} centimeter area 10^{-4} centimeter which is almost about 10,000 times then the an electronic can occupy 10,000 the a volume of electron the what it occupies would be one hour 10,000 by 1000 of centimeter space therefore, we can assume that in general all the electrons they all there all diffused you know they are not fixed exactly they may be moving in that small space in large quantities in different directions etcetera and there is a wide variety of possibilities.

So, the nucleus governs physical properties of the element and the extra nuclear structure is considered as responsible for the chemical properties of the element.

(Refer Slide Time: 20:23)

1.4 The atomic Nuclei

Protons and neutrons together constitute the weight of element. The mass number is the whole number closest in magnitude to the actual weight (in AMU) of the element. Since neutron and proton differ by a unit charge we may write

$$\text{Neutron} \xrightleftharpoons[e^-]{e^+} \text{Proton}$$

However this equation represents an over simplified case. The small masses of electron and positron forbid their functioning in such reactions.

So, now what do we finally, call this structure; the atomic nuclei basically it is protons and neutrons put together constitute the weight of the element, the mass number is the whole number closest to the in magnitude to the actual weight of the element. When we say actual rate we mean atomic mass units, since neutron and protons differ by unit

charge, we may write neutron gaining an electron or losing an electron converts itself into a proton and proton gaining or losing an electron converts it into neutrons.

However this equation is a very very very simplest case, the small masses of electrons and positrons forbid their functioning in such reactions. In general even though such a equilibrium reaction is supposed to take place it does not take place, because of the small masses of the electrons and positrons around the nucleus.

(Refer Slide Time: 21:37)

In 1913, J.J. Thompson [1] showed that neon contains atoms of mass numbers 20 and very small fraction of mass number 22. Since the chemical properties of both atoms were exactly same Soddy suggested the term 'isotope' for such elements meaning there by they occupy the same places in the periodic table. They are chemically identical and differ only in physical properties which are dependent upon the mass.

- Elements of even atomic number are more abundant, more stable and richer in isotopes than the elements of odd atomic numbers.

- Except hydrogen and tritium, neutrons and protons tend to be equal in all elements. Generally neutrons to proton ratios are around 1.2 but never exceed more than 1.6.

So, in nineteen thirteen sorry J J Thompson showed that neon contains atomic mass of about 20 and very small fraction of mass contains number 22. Since the chemical properties of both compound atoms are exactly the same sorry suggested, that array it is the chemical which is having different ways, but having same properties. Now which is against Daltons law which we discussed earlier. So, then they came up with a suggestion sorry he suggested that it could be a isotope; that means, it may carry more number of electrons and does not change the chemical properties at all.

So, such a substance is called as isotope these isotopes, are all there in for our all almost every element in the periodic table you can look up some of your Google and other structures data providers, who will tell you a lot about such isotopes; they are basically identical chemically and differ only in physical properties which are dependent upon the mass. So, elements of even atomic number are more abundant, this is another observation made from the properties. So, elements of even atomic numbers are more

abundant, more stable, and richer in isotopes than the elements of odd atomic numbers. So, except hydrogen and tritium, neutrons and protons tend to be equal in almost all elements; if there is a change the change can be only up to 1.2 or 1.3 in, but not more than 1.6.

So, that is the ratio of the protons and neutrons cannot change should not be more than 1.6 otherwise it will lead to the instability ok.

(Refer Slide Time: 23:42)

- Nuclei with even number of neutrons are more abundant than those of odd number of neutrons.
- Nuclei with even mass numbers are more stable than the nuclei of odd numbers.

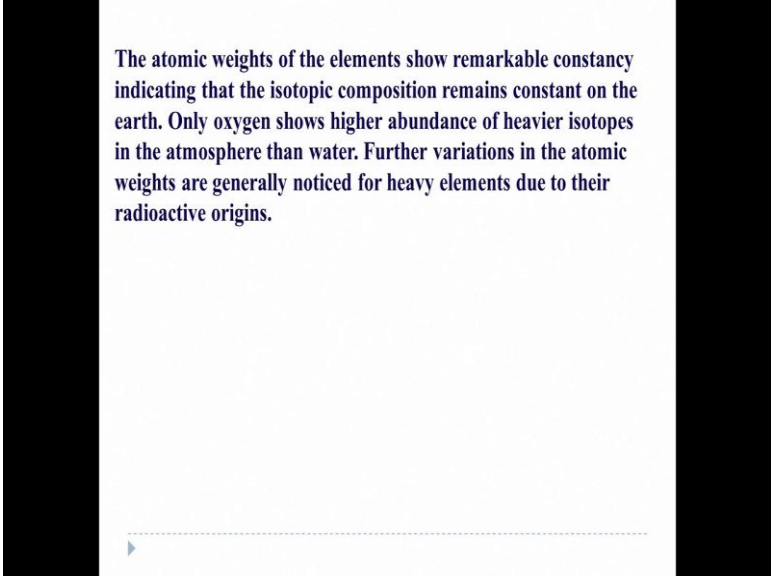
Early mass spectrographic data of hydrogen indicated that its atomic weight is 1.007775 based on the assumption that ordinary oxygen is not an isotopic mixture and has an atomic weight of 16.0000. This value was acceptable because 1.00778 grams of hydrogen combines with 8 grams of oxygen. However subsequently oxygen isotopes of 16, 17 and 18 mass numbers were discovered. Therefore two types of mass numbers are in use. One refers to chemical atomic weight of 16.00000 and the other known as physical atomic weight refers the average atomic weight of 16.00447. The former is universally accepted for the routine purposes and the physical values are used to describe the properties related to atomic nuclei.

So, nucleus with even number of neutrons are more abundant than those of odd numbers, and nuclei with even mass numbers are more stable than the nuclei of odd number these are the fundamental principles. So, what does, how does it convert itself into spectroscopic data. Now this is the slide in front of you says that early mass spectrographic data of hydrogen indicated that atomic weight is approximately 1.00 double 7 triple 75.

So, the combination this much combination this much material can react with iron oxide with oxygen having an atomic weight of 16, and this value was acceptable because 1.00778 gram of hydrogen combines with 8 gram of oxygen; however, subsequently oxygen isotopes with 16, 17,18 they were all discovered and therefore, the two types of mass numbers are in use: one refers to the chemical atomic weight of oxygen with 16, as a reference and the other one is known as atomic weight that refers to the average of the

isotopes, and that is 16.00447. The former is usually accepted for the routine purposes and the physical values are used to describe the properties related to the atomic nuclei.

(Refer Slide Time: 25:21)



The atomic weights of the elements 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. Further variations in the atomic weights are generally noticed for heavy elements due to their radioactive origins.

So, the atomic weights of elements show remarkable constancy, in general indicating that the isotopic composition remains constant throughout the universe all the time anytime anywhere. So, only oxygen shows higher abundance of heavier isotopes in the atmosphere than water this is good for us. Further variation the atomic weights are generally not noticed for heavy elements due to their radioactive elements.

(Refer Slide Time: 25:53)

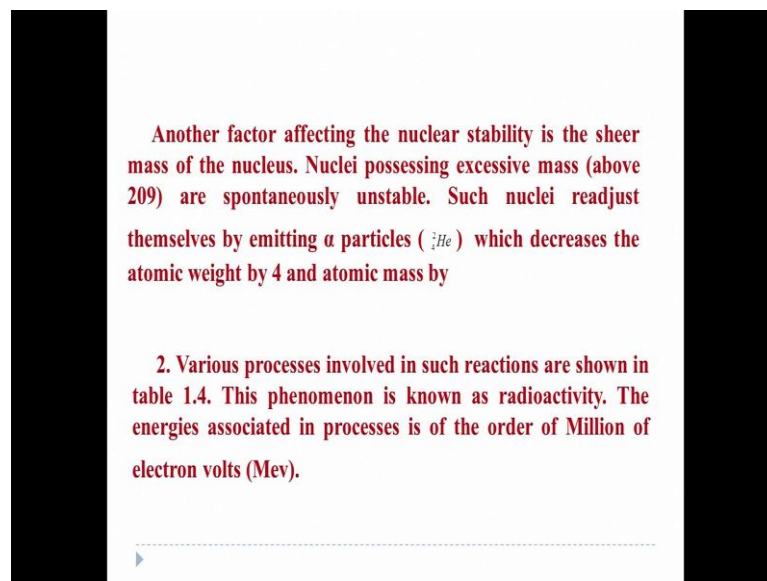
1.5 Nuclear Stability

The presence of stable elements implies that neutrons and protons are held together by attractive forces. At the same time coulombic repulsive forces must also be present. The sum total of these forces would be attractive forces. The energy exchanges between protons and neutrons would be maximum when equal number of the neutrons and protons exist.

Therefore for better stability N: P ratio should be unity. However since protons mutually repel each other a tendency to repel each other exist. For elements containing few protons the tendency towards equalization of protons and neutrons.

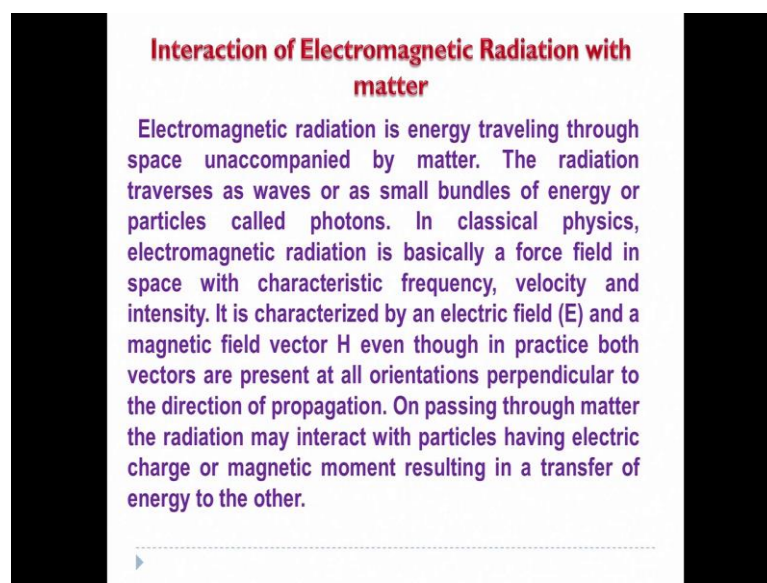
So, the what we have here the nuclear stability is in general understood by nuclear to proton ratio, that is neutrons to proton ratio it should be for better stability, it should be unity and; however, since protons usually you know repel each other, if there are too many protons around each other they will be repelling each other. So, for element containing few protons, tendency towards equalization of protons and neutrons is always there ok.

(Refer Slide Time: 26:30)



So, another factor that affects nuclear stability is the sheer mass of the nucleus. Nuclei possessing excessive mass they would be usual spontaneous the unstable they would you radioactive elements such elements we deal rarely, but such element also loss and keep on losing the energy until they fall into the stable raise stability range. So, this phenomenon various processes are involved by the emission of alpha particles, beta particles, gamma particles etcetera and there until the elements fall back into stable range, the energy is associated in these processes are of the order of several million volts electron volts.

(Refer Slide Time: 27:20)



Interaction of Electromagnetic Radiation with matter

Electromagnetic radiation is energy traveling through space unaccompanied by matter. The radiation traverses as waves or as small bundles of energy or particles called photons. In classical physics, electromagnetic radiation is basically a force field in space with characteristic frequency, velocity and intensity. It is characterized by an electric field (E) and a magnetic field vector H even though in practice both vectors are present at all orientations perpendicular to the direction of propagation. On passing through matter the radiation may interact with particles having electric charge or magnetic moment resulting in a transfer of energy to the other.

So, now what we want to do is having down the structure of the atomic structure, how do you use this information for the electromagnetic radiation or spectroscopy of this substance? So, for that we have to understand what is meant by the electromagnetic radiation, and how does the electromagnetic radiation interact with the matter interact with the matter means it has to interact with the protons, neutrons, electrons etcetera. So, that aspect what happens to the changes in the energy of electron or the electron, magnetic radiation when they have interact with the materials. So, that is part of the spectroscopy. So, that way will be discussing in our next class that is interaction of electromagnetic radiation with matter. So, we will continue our discussion in the next class thank you very much for your patience and have a good day

Thank you.