

Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 02

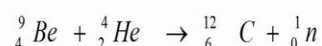
Atomic structure-I

We continue our discussion on Atomic Structure as a prelude to the atomic absorption spectrometry. So, early in the last class what I told you is that atoms are composed of the electrons protons and neutrons and the electrons, so I have described you a little bit about their origin and their properties. Now, continuing that discussion we know that the protons are the other fundamental particles.

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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 , Be , B etc., with α particles yields penetrating radiation consisting of neutral particles of approximately unit mass according to the reaction,



They are found to be identical with hydrogen atoms from which single electrons have been removed. Suppose, you take hydrogen atom and remove an electron what remains of the mass is known as proton. So, just like electrons protons also are present in all types of atomic species and hence considered as fundamental particle, it is mass is 1.00757 atomic mass units and its charge is plus 4.8029.

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Electrons 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 (1.6603×10^{-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.

So, if you look at the electron they are here the charge is minus 4.8029 into 10 raised to 10 and the proton is plus 4.8029. So, one proton and one electron will be completely neutralizing of the charge of each other. So, if I have hydrogen atom I have one proton and one neutron it is the total charge should be 0; that is neutral.

So the neutron bombardment of light elements such as lithium, beryllium, boron, etcetera, with alpha particles yields penetrating radiation. If you take lithium, beryllium boron etcetera you bombard them with alpha particles and alpha, what are alpha particles alpha particles are nothing, but helium atoms. So, if you bombard the such elements with helium, what will get is a sort of radiation that consists of neutral particles of approximately unit mass; that is the minimum mass that is 1.00757 AMU; according to this reaction.

Suppose, I have a beryllium with 9 protons and 4 electrons; 4 protons 9 atomic mass; I hit them with helium containing 4 atomic mass and 2 charge; 2 atomic number, then what I get is a carbon atom with 12 atomic mass and 6 atomic number. So, 9 plus 4 is 13 and here I am getting 12. So, the actual mass difference whatever radiation I am getting out should be having a mass of 1 and charge is 4; here to here 6 is here, so the charge on this neutral this neutron is particle is 0. So, such a particle having charge of 0 and mass of one atomic mass unit is known as neutron.

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These particles are known as neutrons. 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



So, these particles are known as neutrons atomic mass is same outside the nuclei neutrons are unstable; that means, you cannot find neutrons around you. Over the years, a number of unstable particles have been found such as positron, neutrino, antineutrinos, mesons and these are particles incapable of independent existence; that means, during nuclear reactions; all these particles are formed and which have a very short existence. And however, such particles are generated only under certain conditions.

So, further these conditions form part of the advanced to physics; you know science belonging to advanced physics and we are not going into the details because that is not relevant to our course on atomic absorption spectroscopy. So, further composite particles of hydrogen known as deuteron and doubly charged helium nucleus known as alpha particles these are known to exist; that means, we have hydrogen containing 1 proton, 1 electron, but also 1 proton and 1 neutron is also there that is known as neutron and doubly charged helium also is available.

So, like that the atomic mass may be different, but atomic number is same electron numbers of electrons are same. So, these are known as composite particles; composite elements or isotopes very similar familiar word is isotopes.

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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 Rontgen's experiments on the bombardment of a target with cathode rays that is electrons yielded a highly penetrating radiation of shorter wavelength which he called X-rays, these are the electromagnetic part of electromagnetic radiation and for the first time he generated X-rays when he bombarded a metal atom; piece of metal with electrons in cathode rays; so, such radiation is due to the energy released when an inner electron is released and other electrons drop into the vacant slots.

So, the characteristics of X-rays are having still shorter wavelength than the electrons. Therefore, an atom is comes believed to consist of two parts that is; a positively charged nucleus with as which is small in size, the size is approximately 10 raised to minus 12 centimeter and comparatively heavy. So, there is an extra nuclear arrangement of loosely bound electrons going around the nucleus in a space of about 10 raised to minus 8 centimeter and diffusing character; that means, are all the electrons belonging to a atom are spread in a spherical area of about 10 raised to minus 8 centimeter from the nucleus.

So, the nucleus governs the physical properties of the element and the extra nuclear structure is considered as responsible for the chemical properties of the element. So, the electrons, electronic reactions are lead to chemical reactions, chemical properties and the nucleus governs the physical properties such as weight charge etcetera.

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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.

So, the former is used in as a bombarding article particle and the latter is a product of radioactive decay. So, unstable particles and composite particles do not have any role in the ultimate composition of the matter; that means, masons and positrons and etcetera do not have any role in the ultimate composition of the matter, because they are all formed only during particular conditions specific high energy conditions. So, in day-to-day life they do not have a role in the normal chemical reactions of the metals and compounds and elements etcetera.

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1.1 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.

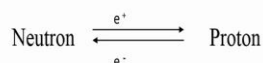
So, now that brings us to the modern atomic theory, so this is basically a sort of acquired a mathematical character and several physical and chemical characteristics can be derived from our current understanding of the atomic structure. In simple terms the structure is based on Rutherford's model; which state that the atom consists of large portion of unoccupied space around it, but populated by revolving electrons; that means, again here we make a distinction that according to the Rutherford's theory the electrons are not located in a particular space around the nucleus, but they are in a state of constant motion around the positively charged, relatively stable nuclear mass that is known as nucleus.

So the nucleus essentially contains protons and neutrons, so protons are positively charged; neutrons are not charged they are neutral in particles.

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1.2 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



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

So, what is the atomic nuclei do? So protons and neutrons constitute the weight of the element basically. So, the mass number is the whole number closest to the magnitude of the actual weight in terms of AMU; Atomic Mass Unit. So, one atomic mass unit is nothing, but one proton; weight of the proton; since neutron and proton differ only by a unit charge, but not the mass we say that neutron; you add a an electron to the neutron, you get a proton; you will subtract a an electron from the neutron.

Now from the proton you get a neutron, so there should be some sort of equilibrium between the neutrons and protons there may be chemical reactions, there may be

electronic transition reactions taking place under special circumstances which will convert protons and neutrons in a given substance; in one proton may become a neutron than at the same time another neutron becomes a proton, so the total charge of the atom remains the remains constant.

So this equation, which I am showing you on the screen represents an over simplified case actually; the small masses of electron and positron forbid their functioning in such reactions; so it is again a sort of simplified view.

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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, Thompson showed that neon contains atoms of mass numbers of 20 and a very small fraction of the mass number of 22; all of them are neon gas only. Since the chemical properties of both are exactly same sorry suggested that we use a term called as isotope, which means that they occupy the same places in the periodic table; they are chemically identical, so it should occupy basically same place in the periodic table and the only difference is; they differ in physical properties because each of the atom some of the atoms have got 20 mass number and others are having 22 mass number. So, the average molecular weight or atomic weight would be different, so he suggested the atoms with different atomic weights are known as the isotopes.

So elements among these things when you study the structure and properties of the atoms; it is noticed that even elements of even atomic number are more abundant, they are more stable and richer in isotopes than elements of odd atomic numbers. A small

observation, but very significant; so, except hydrogen tritium and tritium; neutrons and protons tend to be equal in almost all elements; it means there may be there will be equal number of protons and neutrons. So, generally neutron to proton ratios are around 1.2, but never exceed more than 1.6 that is average.

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•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, nuclei with even number of neutrons are more abundant than those of odd number of neutrons, this is another observation and the nuclei with even mass numbers are more stable than nuclei of odd numbers. So, now we are talking only about the nucleus of an atom, so 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; that is we take oxygen as reference and take the weight of a known quantity of oxygen and determine the weight of hydrogen of the same volume, so then take a ratio.

So it showed that 1.007775 is the weight of hydrogen if you take oxygen in as 16.000 that is an arbitrary number. This value was acceptable because 1.00778 grams; again see that the here 7.5 are converted into 8 and so they become so many grams of hydrogen with compared to 8 grams of this weight is the 1 is to 8 ratio; however, subsequently oxygen isotopes of 16, 17 and 18 mass numbers were discovered.

So, a small correction became necessary to determine the weight of hydrogen, so you know there are two types of numbers available based on 16.000 and other known reference is 16.00447; which takes into account the abundance of oxygen of atomic mass

16, 17 and 18; the former is universally accepted for day-to-day purposes, but for accurate values, we should take 16.00447 as the atomic weight, so in the atomic nuclei can be described by the properties of such considerations.

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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.

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 atomic weights of elements show remarkable constancy that is for sure almost all elements that we know of today, they show the remarkable constancy wherever you make the measurement in any country, anywhere; they show the same weights indicating that the isotopic composition remains constant of any element you take. Only oxygen shows higher abundance of heavier isotopes in the atmosphere than water, this is a sort of aberration, but it is accepted; further variations in the atomic weights are generally noticed for heavy elements due to their radioactive origins.

Most of the heavy elements what we know today like lead the rhenium, (Refer Time: 16:55) actinium etcetera; they all have slight variations in the atomic weights, but normal elements like iron copper, nickel etcetera they all show the same atomic weight wherever and whenever you measure them. So the nuclear stability, if we take a look the presence of stable elements implies that neutrons and protons are held together by attractive forces.

Now at the same time there must be repulsive forces also, whenever a charge is material like a proton is held together by a neutron; it has to be held whereby attractive forces, it does not mean that negative forces repulsive forces are not present. So, but the sum total

of these forces should be attractive forces, suppose there are 20 atom, 20 protons and 20 neutrons and they are held together it is neutral, but still the to be held together attractive force should be greater than the repulsive force that is the logical.

So, the energy exchanges between protons and neutrons would be maximum when both of them are equal. So, neutron to proton ratio should be unity for stable nuclear; however, protons majorly repel each other because the both of them carry positive charges and there is a tendency to repel each other existing also. So, for elements containing few protons, the tendency towards equalization of protons and neutrons are more.

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Another factor affecting the nuclear stability is the sheer mass of the nucleus. Nuclei possessing excessive mass (above 209) are spontaneously unstable. Such nuclei readjust themselves by emitting α particles (${}^4_2\text{He}$)

which decreases the atomic weight by 4 and atomic mass by 2. Various processes involved in such reactions are shown in table 1.4. This phenomenon is known as radioactivity. The energies associated in processes is of the order of Million of electron volts (Mev).

So, another factor that affects the nuclear stability is the shear mass of the nucleus and the nuclei possessing excessive mass are spontaneously unstable. This point you should remember that this is a basic origin of radioactivity also that the above 209; atomic weight most of them are not stable at all and such nuclei readjust themselves by emitting alpha particles; that is they lose a helium atom that is 2 helium with 4 neutrons and with that decreases the atomic weight by 4 and atomic mass by 2.

So, it keeps on losing the helium atoms and the come to lower atomic mass, so this phenomenon is known as radioactivity, the energy is associated in such processes is of the order of several million of electronic volts; it is designated as Mev; Million electronic volts.

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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, electromagnetic radiation is energy traveling through the space, unaccompanied by matter. The radiation traverses as waves or small bundles of energy called as photons; this is another theory of electromagnetic radiation. Now, we know that electrons are also treated as waves, so the electromagnetic radiation which carries a positive and negative field must be carrying a sort of a particle the called as photon and in classical physics electromagnetic radiation is basically a force field that is; it has no independent existence as such, but it has got a characteristic frequency velocity and intensity. So, it is characterized by an electric field and a magnetic field vector even though in practice such vectors are present at all orientations perpendicular to the direction of propagation.

So, I will show you a picture corresponding to this, so this electromagnetic radiation if it passes through an element of our interest; it may react interact with the particles having electric charge or magnetic moment resulting in transfer of energy from electromagnetic radiation to the electron or the from the electron to the electromagnetic radiation.

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All electromagnetic radiations are characterized by wavelength denoted by λ or frequency ν

The term wavelength is defined as the distance between successive maxima or minima. The frequency is the number of cycles occurring per second. The wavelength and frequency are related by

$$\lambda = \frac{v}{\nu} \quad (1.1)$$

where v is velocity of propagation. All electromagnetic radiation have same velocity through vacuum (c) i.e. 2.9979×10^{10} cm/sec. Thus,

So, all electromagnetic radiations are characterized by two force fields one is the wavelength that is denoted by λ and frequency. So, the term wavelength is defined as the distance between successive maxima or minima. The frequency is the number of cycles that occurs per second that is given by λ is equal to velocity divided by frequency. So, where v is the velocity of propagation and the electromagnetic wave all electromagnetic radiations which we will call X-rays, electromagnetic waves, gamma rays, cosmic rays, ultraviolet rays and all these things have the same velocity through vacuum that is 2.997 into 10 raised to 10 centimeter per second.

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$$\lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^{10}}{\nu} \quad (1.2)$$

Frequency is expressed as number of cycles per second or as wave numbers (denoted by $\bar{\nu}$) is given by

$$\bar{\nu} = \frac{1}{\lambda} \quad (\text{cm}^{-1}) \quad (1.3)$$

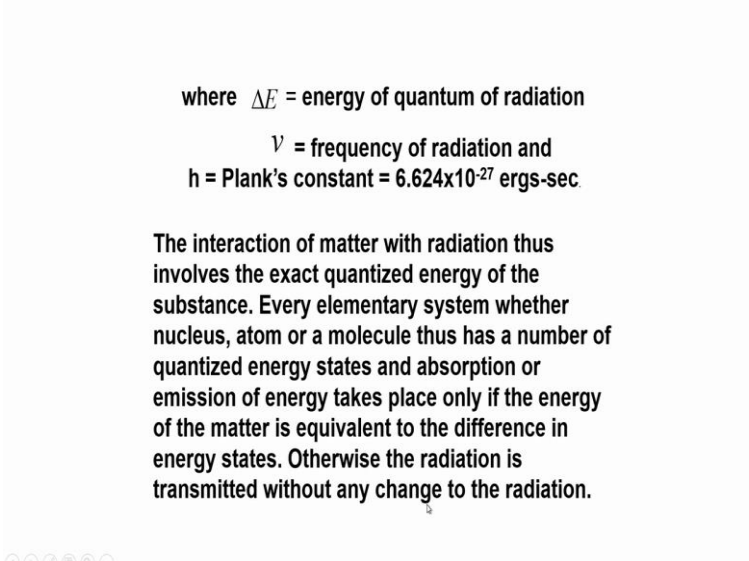
The distribution of spectral intensity in blackbody radiation was best explained by Max Planck in 1900 by uniting the corpuscular theory and wave theory is a relation between the energy of a quantum of radiation to the frequency as given by

$$\Delta E = h\nu = hc / \lambda \quad (1.4)$$

So, now we can define lambda every electromagnetic radiation is governed by this equation that is C is the velocity of light that is 2.9979×10^{10} and when you divide it by the total number of waves; what you get is wavelength that is in between two waves that is two crests maybe or if you measure amplitude the amplitude itself can be taken. So, the frequency is expressed as number of cycles per second or as wave number that is denoted by $\bar{\nu}$ is equal to $1/\lambda$.

So, the distribution of spectral intensity in a blackbody radiation was explained by Max Planck; this is a very important concept in all our future considerations in this course and this spectral intensity was explained by Max Planck in 1900, what he did was he combined the corpuscular theory and wave theory that is a relation between the energy of a quantum radiation what he said is the energy change ΔE is given by a constant multiplied by the frequency and frequency is $h\nu$; h is a constant, ν is a frequency and frequency is nothing, but C/λ , so the velocity of light divided by the wavelength.

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where ΔE = energy of quantum of radiation
 ν = frequency of radiation and
 h = Planck's constant = 6.624×10^{-27} ergs-sec

The interaction of matter with radiation thus involves the exact quantized energy of the substance. Every elementary system whether nucleus, atom or a molecule thus has a number of quantized energy states and absorption or emission of energy takes place only if the energy of the matter is equivalent to the difference in energy states. Otherwise the radiation is transmitted without any change to the radiation.

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So, ΔE is the energy of the quantum of radiation followed and ν is the frequency of radiation; the constant is given by is known as Planck's constant that corresponds to 6.624×10^{-27} ergs per second. So, the inter what he also proposed that the interaction of matter with radiation involves quantized energy; that means, the energy is not continuous every elementary system whether nucleus or an atom or a molecule thus

has a number of quantized energy states and absorption; so, the energy states are located one above the another in between that ten raise to minus 8 centimeter space around the nucleus and the transition from one space to another requires an exact quantity of energy, it does not require a small amount of energy; it has to match that.

Now, if you fall down from one step, you may fall down several steps down, but you will not fall down somewhere in between; it is as simple as that is. Imagine a ladder once you fall from the top, you may fall and at the next you may land at the first step or second step etcetera and the only in jumps; small small jumps.

So, what he suggested is an exact replica of the same idea that every transition of nucleus, every electromagnetic radiation transition takes place only if the energy of the matter is equivalent to the difference between the two energy states. So, otherwise the radiation is transmitted without any change to the radiation.

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The energy or frequency which the incoming photon is absorbed is given by the Bohr equation

$$h\nu = \frac{hc}{\lambda} = E_f - E_i \quad (1.5)$$

where E_f and E_i are the energies of the final and initial states of the substance.

In the case of emission the energy of the radiation is given by

$$h\nu = hc / \lambda = E_i - E_f \quad (1.6)$$

where E_i and E_f refer to the energy states.

In actual practice whenever a radiation of multiple frequency interacts with the matter part of it may be used up in absorption, emission, reflection, refraction, diffraction or in scattering. Thus

So, the energy or frequency which the incoming photon is absorbed is given by the Bohr equation. So, what he says is the energy difference is the difference between the final and initial stages E_f minus E_i here and that is shown in equation 1 is to 5, where E_f and E_i are the energies of the final and initial states of substance. So, in case of emission the energy of the radiation is given by $h\nu$ is equal to hc by λ ; that is also equal to the difference between the two energy states.

So, in actual practice whenever a radiation of multiple frequency interacts with the matter; part of it may be used in absorption, part of it may be used in emission and part of it may be used in reflection, part of it may be in refraction, diffraction, scattering and so many other possibilities that can take place. But all of them in quantized format, so if I write energy look at my next equation.

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$$E = E_{\text{abs}} + E_{\text{emi}} + E_{\text{Ref}} + E_{\text{Ref}} + E_{\text{Diff}} + E_{\text{sca}} + \dots \quad (1.7)$$

Various types of quantized energy changes occurring in each region of the spectrum and the magnitude of energies involved have been traditionally used for a variety of spectrochemical techniques. The energy ranges are generally classified as Gamma rays, X-rays, UV-visible rays, infrared, microwaves and radio frequency rays. The absorption of radiation occurring at different wavelengths and the associated spectroscopic techniques are given in Table 1.

Visible light represents only a part of the electromagnetic spectrum and extends from 380 to 800 nm. Table 1.2 shows an enlargement of the visible region with transmitted colour and complementary hue (observed colour)



If I write a total energy of a given system is the sum of absorbed energy, emitted energy and then reflected energy, refracted energy and then diffracted energy, scattered energy etcetera etcetera etcetera. So, various types of quantized energy changes that occur in each region of the spectrum and the magnitude of energies involved have been traditionally used for a variety of spectrochemical techniques; this is the fundamental basis of all spectroscopic techniques, but including atomic absorption which we are going to study in detail.

So, the energy change a ranges are generally classified as different electro parts of electromagnetic radiation that is gamma rays X-rays, UV visible rays, infrared, microwaves and radio frequency rays etcetera.

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Wavelength	Transmitted color	Complementary hues
< 380	ultraviolet	—
380 – 435	violet	Yellowish green
435 – 480	Blue	Yellow
480 – 490	Greenish blue	Orange
490 – 500	Bluish green	Red
500 – 560	Green	Purple
560 – 580	Yellowish green	Violet
580 – 595	Yellow	Blue
590 – 625	Orange	Greenish blue
625 – 780	Red	Bluish green
> 780	Near IR	Red

So, the absorption of radiation occurring at different wavelengths and the associated spectroscopic techniques, I am presenting to you in the table here. Now, we go back; so the absorbed energy is basically if it is around 380 nanometers; it is less than 280 then it is ultraviolet rays. So, 380 to 435 is violet and the width transmits violet color; its color is yellowish green.

So, similarly if you look at other wavelength ranges now for 380 to 435; 435 to 480 is blue, but it looks yellow orange and then 480 to 490 looks orange and, but it transmits greenish blue like that part of it is absorbed; what is not absorbed is what looks to you; that is a substance that is absorbed when transmitting bluish green will absorb all other radiation that looks reddish.

So, only suppose that between 500 and 560 green is observed then it looks purple you take of this see. In general, visible absorption visible radiation is basically a combination of rainbow colors that is VIBGYOR; violet, indigo, blue, green, red etcetera and these are the wavelengths that absorb the radiations and they look different in different ranges.

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It must be noted that there are no sharp differences in colour at any wavelength but rather they merge into one another in a diffused manner like a rainbow. The absorption of radiation involves transfer of energy to the medium and this process is a specific phenomenon related to the characteristic molecular structure. For a given excitation process a molecule absorbs a discrete quantity of an absorption line. However, since a group of molecules exist in a number of vibrational and rotational energy states each differing by a small amount of energy a series of absorption lines appear over a small range and give rise to an absorption peak or band.

Mono atomic substances normally exist in gaseous state and absorb radiation only through an increase in their electronic energy. These are quantized and appears in various sub shells as shown in Fig 4.4.



So what we note here is that there are no sharp differences between this; where it does not mean if, so for example, if you take a look at this 380 to 435 for what is 435 at 440 would it look violet or would it look yellowish green or yellow. So, the difference is not that sharp, but it looks somewhat in between because our eyes are not capable of differentiating small changes in the color; human eyes are not sensitive enough.

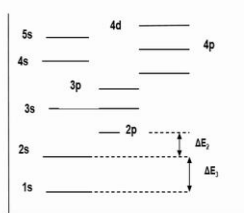
So, it must be noted that there are no sharp differences in color at any wavelength, but rather they merge into one another, in a diffused manner that gives us an impression of a color. So, like a rainbow; in rainbow if you look at rainbow in the sky, you will see that there is no sharp difference between different colors, but they changed slowly over a period of distance to merge into one another.

So, the absorption of radiation actually involves transfer of energy to the medium and this process is a specific phenomenon related to the molecular structure. So, again we are coming, we are trying to correlate the absorption of electromagnetic radiation to the molecular structure and atomic structure. So, for a given excitation process molecule absorbs a discrete quantity of an absorption, so that is since the group of molecules exist in a number of vibrational and rotational energy levels; each differing by a small amount of energy, a series of absorption lines appear over a small range and that gives rise to an absorption peak; that means, even though absorption could be a single wavelength phenomena as imagined by a quantized energy, but there will be a slight variation of the

existence of energy molecules itself; at slightly different energy levels so that you will experience that the transition is not a line a single event, but it is a number of events merged together with slightly different this thing, so we get a peak.

So, the mono atomic substances normally exist in gaseous state and absorb radiation only through an increase in their electronic energy, so these are quantized again and appear in various sub shells like this.

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For poly atomic molecules electronic transitions involve molecular orbital requiring energy in the ultra violet region. These are far more complex involving vibrational and rotational energy levels. Thus the total energy may be considered as a sum of contributions from all states of energy.

For each electronic energy state of the molecule there exist several possible vibrational states and fro each of these in terms numerous rotational energy states.



So, we have different energy states like 1 s, 2 s, 2 p, 3 s, 3 p like that, so the energy difference will be like this the corresponding energy difference. So, for polyatomic molecules electronic transitions involve molecular orbitals requiring energy in the UV region, for atomic absorption they also occur in UV as well as visible region these are far more complex involving vibrational and rotational energy levels.

So, thus total energy may be considered as a sum of contributions from all states of energy. So, for each electronic energy state the state of the molecule; there exist several vibrational energy states which will give you a number of absorption peaks.

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Hence electronic transitions in organic molecules are characterized by the promotion of electrons from bonding or non bonding molecular orbitals to excited state anti bonding orbitals. The bonding orbitals are designated as σ and π orbitals and non bonding excited orbitals by σ^* and π^*

In addition many molecules contain many electrons that are not directly involved in bonding and are mainly located in atomic orbitals of elements like oxygen, sulphur, nitrogen and halogens etc., The generalized shapes of σ orbitals are shown in Fig 1.3 by solid lines and dashed lines.

In the excited state some if not all the electrons occupy antibonding orbitals. Even in the antibonding orbitals the molecule retains sufficient bonding character to ensure the stability otherwise dissociation would occur. The electronic transitions possible in ultraviolet and visible spectrum are σ and σ^* . The energy required for these transitions decreases in the same order as shown below:

Saturated hydrocarbons
Alcohols, Chlorides and iodides
Saturated aldehydes & ketones

So, the absorption peaks are all classified as sigma and sigma star they involve electronic transitions and if they are bond if the electrons are bonded then it is known as bonding orbital and if the electrons are not bonded, then they are known as nonbonding orbital.

For example, any compound you can imagine like methane where all electrons are having a single bond; they are all known as a sigma they assume they have sigma bonds and then a unsaturated organic compounds like ethylene etcetera, they all have a pi bond. So, in addition many molecules contain electrons that are not directly involved in bonding and are mainly located in the atomic orbitals and in the electrons which are not bonded, they can also get excited and go to next higher energy level.

So, such for sigma bonding there are sigma star excited level, for pi bonding there are pi star only, but for non-bonded electrons which will designated as n which are present in elements like oxygen, nitrogen, sulfur etcetera. The non bonded electrons where do they go when they go to excited state, they either reach pi star or sigma star, so the we are talking about molecular orbitals; not atomic orbitals

So, saturated hydrocarbons etcetera alcohols, chlorides, iodides, saturated aldehydes ketones all these things show involve large amounts of energy ranging from 35.71 kilocalories in the visible to visible range to several hundred kilocalories in the ultraviolet.

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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

So, molecular transitions take place in this region, so each electronic level is associated with several vibrational modes, but maximum population is at 0 level consequently 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 or forces or interactions thus a broad absorption band results. So, sigma to sigma star transitions are very energetic and are found only below 200 nanometer: that is in the ultraviolet region vacuum compounds in which all valence electrons are there would be undergoing this type of transitions.

So, we will stop our discussion about the atomic structure right now and in the next class we will see how the transitions will take place in UV and visible region depending upon the atomic and molecular structure.

Thank you very much. We will continue our discussion in the next class.