Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 07
Interaction of EM radiation with matter II

During the discussion on diffraction I had shown you that the phase differences essentially remain entirely constant with time and when they are so, it is said to be a coherent system then only a whenever there is only a coherent system, you get a regular diffraction pattern that is fringes of bright side and left bright and are bright and dark fringes. So, the spacing of those brands depends on the distance between the slits.

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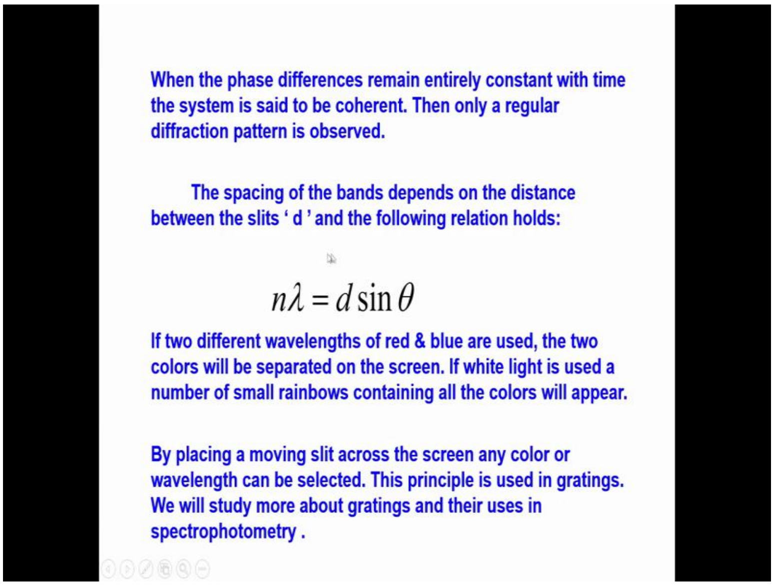

So, we can use this equation n lambda is equal to 2 d sine theta or d sin theta, and if two different wavelengths of red and blue are used.

Now, what I am saying is you use two different sources making them pass through the same hole, pin hole, the two colors will be separated on this screen. So, if suppose we use a white light then what happens we see a number of small rainbows on the screen out across the pinholes. So, by placing a moving slit across the screen, any color or wavelength can be chosen that is the fundamental principle of how we choose a wavelength, whenever we want to make an estimation using a spectroscopic technique. So, in spectroscopic technique we use lenses, we used mirrors, and then we use the diffraction systems and there then subsequently we can also use prisms and other things, but diffraction is a system which we are discussing right now because it is the in thing now that is a fashion.

Prisms are also in use, but whenever we want to use a diffraction system, all I have to do is make a pinhole make the radiation pass through and collect there radiation across the pinhole on the on a screen or something like that, and then if I choose my slit make my slit move from one end to the other end then I get different wavelengths. So, by placing a moving slit across the screen any color or wavelength can be selected, this principle is used in gratings. We will study more about gratings and their uses in spectroscopy later; later means within a few minutes probably.

So, next thing I want to discuss is about the prisms. So, what are we looking at we are looking at prisms as dispersing devices.

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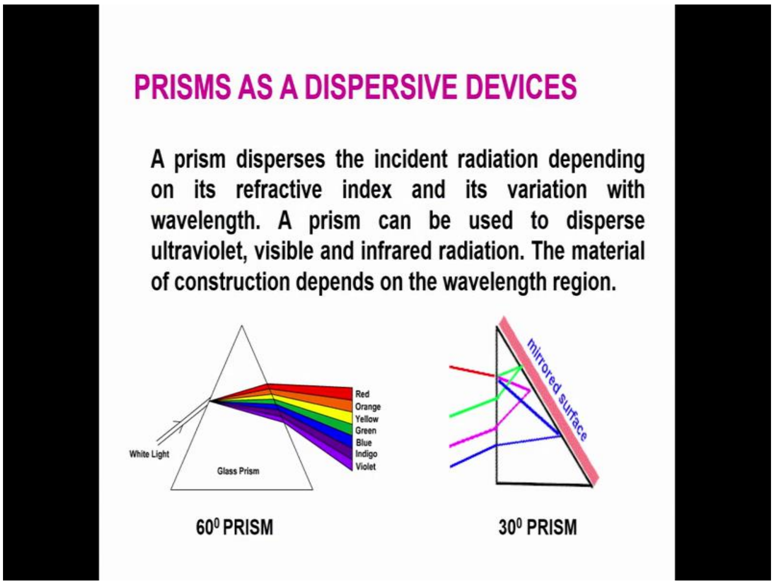

Now, in prisms the array we all know the rainbow colors and in our high school studies we has to we haves seen that even water small simple water droplets coming falling from the sky can act as prisms, which has dispersing a agents for the sunshine which passes through them giving use rainbow colors right.

So, a prism disperses the incident radiation that is the job of prisms. So, I have shown you a picture of the prism here, it is a 3 D prism basically. So, it has got four sides, one on the I am one over what we are seeing here and one on the other side, one on this side, one and the back side. So, such prisms you would have seen in number of places including art objects and several other things and basically this prism is made of quartz or a glass ok.

So, a prism the job of the prism is to pick up the radiation falling on it and disperse the components. So, a depending on the refractive index the and it is variation with it is wavelength we get these scale; that means, suppose the wavelength is uniform dispersion is uniform then the scale also be we will also be uniform. So, what I have to do is I just have to provide a slit in which the slit can be moved arithmetically, that is one step at a time. So, if it is anomalous then the scale will not be uniform, at that point we need different mechanisms to go from one wavelength to another wavelength. So, a prism basically it is use is to disperse the radiation electromagnetic radiation, and what are the ultraviolet, visible, and infrared radiation. So, the suppose you want to use prisms or gratings in X ray you will not be able to use it, it is only meant for ultraviolet visible and infrared radiation this point you should remember.

So, the material of construction again depends upon the wavelength region which we want to separate. Suppose it is ultraviolet I will need a different material such as quartz, if it is visible range I need glass. So, of course, quartz also will work for glass and for infrared radiation etcetera we need different kinds of materials such as sodium chloride and other salts, made into some sort of a conical presumption prismatic shape. So, the material of construction again depends upon the wavelength region; here I have shown you that the white light is falling on this phase of the prism, and then it undergoes refraction at different places depending upon the length the separation will be better. If the prism is big the separation will be better, if the prism is small they would be bunched together somewhere around this thing no.

So, like this in this region they are all bunched together; here as the distance between the two sides increases opposite sides increases, the wavelengths will be separated in a much better fashion. So, if you take white light we end up with red or in yellow I think most of you are aware of the job of prism. Now I can have different kinds of prisms one is like this where the apex angle is 60 degrees, another one is I will take the same thing I cut into exactly half something like this take one portion either left side portion or right side portion and I mirror this, this phase then what happens the incoming radiation will come like this go like this, come back we get reflected on the mirrored surface here goes back and then comes out of the same direction.

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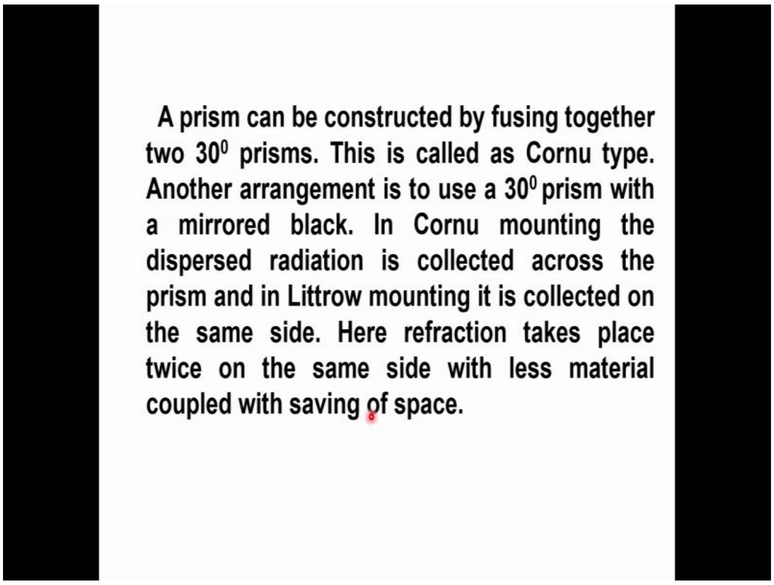

Here it is coming out and moving into the opposite direction. So, there are two types of prisms one which can have a 60 degree apex angle and that is this angle is 60 degrees this angle is also 60, this is also 60, but if I cut it here the angle would be the 90 and this will be 45 and 45 degree angle. So, the 60 degree prism can be constructed by fusing together 230 degree prisms. So, this is called as Cornu type which one is Cornu? The right side is Cornu and this left side is Littrow sorry the it is the other way around it is a fused one is called as Cornu type that is this one fused to half prisms fused together is you gives you 60 degree apex angle and this is Cornu type and if you take a single one mirrored on one side then it is Littrow type.

So, in Cornu mounting the rate dispersed radiation is collected across the prism and in Littrow mounting the dispersion is collected on the same side. Here the refraction takes place twice if you look carefully it will go reaches here goes there and comes back; that means, the total distance traveled by the light beam is both in both cases is same except that in Littrow mounting the space occupied by the prism is much less. That means, if I use a Littrow mounting prism I can reduce the size of the spectrographs or spectrometer.

So, that is the advantage. So, the refraction takes place twice on the same side with less material coupled with saving of the space that is the greatest advantage for Littrow mounting.

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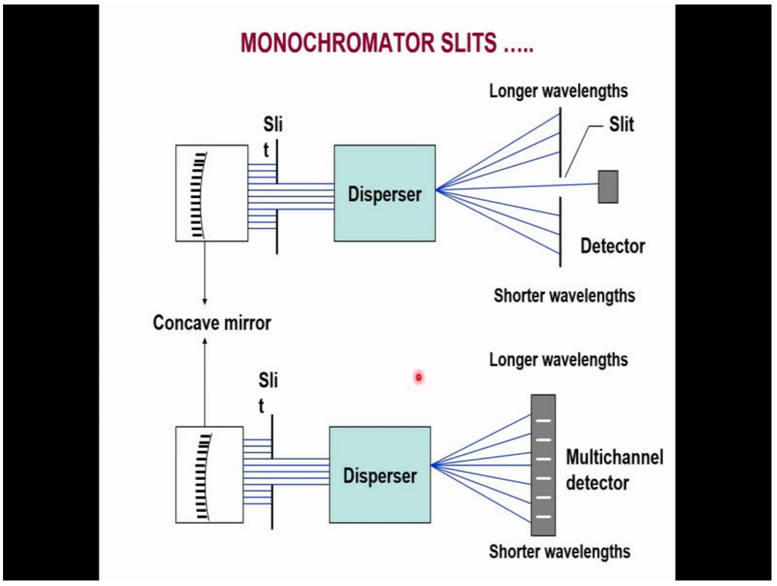

Now, we will also look at monochromator slits. So, what is a monochromator slit? A monochromatic slit is different from an ordinary slit in that the slit the monochromator slit we separate wavelengths from each other. Where as an ordinary slit will only make may pick up a small portion of the light beam light energy and I make it parallel and allow it to pass through a disperser, and this disperser is nothing, but a prism either Cornu or Littrow. Now in this arrangement I have shown you here light source as a concave mirror, and this side is mirrored; that means, all the light is coming this side and because it is concave all the radiation are parallel in this case and I put a slit and in front of this slit I put my disperser that is the prism.

So, a once the radiation comes out of the prism all the wavelengths are spread out uniformly and then longer wavelengths are at the top, shorter wavelengths are at the bottom. Now this is the mechanical slit what we are talking about; this is a monochromatic slit now because if I move the slit down here somewhere here I will be picking up a very short wavelength radiation and if I move it here higher wavelength another higher wavelength like that I can choose any wavelength I want out of the dispersed radiation.

Same thing is true with the concave mirror again here I can put a multi channel detector instead of moving this place slit a taking one slit at a time I can make number of holes in a mechanical position fixed together which will allow me to pick up all the wavelength different wavelengths simultaneously. So, this is known as multi channel slit and the data I need a detector outs across the multi channel so many detectors as many detectors as the wavelengths I want to work with.

So, this is the typical arrangement in almost all spectrophotometers including atomic absorption ok.

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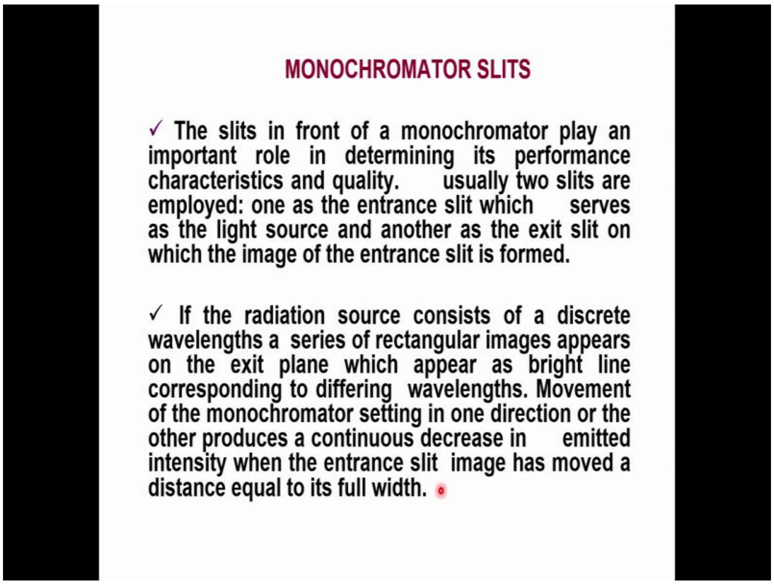

So, the a slit in front of a monochromator plays a very important role in determining it is performance, characters performance characteristics as well as quality. So, usually two slits are employed one is the entrance slit which I had already shown you here in the previous figure, this one is the entrance slit this is exit slit. So, the entrance slit serves as the light source and another as the exit slit shows the image of the entrance slit that is formed essentially it is nothing, but the image of the entrance slit. So, if the radiation source consists of discrete wavelengths by themselves, a series of rectangular images appears on the exit side, this is what I have shown you here the entrance slits it is all parallel downs. So, a rectangular slit is what I need on this side to pick up the different wavelengths.

So, these appear as bright line corresponding to different wavelengths. So, movement of the monochromator setting in one direction or the other direction produces a continuous decrease or increase of the wavelength; that means, if I take a prism if I take a light source put it in a concave the shell with a mirror on the other side, take out the radiation I put a prism in Cornu or Littrow type, put a screen across and then put the wavelengths screen and then what I get is if I move the slit slowly I get different wavelengths continuously or when the entrance slit image has moved a distance equal to it is full width I get the different wavelengths.

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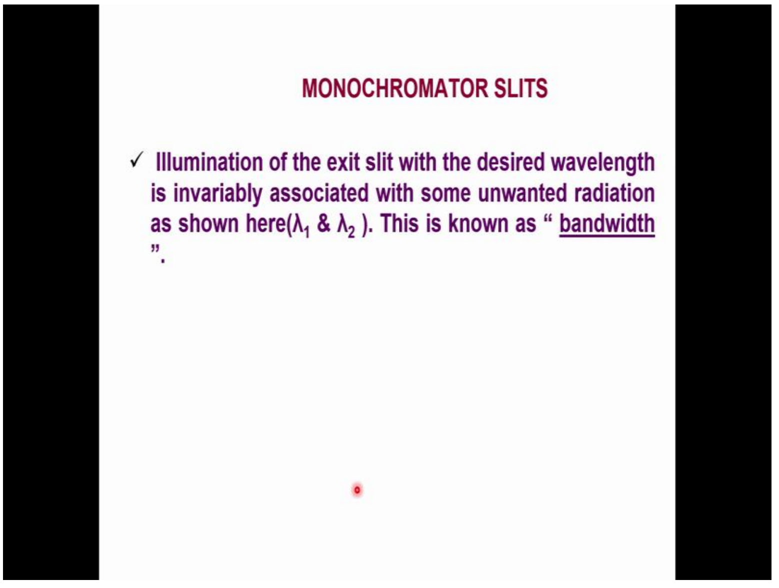

So, illumination of the exit slit with the desired wavelength is invariably associated with some unwanted radiation as shown here I want to show you in the next slide; normally what happens is look at this figure once again any rectangular slit here will also pick up some unwanted additional wavelengths nearby. You know you will never get a true monochromatic radiation.

What is the monochromatic radiation? A monochromatic radiation is a wavelength of single is a radiation of single wavelength and unfortunately and the practically it is not possible to pick up a single wavelength from a monochromatic a slit. So, there is always some wavelength associated with the wavelength what you want to choose, it is associated with some wavelengths of the lowers on the lower side as well as some wavelengths some radiation having higher wavelength also. So, the combination of all the wavelengths put together is known as bandwidth.

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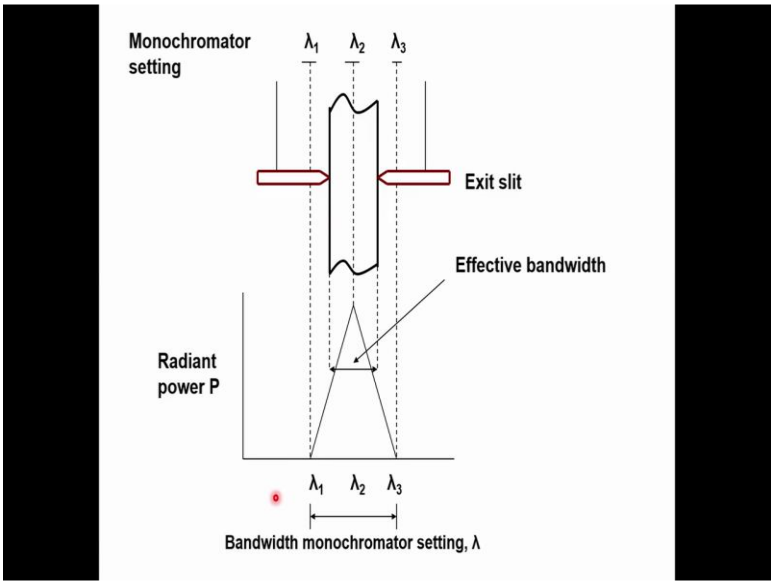

So, this bandwidth I am showing you here and you can see this figure I am assuming that this is the slit exit slit, and then radiation is coming like this and this exit slit I have chose the fix the wavelength like this, this is what I want that is lambda 2. Lambda 2 is here, but unfortunately it is also going to pick up some radiation of lambda one is associated with this because we are because of the distance the wavelengths will conically separate. So, I have put the cone in the opposite direction here. So, if I am choosing this I will also be choosing wavelengths from lambda 1 to lambda 2, also from lambda 2 to lambda 3 on the longer side. So, the actual wavelength or radiant power is the sum of all the radiant powers of each wavelength corresponding to this monochromator exit slit.

So, I as fine as the slit you make you get a better and better wavelength range you will never get a monochromatic light. So, you will get a mixture of wavelengths corresponding to some shorter wavelength plus longer wavelengths, but in the whole group maximum radiation will be the one what you choose from the scale what I wish for. So, the total radiation lambda 2 plus lambda 1 and lambda 2 plus lambda 3 is what is what you are getting, but 50 percent of the intensity is normally what we settle for and that is known as imagine this is the cone and this represents 50 percent of the radiation actually it is does not look like, but I should have drawn it a little below and then it to the line would have come here and that is known as effective bandwidth. So, whenever you want to buy a spectrophotometer or spectrometer you should ask for what is the effective wavelength if our effective bandwidth. So, this is important. So, we should study the in literature whenever you want to by an atomic absorption spectrometer.

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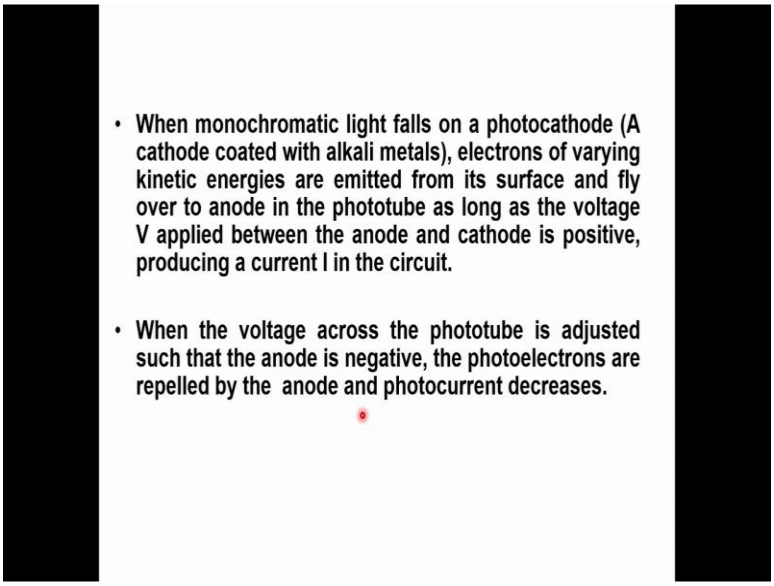

So now we move on to the detector part detector detectors. So, now, imagine that we have a spectrometer and I have the source we switched on we have put a slit collected another put I have disperser collected another fixed one more slit you have collected the radiation. And this radiation is nothing, but a number of photons emanating from the system corresponding to different wavelengths; and these wavelengths we want to detect. Now how do we detect we make them fall on a detector generate the current. So, when a monochromatic light falls on a photocathode, a cathode made of alkali metals.

So, what happens? Electrons of various kinetic energies are released from the surface. You can imagine just like a wind carrying lot of particles coming and hitting your glass in your window at home and they make the pockmarks right whenever we metal sand or some other particles come and hit your window it becomes fogged right. So, similarly if I make a in electrode and make the radiation fall on that, they will fall on the alkali metals electrodes another make them fall on that it will release electrons. So, this electron being a negatively recharged it will generate current and this current is measured.

So, if the wavelength is very short the radiation is highly energetic so more current will be produced. If the radiation is of longer wavelength they are less energetic less current will be produced. So, this is a way of detecting the wavelengths and then correlate the wavelength whatever we have connected to the intensity of the radiation. So, you know what we are essentially doing is to increase it to take advantage of the kinetic energy of the electrons emitted from the surface that fly or once the electrons are released the they are attracted by the anode because electrons cannot exist simply in space.

So, if a alkali metal releases electrons this move into the space and reach towards a an electrode which is having positive charge that is known as anode an electrode having a positive charge is known an anode so the electrons will be moving from the negative electrode to the positive electrodes, that is what we are showing here. So, the fly over to the anode and if you put both the electrodes in a phototube as long as we apply a voltage between the anode and cathode is positive as long as it is positive if a current I is produced in the circuit.

So, when the voltage across the phototube is adjusted such that anode is negative then what happens? Photoelectron electrons are repelled and photocurrent decreases. So, it is essential that in a phototube both anode and cathode should be there, cathode anode should be maintained at a higher potential than the cathode; then only the electrons will be attracted towards the higher energy anode.

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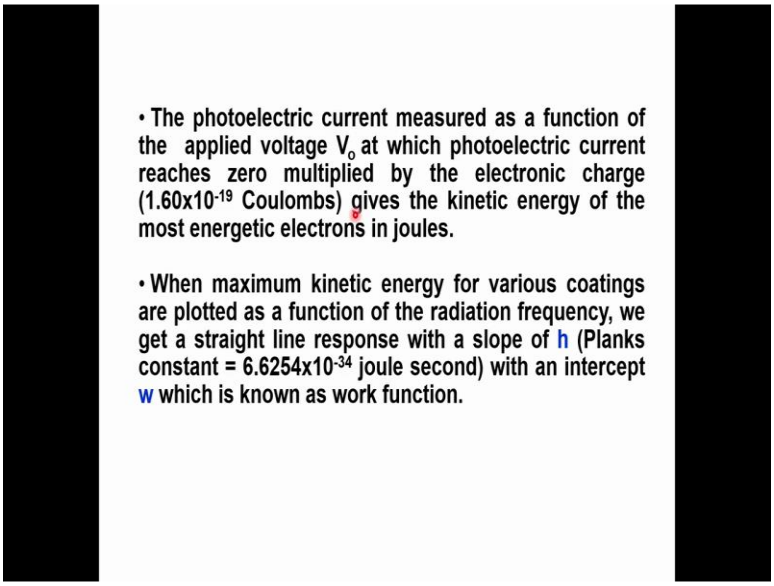

So, the principle is essentially same the photoelectric current is measured as a function of the applied voltage, we call it V 0 you can call it anything, but it is only a notation which I am using for my personal reasons, because I am very familiar with V 0, at which the photoelectric current reaches zero multiplied by the electronic charge that is 1.60 into 10 raised to minus 19 coulombs.

So, the total a kinetic energy of the most electronic most energetic electrons are measured in joules. So, when maximum kinetic energy for various coatings are plotted as a function of the radiation frequency, you plot the energies of the radiation electrons then we get a straight line response with a typical slope that slope should be of planks constant that is 6 into 6.6254 into 10 raised to minus 34 Joule second with the intercept w which is known as work function. This work function is a very special material property of the matrix, suppose I make an electrode of the alkali metals the work function is low; that means, electrons it minimum amount of energy can impinge on the electrode and release the electrons.

So, if it is metal like copper then they need higher energies to release the electrons from the metal. So, this work function is a very special property and if the plots what you get of the energy, energy plot can be described by this equation that is KE m is equal to h nu by minus w or E is equal to KE m plus w or that is should be equal to the difference between the energy of the radiation that is h c by lambda.

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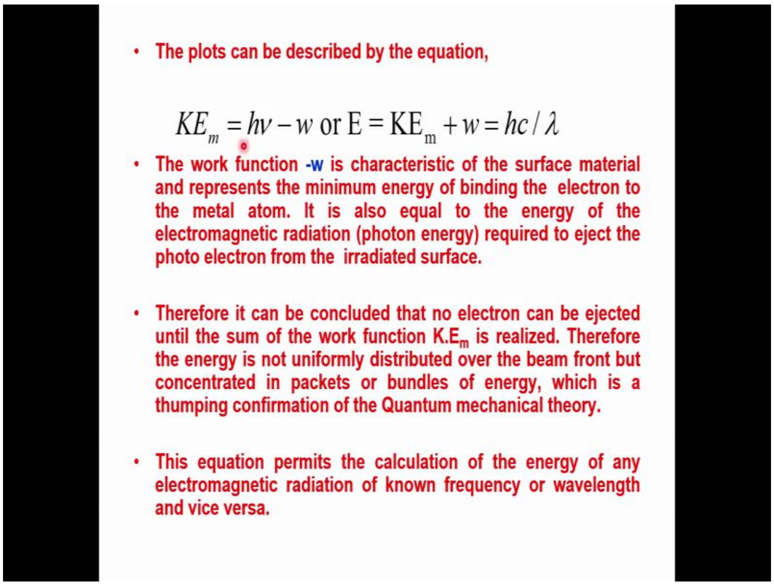

So, the work function minus w is characteristic of the surface material which I have already told you, and that represents the minimum amount of energy of binding the electron; that means, if you want to release an electron from a metal coating what you should do is, you should apply enough energy to exceed the work function that is w zero then only the electrons will be released otherwise what happens what happens to the energy that is supplied if it is less than work function.

You think about it, but I will have to give you the answer the answer is the electrons will vibrate they will absorb the energy and just vibrate. Suppose you are standing on a heated metal plate what happens, you either jump up and down to reduce the heat or you jump out of the heating system. So, if the heated plate is very long then we try to jump up and down and try to survive. That is how most of the electrons survives if the energy supplied to the electrode is less than it is work function. So, to release the electron from a metal you have to supply energy much more than the work function.

So, above the work function quantity you can supply any amount of energy, and then if you supply more energy more electrons will be released otherwise if you supply less energy less electrons will be released. So, the energy of the electromagnetic radiation required to eject the photoelectron is also it is approximately equal to the work function of the irradiated surface; that is the metal electrode from which they are made. Therefore, we can conclude that no electron will be really ejected until the sum of the work function k dot into e m is realized. The as long as it does not exceed the electrons will not be released, and that quantity is the multi or multiplication of the electromagnetic radiation energy work function energy multiplied by the kinetic energy.

So, the energy is not uniformly distributed over the beam front, but concentrated in packets or bundles of energy which is; that means, it is quantized that it is a thumping confirmation of the quantum mechanical theory, you keep on supplying enough energy continuously over a pair to a metal nothing will happen above that above the critical K dot into E m the electrons will be released; that means, in between there are no in between states through which continuous ejection of the electrons take place. So, that is a point we should remember because in all quantum mechanical theory we always say that the electrons behave in a quantized manner.

So, if the electrons are to be absorbed still they need an energy corresponding to the difference between the energy levels only when it is supplied they to get absorbed, and if they have to be released they will they released energy also will correspond to the quantized energy difference between the two energy states, through which the electrons will pass through.

So, the quantum mechanical theory itself is proven by this work function concept. So, the this equation what I had shown you earlier that is K into E m is equal to h nu minus w r, w e is equal to KE plus w, that is equal to h c by lambda this equation permits the calculation of the energy of any electromagnetic radiation of known frequencies is. If you know the frequency or wavelength see the; remember this last equation h is constant c is constant and lambda is the wavelength. So, either you should determine the wavelength or frequency both are connected they interrelated as I taught you in the last class and this equation permits the calculation of the energy of any electromagnetic radiation of known frequency or wavelength and vice versa.

If you know the frequency you can calculate the energy, if you know the energy you can calculate the wavelength or frequency either wavelength. So, the concept of work function is very important in most of the detectors and where do we use a detector? We use a detector in a spectrophotometer or spectrometer or emission spectrometer spectrographs and so many other places wherever we have to determine the energy of an electron or a photon we need the concept of work function.

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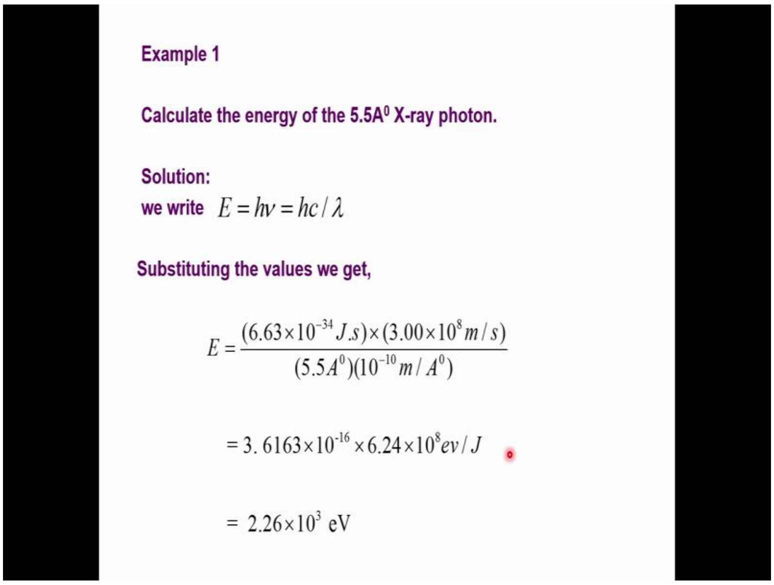

So, we can I am going to give you a small example here that is an X ray photon is having 5.5 angstroms; what is 5.5 angstroms it is the wavelength. So, I can calculate E is equal to h nu or h c by lambda, we know the value of h that is the 6.63 into 10 raised to minus 34 joules per second Joule second sorry and then c we know value of c is the velocity of light that is 3 into 10 raised to 8 meters per second or you can also write 3 to 10 raise to 10 centimeters per second this joules also you can express in hertz. So, 5.5 extra minutes we have using here that is the wavelength given delta, and you have to convert that you have to convert multiplied by 10 raised to minus 10 this table I have shown you in the earlier class.

So, if I substitute all these values what I get is 2.26 into 10 raised to 3 electron volts; that means, if I have a wavelength an X ray radiation of corresponding to 5.5 angstroms the corresponding energy of that radiation is 2.26 into10 raised to 3 electron volts.

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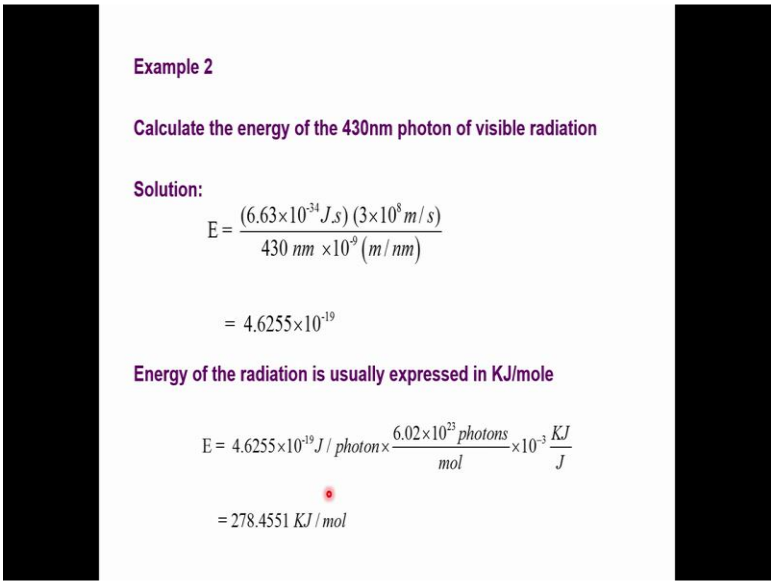

Now, I can show you another example; here I am showing you calculate you have to calculate the energy of the 430 nanometer photon of visible radiation. Now I think we should remember that 430 nanometer is a visible range. So, if you remember my earlier slide the ultraviolet range starts from 180 to 350 and then from 350 to 800 nanometers is the visible range. So, this is around 430; that means, it is it corresponds to somewhat orangish color of the where a rainbow, and if I have that kind of radiation the top portion that is numerator will remain the same because it is nothing, but planks constant multiplied by the velocity of radiation and this we can convert into 430 nanometer that is a given photon converted into meters, I have that works out to approximately 4.6255 into 10 raised to minus 19.

So, in the energy of the radiation is usually expressed in kilo joules per mole; that means, if I have what is one mole? A one mole of any substance should contain 6.23 into 10 raised to 23 or 6.0 to if you want to use the current number correct number, it is 6.02 into 10 raised to 23 is the number. So, if you take one mole of water it will have 6.02 into 10 raised to 23 molecules of water. If you take copper one mole; that means, 6.02 into 10 raised to 23 atoms will be there; like that if I take photons one mole of photon should be 6.02 into 10 raised to 23 photons.

So, I can express this energy see 4.6255 into 10 raised to minus 19, I have to multiply it by the mole fraction. So, 6.02 into 10 raised to 23 photons per mole and this is so many joules per photon. So, how many how much photons what is the total energy of 6 so many photons and you can convert from Joules to kilojoules also that is so, you have to multiply by 10 raised to minus 3 or divided by 1000, and what you end up is approximately 278.4551 kilo joules per mole.

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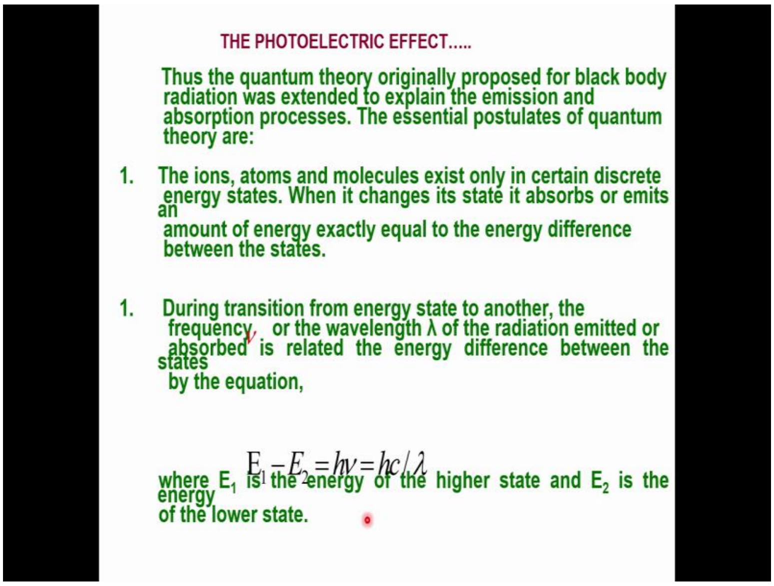

So, this is how most of the energies of the radiation is calculated; we will continue our study discussion on the photoelectric effect after a small gap of about 5 minutes.