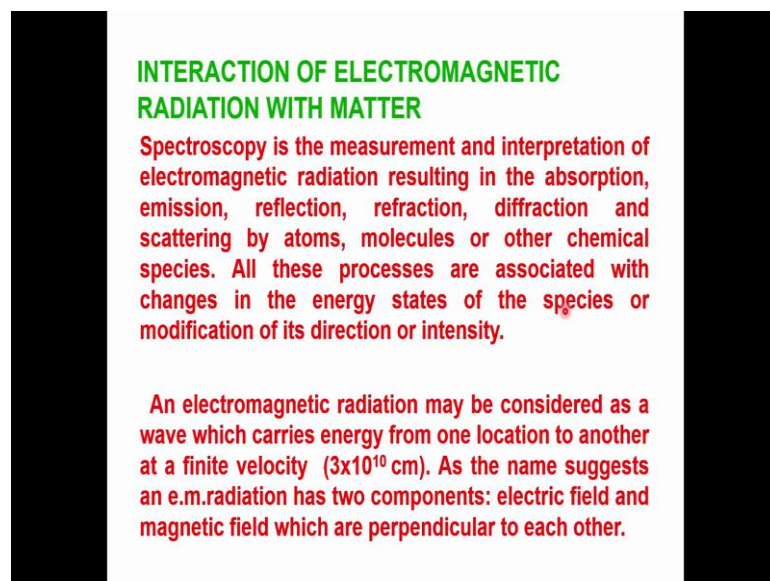


Trace and ultra trace analysis of metals Using atomic absorption spectrometry
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Lecture – 05
Electronic arrangements in elements II

Greetings to you, we had discussed about the electronic structure of the atoms in the last class and previous class also.

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INTERACTION OF ELECTROMAGNETIC RADIATION WITH MATTER

Spectroscopy is the measurement and interpretation of electromagnetic radiation resulting in the absorption, emission, reflection, refraction, diffraction and scattering by atoms, molecules or other chemical species. All these processes are associated with changes in the energy states of the species or modification of its direction or intensity.

An electromagnetic radiation may be considered as a wave which carries energy from one location to another at a finite velocity (3×10^{10} cm). As the name suggests an e.m.radiation has two components: electric field and magnetic field which are perpendicular to each other.

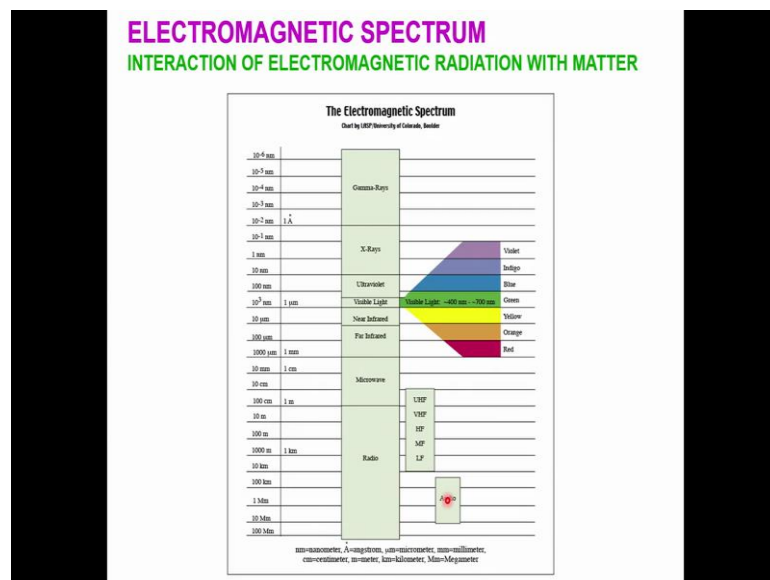
What we I had where I had stopped is the interaction of electromagnetic radiation with matter because spectroscopy is the measurement and, measurement and interpretation of the electromagnetic radiation resulting in the absorption, emission, reflection, refraction, diffraction etcetera by atoms and molecules or other chemical species. So, all these processes are associated with changes in the energy states of the species or modification of its energy or intensity.

So, what we are essentially saying here is the atoms molecules and other chemical species will react with electromagnetic radiation and the changes occurring in the atomic structure or the electronic structure could be related to changes in the electromagnetic radiation because the change will be corresponding that is one is to one. So, what is an electromagnetic radiation? So, what we want to say is an electromagnetic radiation is

considered as a wave which carries energy from one location to another at a finite velocity this velocity is 3×10^{10} .

So, as the name suggest the electromagnetic radiation has 2 components one is an electric part that is electric field and another is a magnetic field. So, each of them are perpendicular to each other and I think all of us are familiar with what is an electromagnetic radiation I do not know how many of you are aware, but every day we are exposed to electromagnetic radiation and any time of the day we are expose to electromagnetic radiation we see electromagnetic radiation all around us.

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So, what is an electromagnetic radiation it is nothing, but some sort of a light which we see for example, the rainbow colours what you see in the sky they are all electromagnetic radiations the ultra violet rays what you get from the sun in the morning they are electromagnetic radiations and then visible light through which you and I see each other they are also electromagnetic radiations and then you must have heard of several other types of electromagnetic radiations which include infrared radio waves, microwaves, cosmic waves, cosmic rays all these are as a group they constitute electromagnetic radiation

So, each electromagnetic radiation some of them we see them some of them we do not see them because our eye is not sensitive enough to capture the radiation. So, how do we define what is electromagnetic radiation look at this slide here I have written an electro I

had shown you an electromagnetic radiation this slide here you can see on the top I have written the electromagnetic spectrum chart by university of the colorado boulder and that consist of gamma rays x rays ultra violet rays and then visible light, somewhere in the middle and near infrared far infrared microwaves and radio waves.

Now, here we you see the I have listed the frequencies on the left side for example, gamma rays have got in the wavelength of $10 \text{ raise to minus } 6$ nanometers the range from up to $10 \text{ raise to minus } 2$ nanometer. So, $10 \text{ raise to minus } 2$ nanometer is one angstrom unit. So, the effect of gamma rays end up maximum wavelength of a gamma ray is one angstrom unit and then we have x rays that is $10 \text{ raise to minus } 1$ to 10 nanometers.

So, this is approximately about 100 nanometer total because $10 \text{ raise to minus } 2$ $10 \text{ raise to minus } 1$ and 1 nanometer approximately 100 nanometers range and the radiation which have a wavelength of this range are called as x rays you may not be able to see them, but you will be able to see the x ray effect of x rays on photographic plates when you go to a doctor detect the x ray.

Now, x ray is a here you can see that the x rays have got longer wavelength than gamma rays gamma ray is $10 \text{ raise to minus } 2$ where as x ray is extend up to $10 \text{ raise to up to } 10$ nanometers. Now as you go down I have written here ultra violet rays which range from 10 to 100 nanometers and then we also have among the ultra violet also we have the far ultra violet and near ultra violet that is vacuum ultra violet it is called I have not shown it here, but vacuum ultra violet ray rays are up to 10 or 20 nanometers followed by ultra violet and then after the ultra violet range we have visible light.

Now, the visible light the range is from almost up around 1 micrometer 1 to 1000 micrometer up to $10 \text{ raise to minus } 3$ micrometers and the visible light I have shown on the right side expanding cone into violet, indigo, blue, green, yellow, orange and red. So, visible light what we see around you what you see what I see all of us see comprise of these 7 colours violet indigo etcetera, but the range from one micro around one micrometer range then we have if you come back to this middle stripe after the visible light there is near infrared light that is up to 10 micrometers and after that I have far infrared that is up to 100 micro 100 micrometers that also extends further down the line up to 1 millimetre.

So, all these ray radiations electromagnetic radiations corresponding to this range 10 micrometers to 1 millimetre or 1000 micrometer are known as far infrared then there are ways electromagnetic radiation having still larger wavelength that is from 1 centimetre to 1 meter. So, these are called microwaves you are familiar with the microwave cooking etcetera and it is not very unusual and down the line we have from 1 meter to 1 kilometre and up to 100 mega meter also we have what is known as radio waves. And the microwaves and radio waves comprise of ultra high frequency v h f high frequency medium frequency low frequency etcetera and still down the line we have from 100 kilometre to 1000 kilometre it is audio waves; that means, the electromagnetic radiation except this part are not visible to us.

But they are in existence and the all constitute the same species except by differing in wavelength and frequency some of them we see some of them we do not see and our visible eye is limited to only a small portion of the electromagnetic radiation any other eye radiations we are unable to feel at least see the see it with our naked eye feeling yes for example, infrared heating we are all aware it can be done microwave heating can be done microwave towers you would have seen all around us etcetera radio waves we have heard of a all these the whole thing constitutes an electromagnetic spectrum.

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| PROPERTIES OF E.M. RADIATION | | | |
|------------------------------|--------------------|-----------|--|
| Name of the unit | Symbol | Unit for | Used in |
| Nanometer | Nm | λ | UV, visible, near-infrared |
| Angstrom+ | \AA | λ | X-ray, UV-visible (in older work) |
| Milimicron | m μ | λ | Visible (in older work) |
| Micron, Micrometer | $\mu, \mu\text{m}$ | λ | Infrared (common in physics literature) |
| wavenumber (reciprocal cm) | cm^{-1} | μ/c | Infrared, UV- visible (less common) |
| Electron volt* | eV | E | X-ray, γ -ray |
| Hertz | Hz | length | Radiofrequency ,microwave |
| Cycles per second | Cps | length | Radiofrequency (less common in current literature) |

So, the properties of electromagnetic radiation I define them like this that is the name of the unit, normally this is the how the electromagnetic radiation is described it is

wavelength. So, the nanometer symbol is Nm unit for wavelength, and this type of electromagnetic radiation is used in UV visible and near infrared radiation infrared range. We can also write angstrom symbol is like this and then it is also unit for wave wavelength and it is useful if I write angstrom if I have to describe any x ray, I have describe it has having 10 angstroms, 20 angstroms like that that is it is wavelength.

Similarly, in UV visible also we have described in terms of angstroms, but that is all in older work. For example, if you study literature scientific literature around about 40 50 years before people will have describe UV visible range in terms of angstrom units; 4000 angstroms, 6000 angstroms like that, but for convenience nowadays we do it in nanometers and their SI units also. So, next is milimicrons, units are again wave for wavelength and that is in the visible range, but again it in the older work we do not we no more use this terms in our scientific literature and then we can we do is microns and micrometers that is also unit for wavelength, but that is useful for infrared radiation only.

So, such microns and micrometers are used in organic chemistry as well as in physics literature; then we use a term what is known as wave number that is centimetres inverse symbol is micrometer by wave velocity of light that is c , again it is used in infrared radiation. It is also used in UV visible radiation, but fairly less common.

Then for describing high energy radiation we used instead of wavelength we used electro volts, electron volts. So, that is the unit for energy and it is used for x ray and gamma rays, then we use hertz that is radio frequency it is the frequency for symbol for frequency Hz it is for length and radiofrequency and microwaves will describe them in terms of hertz; and cycles per seconds Cps that is used in radiofrequency, but that is also again less common in the current literature.

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Interconversion of Energy and Wavelength

| | nm | Å | cm ⁻¹ | eV | MHz | J* |
|----------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| nm | 1 | 10 | 10 ⁷ | 1.240 × 10 ³ | 2.9979 × 10 ¹¹ | 1.986 × 10 ⁻¹⁶ |
| Å | .1 | 1 | 10 ⁸ | 1.240 × 10 ⁴ | 2.9979 × 10 ¹² | 1.986 × 10 ⁻¹⁵ |
| cm ⁻¹ | 10 ⁷ | 10 ⁸ | 1 | 1.240 × 10 ⁻⁴ | 2.9979 × 10 ⁶ | 1.986 × 10 ⁻²³ |
| eV | 1.240 × 10 ³ | 1.240 × 10 ⁴ | 8.0655 × 10 ³ | 1 | 2.418 × 10 ⁸ | 1.602 × 10 ⁻¹⁹ |
| MHz | 2.9979 × 10 ¹¹ | 2.9979 × 10 ¹² | 3.3356 × 10 ⁻⁵ | 4.1355 × 10 ⁻⁷ | 1 | 6.626 × 10 ⁻²⁸ |
| J | 1.986 × 10 ⁻¹⁶ | 1.986 × 10 ⁻¹⁵ | 5.034 × 10 ²² | 6.241 × 10 ¹⁸ | 1.509 × 10 ²⁷ | 1 |
| Spectrometric region | UV-vis | X-ray UV | Infrared | X-ray γ | Radiofrequency (NMR) | |

*4.184 J = 1 cal

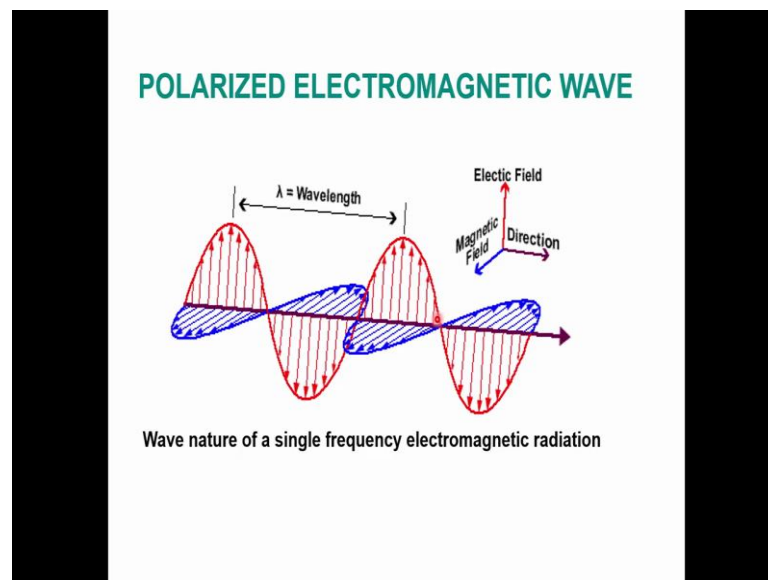
Now, all these energies refer to because all these energies refer to the wavelengths there should be some sort of interconversion of energy and wavelength for example, if I write it in nanometer, 1 nanometer corresponds to 10 angstroms and 10 raised to 7 centimetres inverse it corresponding energy is 1.240 into 10 raised to 3, and it is frequency would be 2.9979 into 10 raised to 11, and it is energy in joules is 1.986 into 10 raised to minus 16.

Similarly, if I choose any other column here that is centimetres inverse it can be described in terms of nanometers, in terms of angstroms, in terms of electron volts and energy and frequency. Same thing is true with respect to frequency that also can be converted there is some inter convertibility table you need not by heart this, but it make sense to know that all these forms of energies are interchangeable interconnectivity is there.

So, spectrometric region this nanometers is the wavelength range used in UV visible spectrometric, angstroms in UV, and x ray centimetres in infrared, electron volts for X ray and megahertz for radiofrequency. The corresponding analytical techniques are also you can easily identify here for example, UV visible region this for colors, this is for X ray is for bones etcetera hard materials infrared is for suns radiation etcetera all these things can be understood.

Now coming back to electromagnetic radiation we say we call it an electromagnetic radiation because it has 2 components, one is electrical field another is magnetic field; that means, whenever an electromagnetic radiation is proceeding towards us in a particular direction.

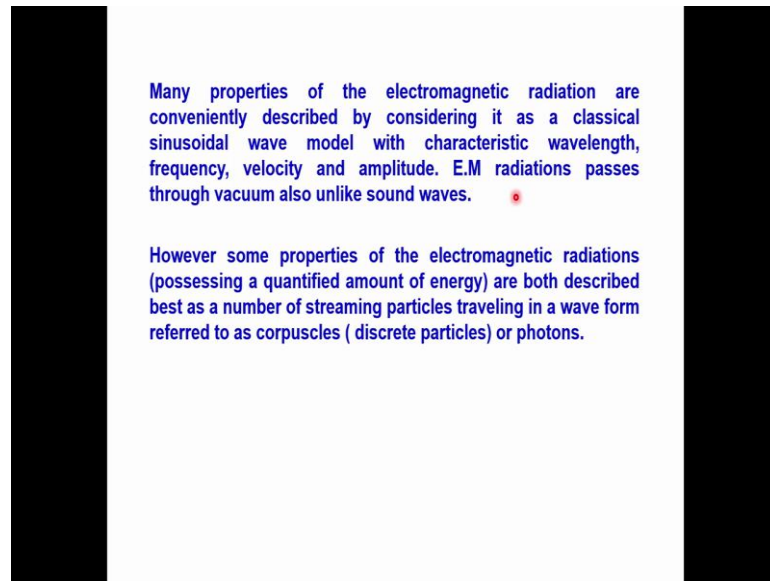
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There is a component known as electric field and another component is known as magnetic field, here I had try to depict here the electric field like that in the x axis in red colour.

Now, the magnetic field is perpendicular to that and then it is in blue colour. So, this is the wave nature of a single frequency of electron the electromagnetic radiation. So, whenever we see an electromagnetic radiation going, I have to imagine that there is a electrical field like this and then there is a magnetic field perpendicular to that like this. So, if I am sitting here on a chair on a table along the horizontal lines there is one magnetic field and they are in the vertical space there is electrical field. This is how imagine and you can see the directions of the electric field and magnetic field here in this area. So, the magnetic field stretches upwards and electric field stretches upwards and magnetic field stretches horizontally; there is no hard and fast rule that it should stretch only electric field should stretch upwards, it is only relative as for as we are concerned.

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So, many properties of the electromagnetic radiation are conveniently described by considering it as a classical sinusoidal wave. This wave type of wave one it starts from 0 reaches maximum, again reaches 0 goes to minus 1 and again reaches 0 like this in terms of units this is known as sinusoidal wave. And same thing is true even with the magnetic field that is shown in blue colour here; that means, its value keeps on increasing until it reaches 1 and falls to 0 and then it reaches minus 1, more than that the values it would not be a bigger, but for microwave this amplitude will be bigger and this distance wavelength is also bigger. But otherwise all the properties are essentially similar like this except in terms of quantity.

So, we say that all electromagnetic radiations are conveniently described by considering it as a classical sinusoidal wave with characteristic wavelength, because we know per a centimetre how many crests will appear, how many troughs will appear; below the scale we call it troughs, above the scale we call it crests and troughs. So, the characteristic of an electromagnetic radiation is its wavelength, its characteristic is frequency, characteristic is velocity and amplitude. If you describe anywhere electromagnetic radiation with one single wavelength, will be describing all other properties also simultaneously because they are fixed for particular wavelength, and same thing is true with respect to all other parameter also.

So, also electromagnetic radiations are pass through vacuum also unlike sound waves. So, electromagnetic radiation does not need a medium; however, some properties of the electromagnetic radiations are also described as a number of streaming particles travelling in a wave form referred to as corpuscles or photons. Now you can imagine a wave if you imagine a wave in a pond, you can see that the pond surface is having troughs and crests troughs and crests etcetera or if you through a stone in a pond, it will generate waves which will have troughs and crests; that and for that there is a medium required for example, water if the water is not there you will not be able to see the troughs and crests correct.

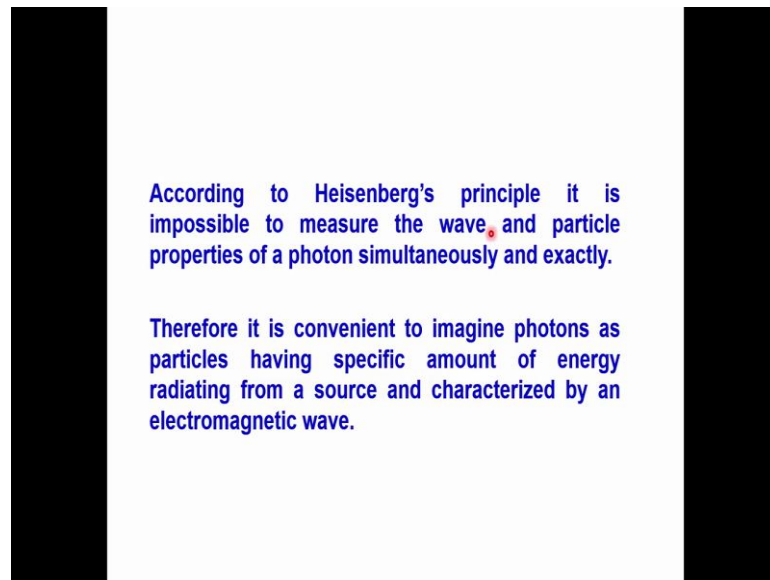
So, if the medium is not there then also the electromagnetic waves will be going through the same motions in the air. In this case air acts as a medium, but we do not see the air, but the waves will be going through the same. Extending the analogy suppose air is not there then what happens; will the electromagnetic radiations still need a medium whether visible or not to move from one point to another; answer is yes because in between keep on receiving radiations from the sun on the earth even though there is nothing in between, you can almost describe it almost as vacuum.

So, if you take a radiation create a vacuum in between put a detector on the other side, you will see the still see the radiation on the other side this is known as vacuum transmission. So, electromagnetic waves have got wavelength frequency they need a medium and they need not need a medium also. Now I can imagine that going back to this figure you can also imagine; I can imagine a light particle a particle made of single light moving up like this up like this, but it keeps on moving in this direction right. So, when this if I assume that this is a particle may it reaches here, what happens to another particle will replace this from the source. So, I can imagine that every electromagnetic radiation is a stream of particles which keep on travelling through the same mechanism having same amplitude etcetera in the same medium; that means, a number of light points are imagining you can imagine a number of light points being thrown from the source towards a particular direction.

So, the imagination can also extend we can extend the imagination to the electromagnetic radiation that they are not only waves of energy, but they could be particles of energy carrying certain amount of energy a fixed amount of energy along with them, so this known as corpuscles theory. So, some properties of the

electromagnetic radiations we can easily define them or describe using particle theory or using a wave theory. Both of them are possible the particle theory is explained by using the by imagining that the source is emanating a number of particles throwing out and these particles are known as photons.

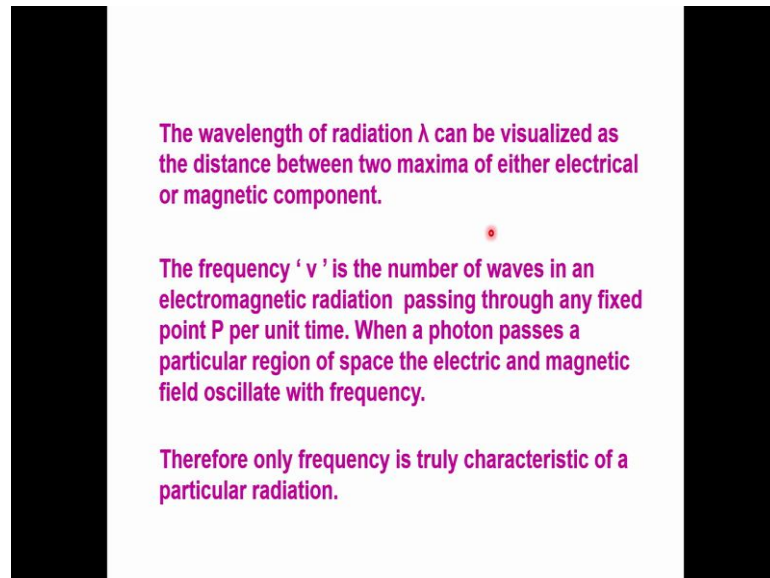
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So, both of them are possible and characteristic wave a typical wave will have can behave both has particle as well as a wave. In some cases it makes more sense to measure it has a wave and in some cases it make sense to use them as particle particles corpuscles particles.

Then can we use both the answer is no why because according to Heisenberg's principle it is impossible to measure the wave and particle properties of a photon simultaneously and exactly. It has got lot of quantum mechanical connotations, but essentially stated it means that you cannot pin point the position of a wave corresponding to it is a position as well as energy. So, wave and particle properties of a photon simultaneously it is not possible, there is always certain amount of error associated when you want to measure the wave pa wave size as well as particle size at the same time therefore, it is convenient to imagine photons as having specific amount of energy radiating from a source and characterized by an electromagnetic wave.

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Now, the wavelength of radiation λ can be visualized as the distance between 2 maxima of either electrical or magnetic components; this one, this is one maxima this is another maxima, this distance measured either (Refer Time: 27:18) or centimetres or milimicrons whatever it is the difference between the distance between the 2 crests or 2 troughs for example, I can do it from here to here from this crests to this crests. So, both of them should be same. So, it is possible to measure this and it can be visualized as the distance between 2 maxima of either electrical component or magnetic component both of them should be same for a given electromagnetic radiation.

Now, the frequency ν is the number of waves in an electromagnetic radiation passing through any fixed point per unit time so; that means, you fix a particular place and how many waves pass through that point per cent per second or per minute or something like that. So, when a photon passes a particular region of space, the electric and magnetic fields oscillate with the frequency; you can show this thing by a simple lime experiment and therefore, only frequency is truly characteristic of a particular radiation that is what we said, if you calculate the frequency electromagnetic radiation is fixed.

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Mathematically an electromagnetic wave can be described as a sine wave,

$$A = A_0 \sin \theta$$

where A is the amplitude at any point

A_0 is the peak amplitude

θ is the continuous variable



Now, mathematically how do you write an electromagnetic radiation? We write it as a sine wave I have already explain to you that the amplitude for a sine curve it reaches a maximum and then a minimum and then the all the values are correspond in between. So, we write A is equal to A_0 in to $\sin \theta$; that means, when θ is 0, $\sin \theta$ is 0. So, it the value of amplitude will be 0. So, as the θ increases $\sin \theta$ also increases reaches a maximum of one and then in that case A would be equal to A_0 that is the maximum and then again it will decrease oh as you proceed along these thing.

So, A_0 is the peak amplitude, and θ is a continuous variable by which the photon moves forward.

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Alternately

$$A = A_0 \sin \omega t$$

Where $\omega t = \theta$ and ω is the angular velocity in radians/unit time.

A complete cycle occurs when ωt changes from 0-360°. This is called one oscillation or one period. Hence the time over which one complete occurs is given by,

$$t_{\text{cycle}} = \frac{2\pi}{\omega}$$

or $\nu = \text{frequency} = \frac{1}{t_{\text{cycle}}} = \frac{\omega}{2\pi}$

Now, alternately you can also write A is equal to $A_0 \sin \omega t$, and this ωt is equal to θ and ω is the angular velocity in radians per unit time. You can imagine that the radiation is going through a 360 degrees first 0 to 180, if you imagine a range from 0 to 360 degrees from 0 to 90 it reaches maximum, 180 it reaches 0, 270 it reaches minus 1 and 360 again it reaches 0. So, this cycle keeps on increasing and occurring again and again. So, it will be describing a sinusoidal wave as we have said earlier.

And then a complete cycle occurs when ωt changes from 0 to 360 degrees and this is called one oscillation or one period, that is the path described by an electromagnetic radiation from 0 to 360 degrees is 1 oscillation, hence the time over which one complete oscillation occurs is given by ω divided by 2π that is number of cycles or that is known as frequency, $1/t$ is the frequency we call it and then that is described by 2π by ω is only a simple mathematical representation of the radiation.

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For any wave moving at a constant velocity v , we can write

$$v = \nu \lambda$$

where ν is the frequency in ms^{-1} , ν is in Hertz (cycles per second or s^{-1}) and λ in meters

The frequency is proportional to the energy E of the photon given by

$$E = h \nu$$

where $h = 6.62 \times 10^{-27}$ ergs when E is expressed in ergs and
and $= 6.63 \times 10^{-34}$ joules. E is expressed as joules.

Sometimes it is convenient to use "wave number" denoted by $\bar{\nu}$ to describe the radiation for example in infrared spectrometry. Then the photon energy is expressed

And then for any wave moving at a constant velocity v , we can write the velocity is the number of cycles per second followed by wavelength multiplied by wavelength. V is the frequency in meters per second and ν is in hertz that is cycles per second and λ is in meters. So, the frequency is proportional to the energy and that is again given by E is equal to $h \nu$, ν is the frequency. So, the energy of any electromagnetic radiation h is a constant that is known as planks constant. So, the energy of a given system corresponds to a fixed frequency of a fixed part of the electromagnetic radiation.

So, in this equation h is planks constant that is a determined experimentally a 6.62×10^{-27} ergs, when e is in expressed in ergs and that is also equal to 6.63×10^{-34} joules that is when E is expressed as joules. Sometimes it is convenient to use wave number denoted by $\bar{\nu}$ sometimes it will called denoted by $1/\lambda$ frequency that is wave number.

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It may be noted that regardless of the units of expression any electromagnetic radiation of frequency will have unique wavelength and energy.

The longer the wavelength, the lower is the energy and frequency.

Energy is closely related to temperature of any object. It can be expressed as

$$E \propto K_B T$$

where K_B = Boltzmann's constant
= 1.380×10^{-16} ergs K^{-1} atom $^{-1}$ or 1.380×10^{-23} joule K^{-1} atom $^{-1}$

If we consider energy per mole of the material,

$$E \propto RT$$

where R = the gas constant
= 8.3145×10^7 erg K^{-1} mol $^{-1}$ or 8.3145 joule K^{-1} mol $^{-1}$

It may be noted that regardless of the units of expression of any electromagnetic radiation of frequency, frequency will have unique wavelength and unique energy and unique frequency; every frequency will have unique wavelength and unique this is what you have trained since long time and the longer the wavelength the lower is the energy and frequency.

So, frequency is closely related to the temperature of any object, it can be expressed as a Boltzmann constant expression a is proportional to $K_B T$ where K_B is Boltzmann constant described by 1.380×10^{-16} ergs per degree, that is Kelvin per atom. If we consider the energy per mole of the material you can also write that E is proportional to RT that is roomed R is gas constant and T is the temperature in absolute scale.