Physico-Chemical Processes for Wastewater Treatment
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Lecture 53
Disinfection - II

Good day everyone and welcome to these lectures on Physico-Chemical Processes for Wastewater Treatment. In the previous lecture, we started the disinfection section. So, various types of chemical compounds in particular chlorinated compounds or chlorine and its various compounds are used for disinfection, along with the ozone, ultraviolet radiation etc. And in the previous lecture, we started the disinfection chemistry with respect to chlorine, and we understood that if the hypochlorite in the form of sodium hypochlorite or calcium hypochlorite, if it is added, so, depending upon the pH it will get converted into HOCl or the chloride ion, so, that is there.

Now, I will continue with the chemistry part, further understand the chemistry with respect to other type of species if they are present in the water. So, going further, now, in particular, for disinfection, the chlorine ammonia reactions are very important to understand, because if the ammonia or nitrogenous compounds are present in the water, so, chlorine actually reacts with them, while the chlorination process is going on. So, in this way different types of chloramines get formed.

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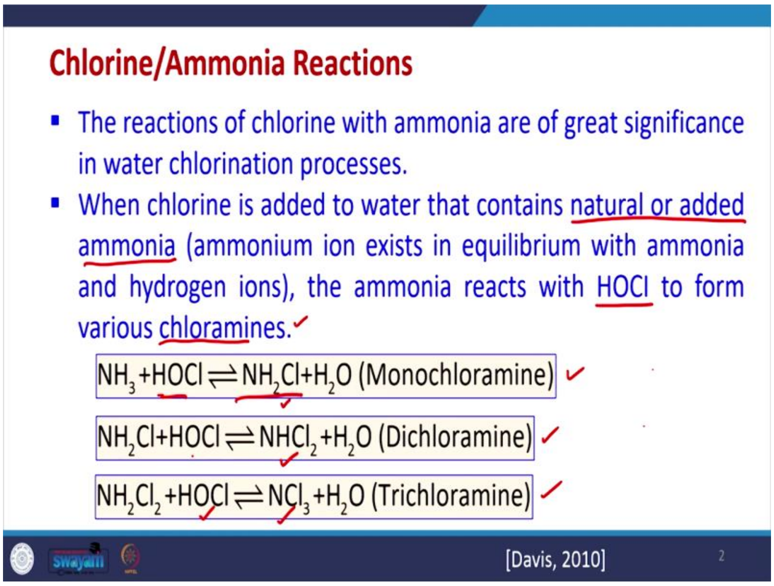

So, different types of various Chloramines maybe monochloramine, dichloramine trichloramine, so, they may get formed depending upon the amount of ammonia present and the amount of HOCl which has been added. So, these chloramines they have order, and also the use of the chlorine which has been added. So, this way the amount of chlorine which is actually available for disinfection become less so, this is very, very important to understand this chlorine ammonia reaction.

Now, when the chlorine is added to water that contains natural or added ammonia, so, ammonium ion may exist in equilibrium with ammonia or hydrogen ions depending upon the pH. So, this chlorine react will react with ammonia and this chlorine may be in the HOCl form because this is the dominant form in the usual pH range in which the water treatment is done. So, different types of chloramines will get formed.

Now, ammonia reacts with HOCl to form monochloramine here we can see a plus H2O Then again if more amount of HOCl is present, so, this will further react with monochloramine to form dichloramine and if more amount of HOCl is available, it will form trichloramine. So, these different types of poli chloramines may get formed if ammonia is present in the water.

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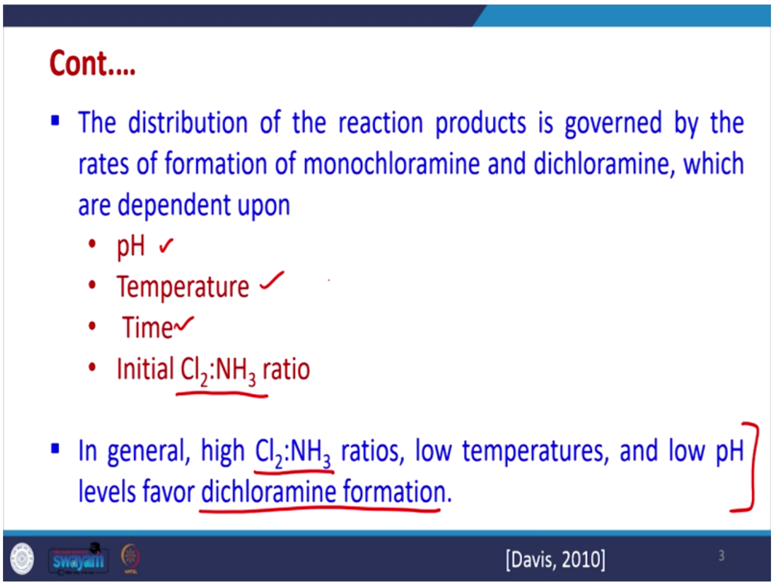

Now, the distribution of the reactant products that whether mono tri or di, which type of chloramine will be formed that is dependent upon the pH, temperature, time for which this reaction is available, and the ratio of Cl2 to NH3, so this ratio is one of the very important parameter along with the pH, because temperature is the usual range in which operation is being done and generally time is also sufficient enough. So, in general the high chlorine to ammonia ratios and at lower temperature and low pH they will form more dichloramine formation will happen. So, this is the general chemistry of that, we will not go detail of this chemistry, but this is for understanding.

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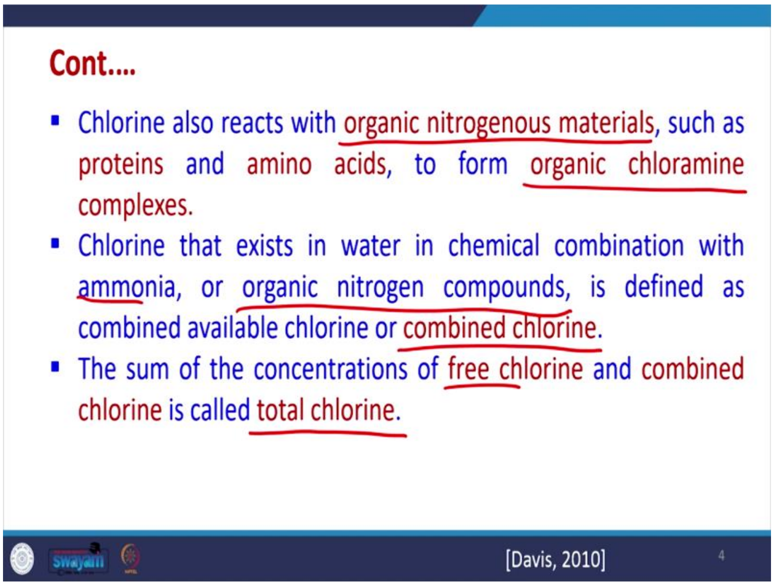

Now, these chlorine also react with various organic nitrogenous materials, which are present in the water and generally they will be present in the water because the water may contain different types of proteins and amino acids and if they are present the chlorine will react with these proteins and amino acids also to form organic chloramine complexes, so this is possible. And chlorine that exists in the water in chemical combination with ammonia or organic nitrogen compound is defined as combined available chlorine or combined chlorine. So, this is different than free chlorine.

So, we have free chlorine which is either HOCl or OCl minus then we have combined chlorine which is the chlorine combined with the ammonia or organic nitrogenous compounds. So, and the combination of free chlorine and combined chlorine is called as total chlorine. So, this is the simple information.

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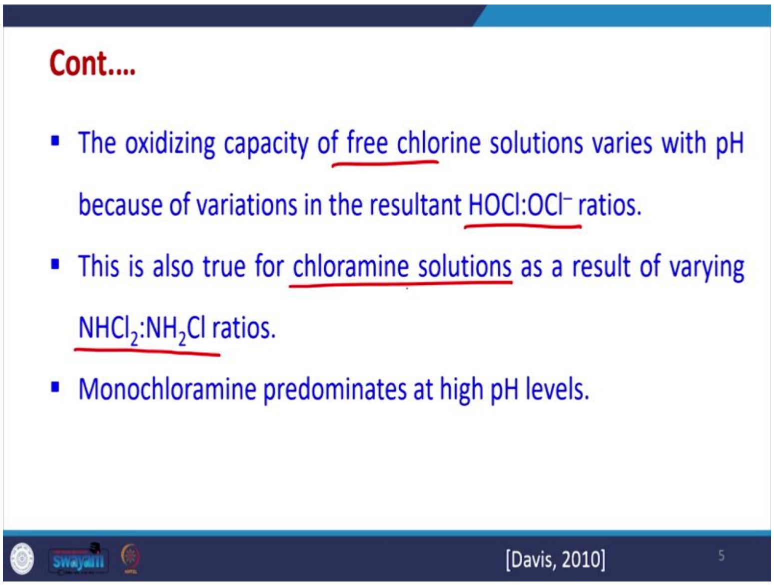

Now, going further the oxidizing capacity of free chlorine available in the solution varies with pH and because of the variation in the resultant HOCl and OCl ratios and because of the uses of the HOCl with the ammonia or other nitrogenous compounds the amount of actually free available chlorine will be lesser and this is for free chlorine it depends upon this ratio. Similarly, for chloramines solutions, so, this will be dependent upon the oxidizing capacity will be dependent upon these ratios which are there. So, the, in a general the monochloramine they predominate at higher pH level, as well as the dichloromethane that dominates at lower pH levels.

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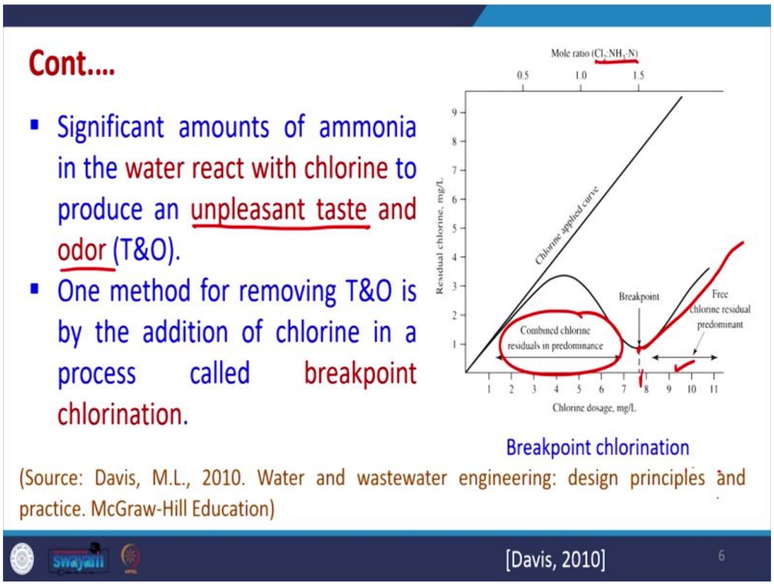

Now, significant amount of ammonia in the water if it is present it will react with the chlorine to produce an unpleasant taste or odor. So, if ammonia is present or any nitrogenous compounds etc, are present. So, they may react with the they will react with the chlorine and they will form compounds which actually have unpleasant taste as well as odor, and one the method for removing this taste and odor is to add more amount of chlorine so that a breakpoint is reached. And after that this breakpoint, where the concentration becomes less and we have more free chlorine which is predominant.

So, this is combined chlorine section where the reaction is happening, but after a breakpoint is reached, after that, we have only free chlorine which is available and which can be used for disinfection as well. And we can see here the ratios at which the molar ratio of chlorine to ammonia nitrogen at which this breakpoint may occur.

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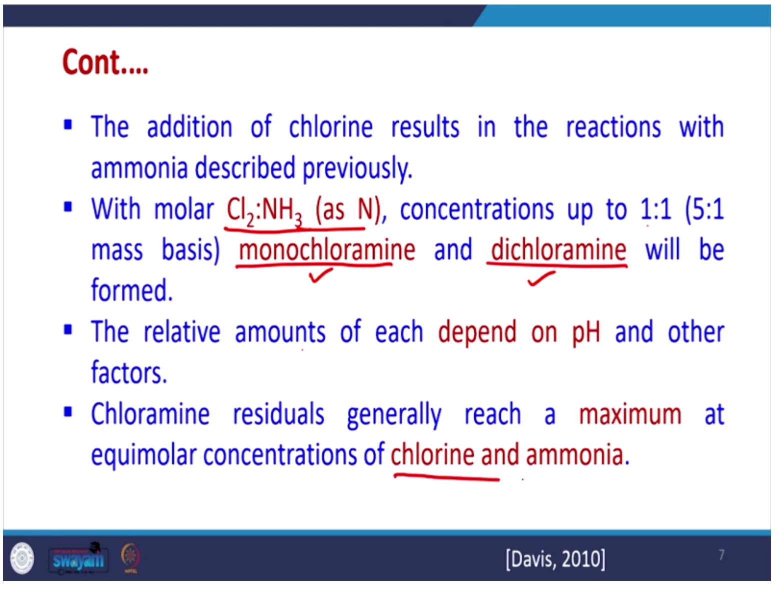

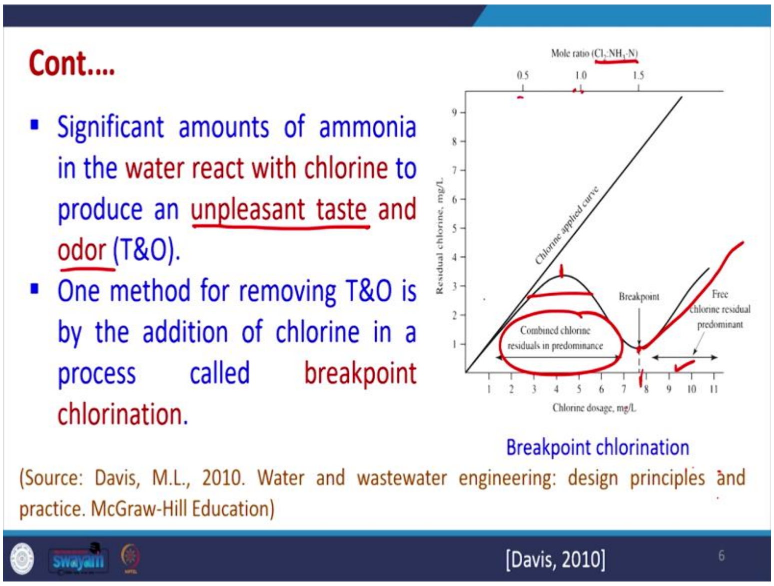

Now, going further the addition of chlorine results in the reaction with the ammonia already we have described, with different molar ratios of chlorine to ammonia as nitrogen, the concentration up to 1.1 molar ratio monochloramine and dichloramine will get formed. So, relative amount will depend upon the pH whether it is di or mono. So, already we have told that higher pH mono will be dominant, lower pH dichloramine will be dominant.

Now, the chloramine residuals generally reach a maximum at equimolar concentration of chlorine and ammonia. So, we can see here in the figure this is reaching maximum around 1. So, this these ranges 0.5 to 1. So, they are reaching maximum around these ratios. So, this is the ratio at maximum concentration maximum combined chlorine will be formed.

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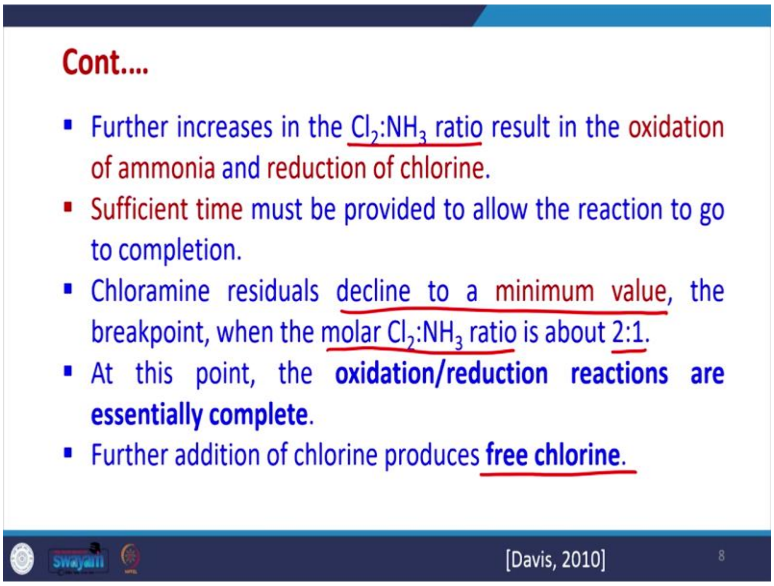

Now, after that further increase in the this Cl2 to NH3 ratio will result in the oxidation of ammonia and reduction of chlorine. So, sufficient time must be allowed for this to complete. So, chloramine residues they thereafter they declined to a minimum value and this will occur this breakpoint will be there around the ratio molar Cl2 to NH3 ratio of 2 is to 1. So, under this condition, we will be reaching a breakpoint and at this point, the oxidation reduction reactions are essentially complete. And if we add further chlorine, it will be totally available as free chlorine and it will be used for disinfection as well, so this is there.

So, we always try to have free chlorine, good amount of free chlorine available so that, that can be used for disinfection more. Now, suppose we use chlorine dioxide, so till now we have studied regarding the chlorine, now suppose are hypochlorite, now suppose we add chlorine dioxide. So, what are the essential chemistry of that, we are going to learn.

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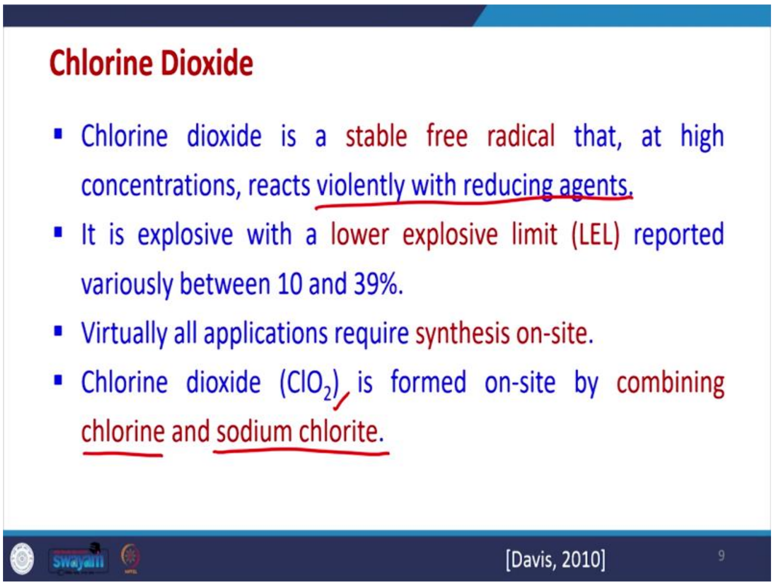

So, chlorine dioxide is a stable free radical and higher concentration, reacts violently with the reducing agent, so this is one of the basic characteristics of chlorine dioxide. It is explosive with the lower explosive limit reported between 10 to 39 percent and virtually all applications require synthesis on site. So, if chlorine dioxide has to be formed it has to be formed on site before usage, and this formation takes place by combining chlorine with sodium chloride. So, this way we can find out the chlorine dioxide. Generally, is not a very preferred chemical for disinfection.

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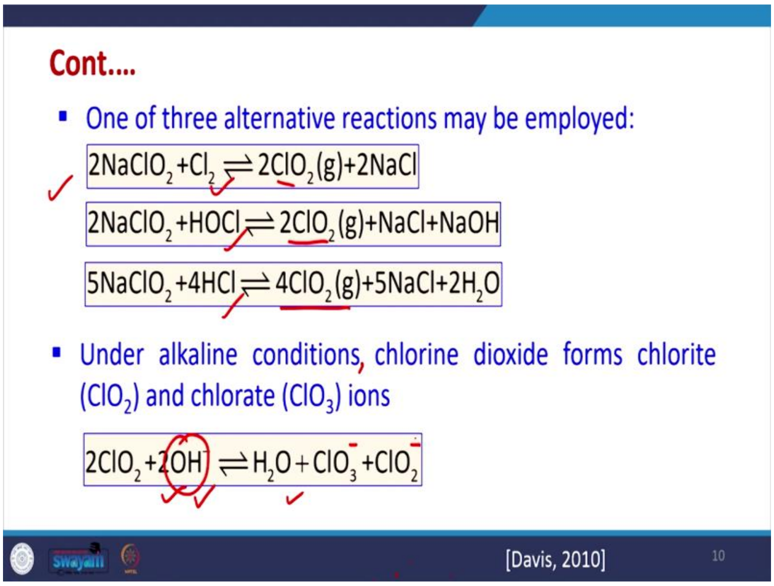

But if it has to be used, it has to be made on site. One of the three alternative reaction via which the chlorine dioxide can be formed, it is shown here. So, we can see the sodium fluoride reacting with Cl2, HOCl, HCl, so with reaction with any of these we can find we can make chlorine dioxide on site itself.

So, under alkaline conditions, if alkaline conditions are prevailing in the reaction that chlorine dioxide forms chloride and chlorate ions as per they are given here. So, we have chloride and chlorate ions, so, chlorate ions and chloride ions both are formed depending upon the pH under high alkaline condition when OH minus radical is available. So, this is possible and these may get formed.

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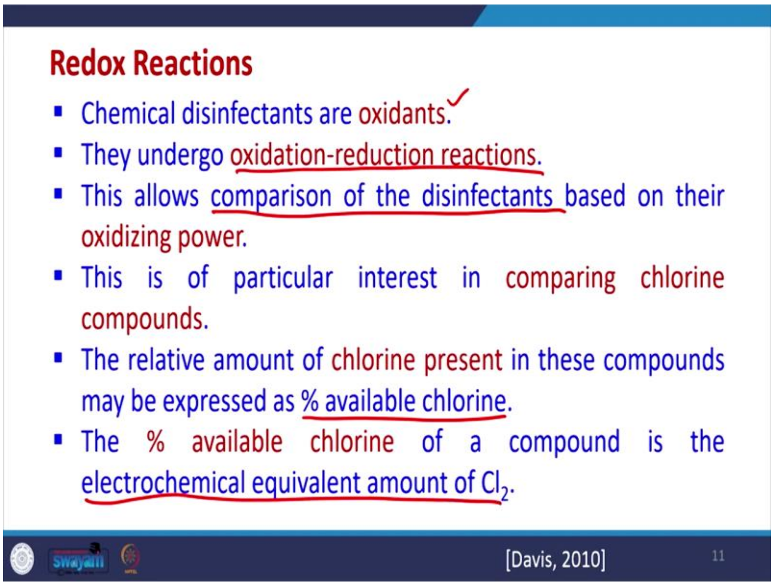

Now, going further ahead, there are certain redox reactions which happen where we are using any chlorine species in particular and these chemical disinfectants which are used which are generally like came all the chlorinated compounds chlorine and its related compounds are used as disinfectant, so they are essentially being used as oxidants.

Now, since they are used as oxidants, they are, they undergo oxidation reduction reactions. So, we can use these redox reactions and some more information from them for understanding their oxidizing power and if we can find out their oxidizing power we can compare different types of disinfectants, this is possible or using the oxidizing power and this is in particular very important for comparing various types of chlorine compounds which are used as a disinfectant.

Now, that relative amount of chlorine present in these compound may be expressed as percent available chlorine. So, any other chlorine compounds we can find out the relative amount of chlorine element and then we can calculate. The percentage available chlorine of a compound is the electrochemical equivalent of the Cl2. So, this is important.

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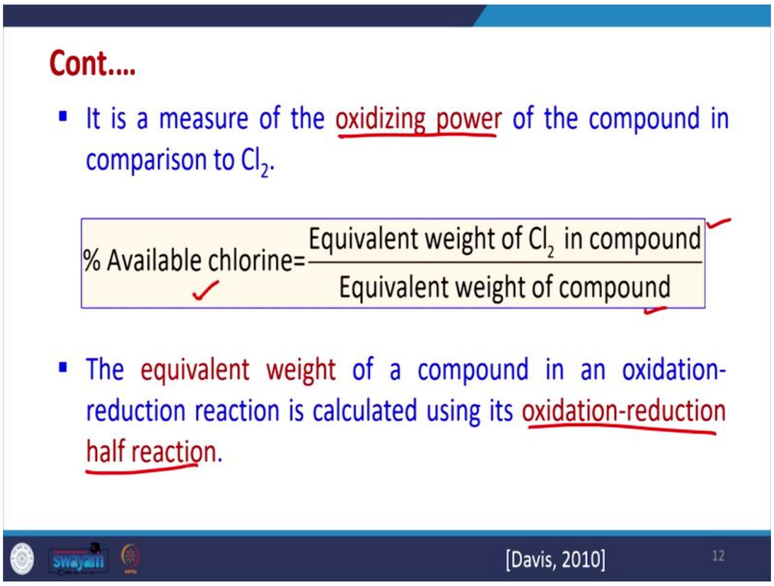

Going further, it is used as a measure of oxidizing power of the compound in comparison to Cl2, so, percentage available chlorine, so, we find out, then we find out equivalent weight of Cl2 in the compound and the equivalent weight of the compound itself. And by this we can find out the percentage available chlorine and if so, and this is a measurement of oxidizing power, the equivalent weight of compound in an oxidation reduction reaction is calculated using its oxidation reduction half reaction only, this is done.

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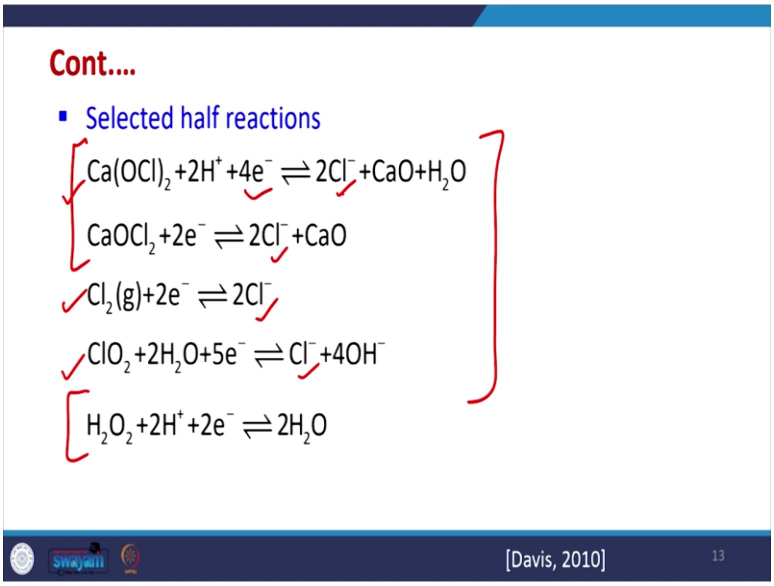

Now, some of the selected half reactions are given here, for different types of compound. So, we can see here for calcium chloride, and for Cl2 for ClO2 and for hydrogen peroxide it is given here, so you can see here that each are the reaction are given and in each of these reaction they are converted into react to Cl minus ions. So, we are trying to find out the chemistry there in which the compound combines with the electrons to form chlorine ion. So, this is the these are the half reactions we consider for calculating the oxidizing power or percentage available chlorine. So, this is these are there.

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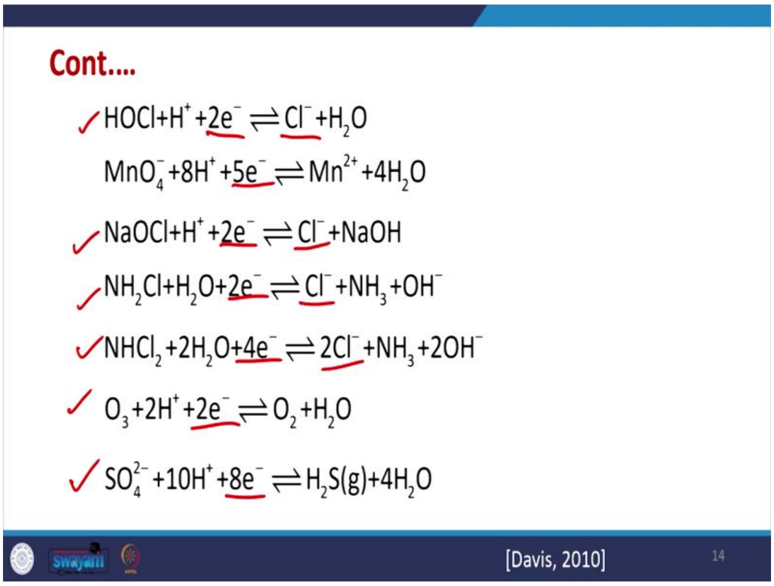

Now, these are the further reactions you can see here. So, for different types of chlorinated compounds, other types of chemicals as well. So, HOCl you can see NaOCl, NH2Cl, NHCl2, SO42 minus, O3 we can see here in each of the reaction the electrons are combining with the respective species in the presence of H plus or H2O and they are we are trying to get them converted into respect to chlorine species in particular for all the chlorinated compounds. So, this way we can write the half-reactions for different compounds and then we calculate the oxidizing power.

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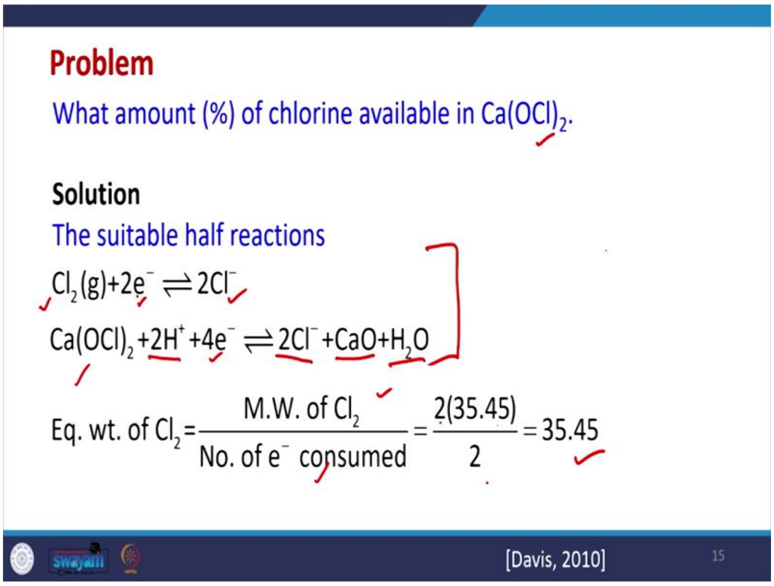

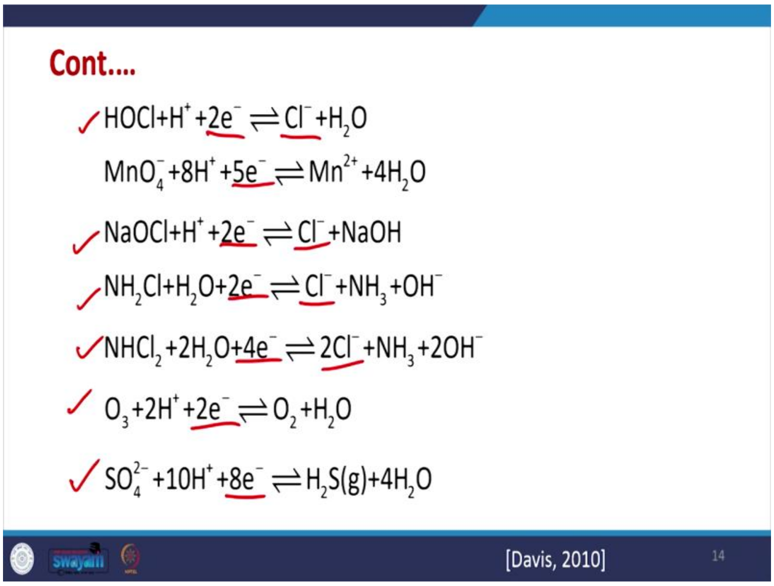

So, this question is given here and we will try to understand or solve this question for using these half-reactions equations which we have considered right now. And this way we can the same method can be used for different other compounds as well. So, for CaOCl2 the suitable half-reactions are given here and we can see here Cl2 gas combining with 2 electron to found 2Cl minus and similarly, CaOCl2 combining with 4 electron presence of 2H plus minus ion to form 2Cl minus ion and then CaO plus H2O, so, these are the half-reactions with respect to CaOCl2. Now, what is the equivalent weight of Cl2? So, molecular weight of Cl2 is known. So, it is 35.45 into 2 and the number of electrons that it is consuming in this reaction is 2. So, this is what is given. So, its equivalent weight is 35.45.

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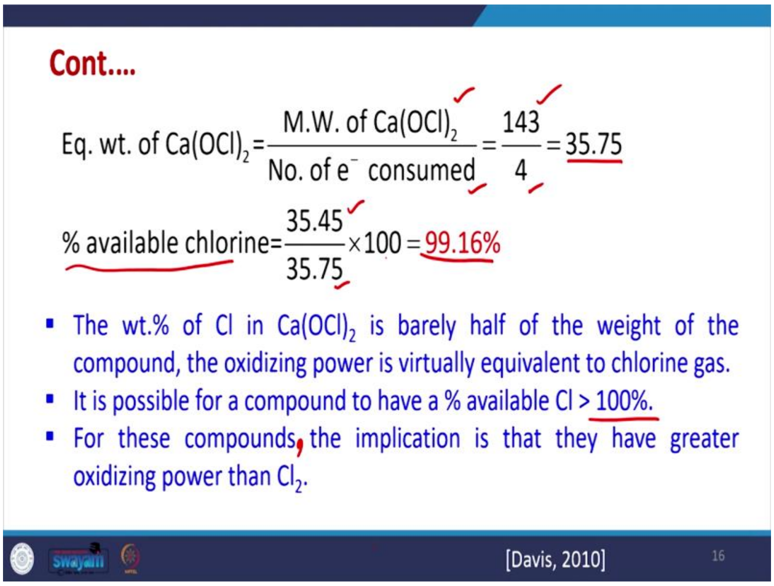

Now, going further, the equivalent weight of CaOCl2 is molecular weight of Cl2 CaOCl2 a number of electrons consumed. So, it is consuming 4 electrons and its molecular weight is 143. So, if you divide it, it is 35.75. So, again they are same. So, what is the percentage available chlorine? In the case of CaOCl2 is 35.45 divided by 35.75, so, into 100, so, it is 99.16. So, the weight percentage of chlorine in CaCl2 to is nearly half of the weight of the compound, so, this is only half only, but the oxidizing power is virtually equivalent to chlorine gas itself.

So, it is possible for a compound to have a percentage available chlorine greater than 100 percent also or nearly equal to 100 percent. And for these compounds the implication is that they have very high oxidizing power in comparison to Cl2 themselves. So, if they have more than 100 percent oxidizing power, so since we are comparing with respect to Cl2, so this way they can hire more oxidizing power than the Cl2 itself and by performing such calculations for other types of compounds also we can cross-check that, which compound itself is having more oxidizing power, because we are comparing the oxidizing power of different compounds with respect to Cl2 only via using this reaction this equation which was given earlier.

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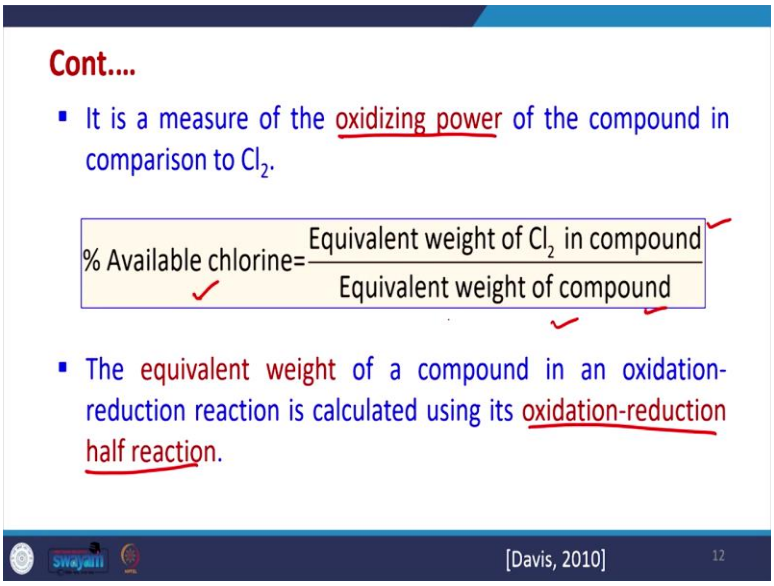

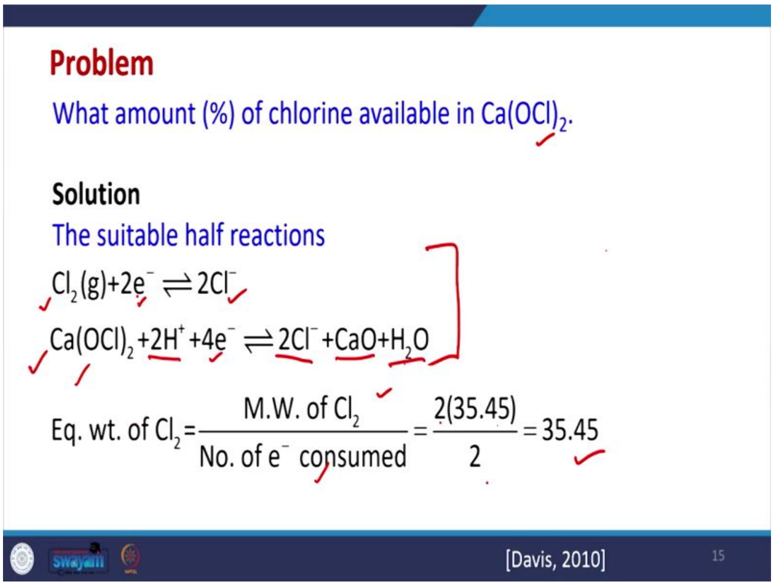

So, and for this doing this, we use the Cl2 half-reaction and plus the reaction with respect to that particular compound which is given here. So, this is giving a good idea for the comparing different types of chlorinated species and their oxidizing power. Now, going further ozone is also one of the chemicals or gas which is used for disinfection and the ozone that means O3.

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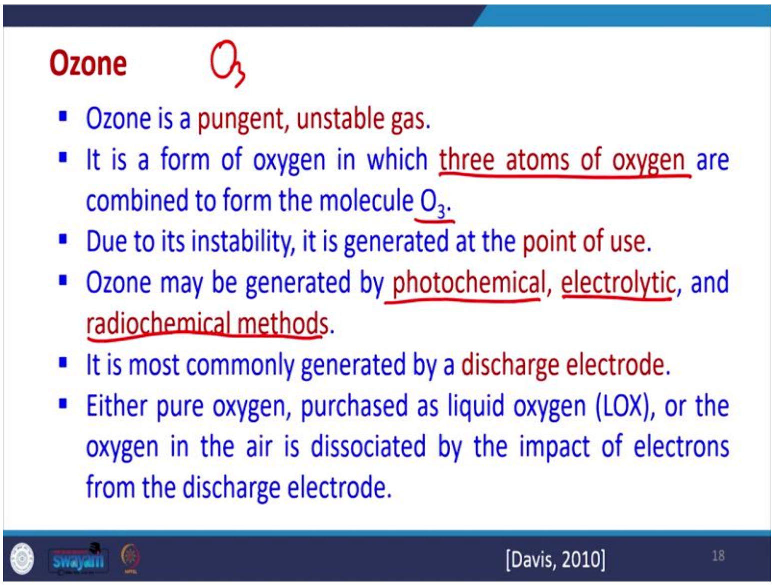

The good thing is that it has ozone is generally considered to be very good compound because it saves us from ultraviolet radiation which is coming from the sun and ozone layer is there, but ozone if it is present at the ground level, if any amount of ozone gas is present at the ground level and that it is considered to be bad because it will react with different living organisms maybe plant, etc and also with human beings if present in high concentrations, it will cause problem to them as well.

Now, so that means the formation of ozone at a ground level is considered to be a air pollutant and it is undesirable and but because of this its potential to react with different species and different types of pathogens, it is considered or it can be used as a disinfectant also because, it is highly reactive and it can react with virtually most of the compounds and thus it can react with the pathogens also and distract them. Now, ozone is a pungent unstable gas and it will stabilize very quickly farming oxygen.

So, it is a form of oxygen in which three atoms of oxygen are combined to form the molecule O3 and because it is a highly unstable gas, so it is generated if you have to use the ozone it has to be generated at the point of use itself. So, we have ozone generators which are used for generating ozone and then they are used for treatment of the water. Ozone maybe generated by a photochemical, electrolytic and radiochemical methods. So, any of these methods can be used for generating ozone and it is commonly generated by using discharge electrode system is there so under which the ozone is generated.

So, we can use either pure oxygen or liquid oxygen or oxygen present from the air and it is dissociated by the impact of electrons from the discharge of electrode and these O minus these oxygen ions which get generated they react with again oxygen molecule to generate ozone.

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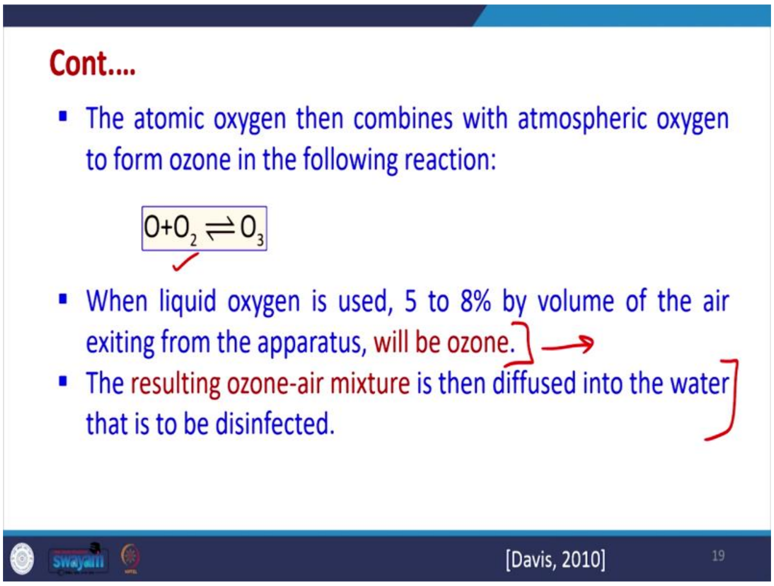

So, this ozone has to be used on site. So, this is the reaction the atomic oxygen then combined with atmospheric oxygen, so, to form the ozone via this reaction, when liquid oxygen is used, 5 to 8 percent of the volume of the air exiting from the apparatus will be ozone. So, we have to take precaution that this should not leave out of the system except going into the water for treatment. The deserting ozone air mixture is then diffused into water and that has to be treat. So, we have to see that all the ozone which is generated is used only for treatment of the water and for disinfection only not for any other purpose.

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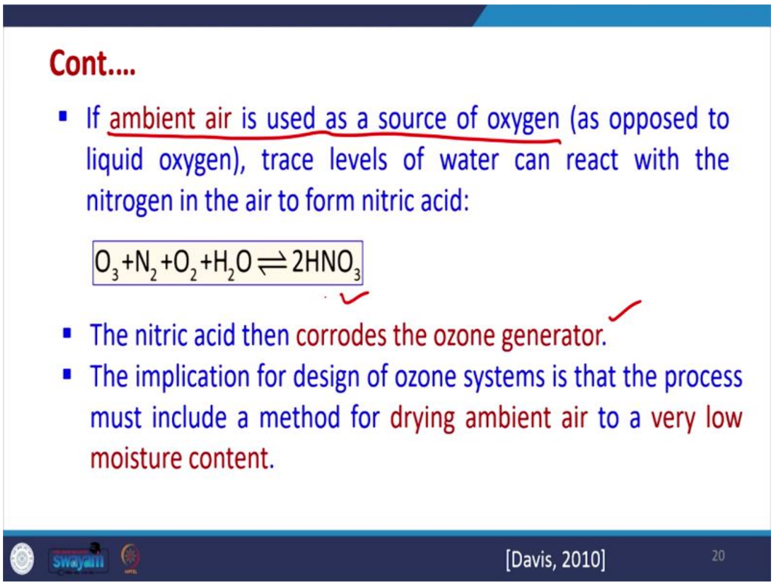

The ambient air is used as a source of oxygen as opposed to liquid oxygen. So, this is there. If suppose, we are using then, then that trace level of waters can react with the nitrogen in the air to form nitric acid. So, this is the side reaction if it is possible if we are using ambient air as a source of oxygen for ozone generation. So, this reaction is possible which is not desirable and this nitric acid may corrode the ozone generator itself.

So, this we have to take care, the implication of design of ozone system is that, the process must include a method of drying the ambient air before using it. So, ambient air should be free of moisture or it should have very, very low amount of moisture, otherwise this nitric acid formation may happen and it will corrode the ozone generator system.

And thereafter, the ozone generated is passed through the water and it is diffused into the water and water which contains the pathogens, they actually get oxidized, along with the pathogens if other amount of organic species, etc are present, so that they will also get dissociated and get distracted along with the ozone, going further.

The ultraviolet radiation is another technique which is commonly used for water treatment or wastewater treatment and ultraviolet radiation has been used since long. And in the COVID scenario the use of ultraviolet radiation for disinfecting the surfaces of various types of surfaces including metallic surface, the surface of the paper, the surface of the furniture’s, etc, everything can be disinfected via ultraviolet radiation. So, this is used since long.

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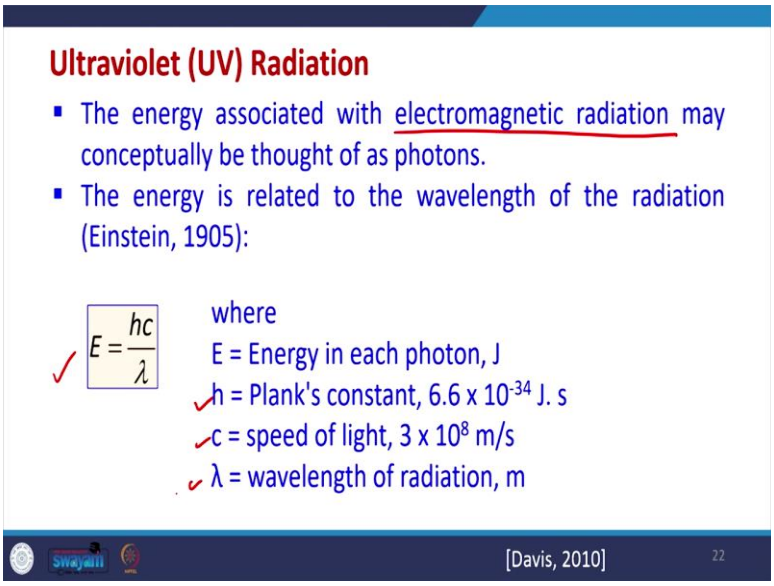

The energy is related to the wavelength of the radiation (Einstein, 1905):

$$E = \frac{hc}{\lambda}$$

where

E = Energy in each photon, J

h = Plank's constant, 6.6 x 10^{-34} J. s

c = speed of light, 3 x 10^{8} m/s

λ = wavelength of radiation, m

A little bit of the knowledge we are repeating here the energy associated with electromagnetic radiation, maybe it is thought to be in the form of photons, the energy is related to wavelength of radiation via this equation. So, we have we studied this equation since long so, E is equal to hc by lambda where h is the Plank constant, c is the speed of light and lambda is the wavelength of the radiation that we are going to use.

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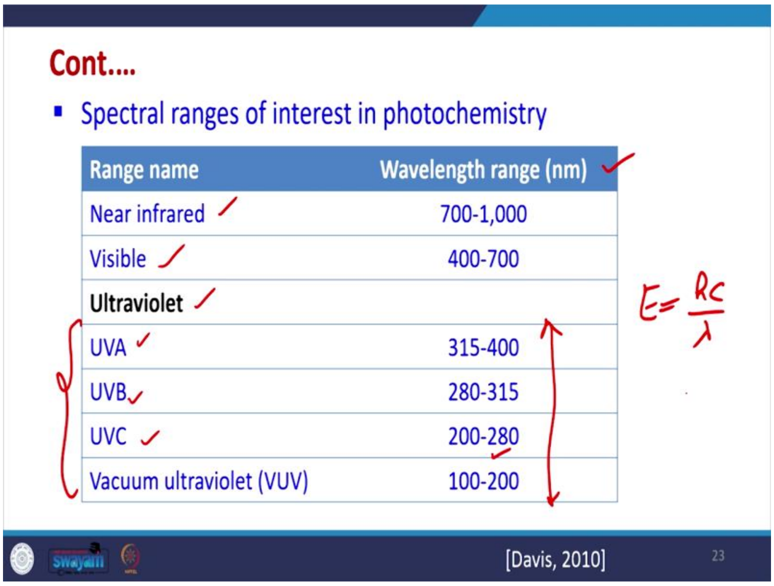

Now, the spectral range of interest which are used in the photochemistry you can see here, so, we have different wavelength range and the range include from near infrared, visible ultraviolet, so within ultraviolet we have UVA, UVB UVC then vacuum ultraviolet. So, and these are the wavelength in which we can use the ultraviolet. Now, depending upon the lambda that we are using, the energy will change because E is equal to hc by lambda.

Now, this lambda as we go suppose, we are using UVC, so, the amount of energy that the wave contains is very high. So, it will be able to distract most of the pathogens, so depending upon the type of pathogens, which are there, and also depending upon the intensity which is generated. So, the energy will also be different and they will be able to distract different types of pathogens, depending whether they are bacteria, virus or any other thing. So, this way we can distract most of the pathogens, which is there using the ultraviolet radiation.

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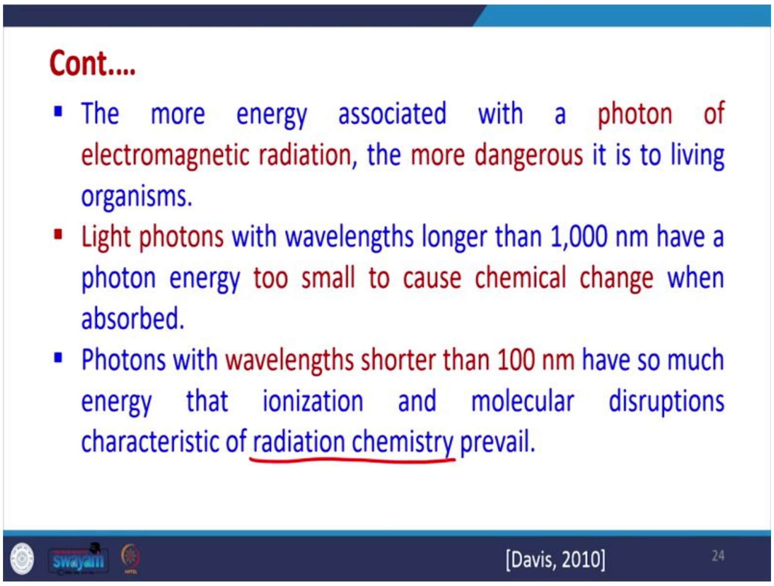

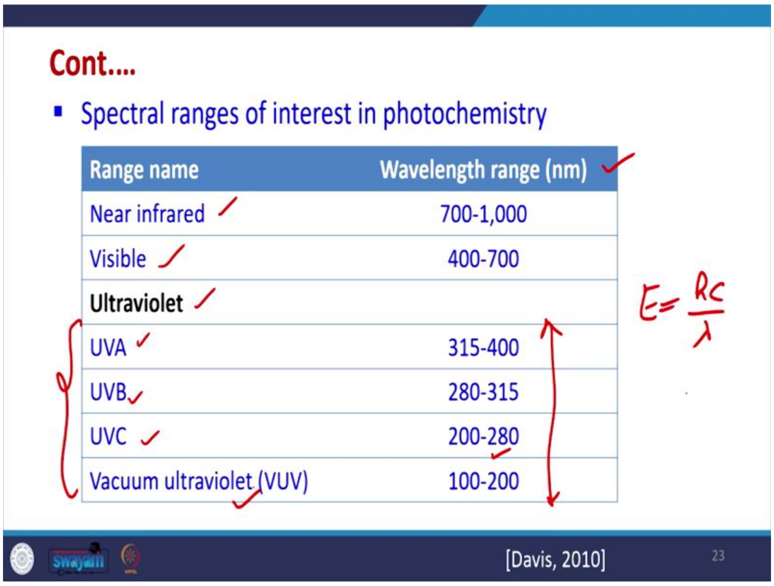

Now, the more energy is associated with a photon of electromagnetic radiation, the more dangerous it is to the living beings. So, if energy is high, so, it will distract everything, but it is dangerous to the living organisms. Light photons with the wavelength longer than 1000 nanometer have photon energy, which is very small enough to cause any chemical change when absorbed, but photons with wavelength less than 100 nanometer have so much energy that ionization and molecular disruption characteristics may happen.

So, this is possible and radiation chemistry conditions may prevail if we are using such ultraviolet radiation conditions. So, depending upon the type of pathogens, which are present in the water or in the air so depend different types of UVA, UVB, UVC lights are used or we can go to vacuum ultraviolet lights also for distracting or for disinfecting.

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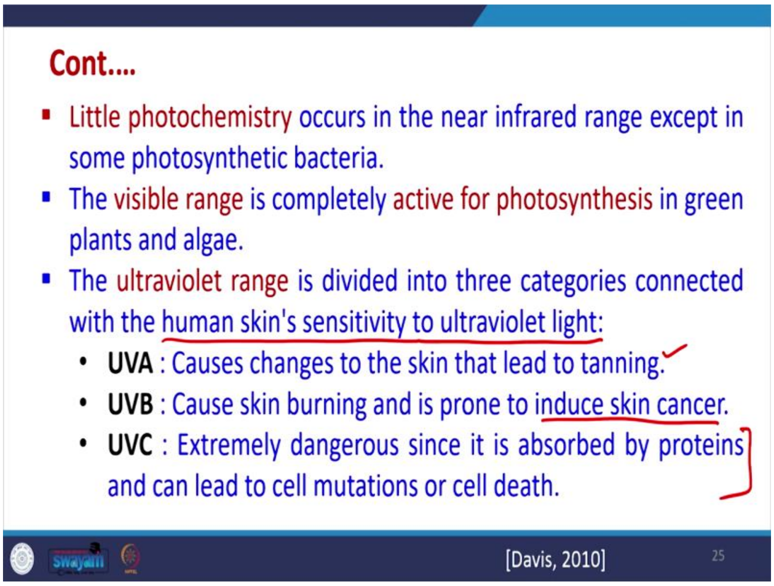

Now, little photochemistry occurs at the near infrared region except in the some photosynthesis bacteria the visible region is completely active of photosynthesis in the green plants and algae. The ultra violet train has been divided into three categories connected with the human skin's sensitivity to the ultraviolet light. So, this is called as UVA, UVB, UVC. Now, UVA has lesser energy as compared to UVC. Now, UVA if the this particular light is used, it will cause changes to the skin that may lead to tanning only. So, this is UVA.

Now, UVB it causes skin burning and is prone to induce the skin cancer. So, if UVB intensity is there, so, that means, if we are going to under that conditions a skin cancer may happen. Under UVC, extremely dangerous because it is absorbed by the proteins and can lead to cell mutations or cell death and instant a very quick skin cancer and that type of problems may happen. So, UVC has to be avoided in all conditions. And but, the same is though it is dangerous to us, but we can use the same technique for disinfecting on metallization, mineralizing various pathogens which are there in the water.

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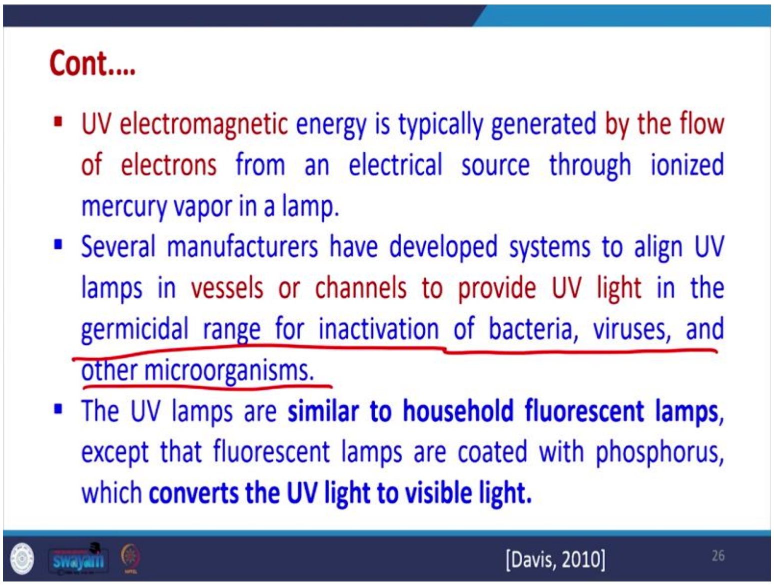

So, the UV electromagnetic energy is typically generated by the flow of electrons from an electrical surface through ionized mercury vapor in a lamp. Several manufacturers have already developed systems to align with UV lamps and in vessels or channels to provide UV light in the germicidal range of inactivation of bacteria, viruses and other microorganisms. The UV lamps are very similar to household fluorescent lamps that we use, except that fluorescent lamps are coated with phosphorus, which converts a UV light to visible light, but here they are not converting anything. So, we can use these lamps.

Now, when we are using these type of materials, so we can use them in the water in different way, the way we have studied in the advanced oxidation processes, they are very similar to advanced oxidation processes, and here we are oxidizing bacteria, viruses and other microorganisms. So, this way we understand that we can use the UV light, the only problem with UV light uses for disinfection is that the intensity of the light will decrease as the depth of the water increases. So, we have to see that the system should be properly designed. So, these are the hindrances which are there with respect to use of UV light for disinfection.

So, these some of these parameters already we have discussed previously for water treatment with respect to water treatment, how the photochemical or photo-oxidation? Why it cannot be used beyond a certain value? And what are the problems and associated research challenges which are there where people are working? So, today we have learned regarding the reaction of chlorine with ammonia in which different chloramines get form.

So, we learn regarding these and we came to know that there is a form which is called as combined chlorine the one in which chlorine combined with different ammonia or other nitrogenous compounds. So, they form different types of chlorine and they are called as combined chlorine. There is another free chlorine which is like HOCl or OCl minus ion. So, if they are there they are called as free chlorine.

Now, free chlorine and combined chlorine together all is called as total chlorine. Now, if any of the water contains any amount of nitrogenous compounds or ammonia, so, chlorine hypochlorite or any other chlorite will always react with that and some break-even point will be reached beyond which the reaction of chlorine with ammonia will stop and that ratio is typically 2 is to 1.

So, if suppose one molar ratio of nitrogenous compounds are present, so, we have to use twice of that chlorine and after that only free chlorine will be available for direct disinfection. So, this is the basic understanding we got, after that we studied a little bit of the redox reactions, and through that we have calculated, learn to calculate the oxidizing power of different chlorine compounds and through that we can compare different chlorine compounds with respect to their potential for oxidation.

So, this we have done, and in the last we have studied the ultraviolet radiation, how they are used and how they are generated in system, and in addition to that we studied the ozone system as well. So, we will continue with that disinfection with various types of these chemical compounds or using the ultraviolet radiation and the chemical in particular that disinfection kinetics we will study in the next lecture. So, thank you very much.