Course on Analytical Chemistry
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Module 7
Lecture No 35
Thermal Methods of Analysis – I (Contd.)

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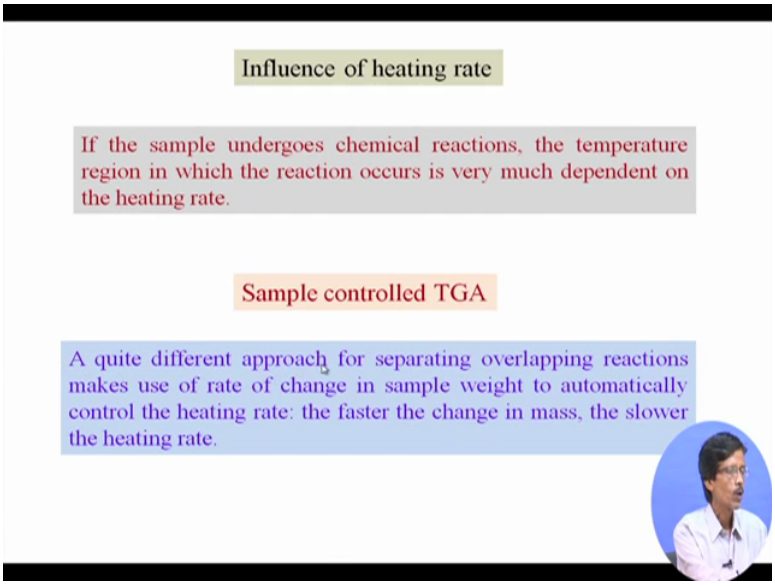

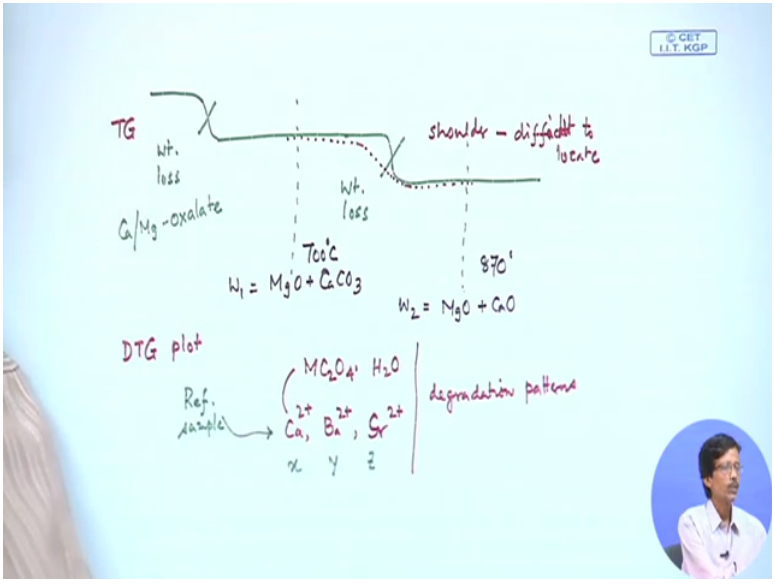

Hello and welcome back to the class where we are continuing about corresponding TG analysis and we have seen that we must have certain level of heating of the Crucible, so what we see that a particular type of heating rate you can have and what we see that a typical plot what we have seen in case of your oxalate it can be all different oxalates or mixture of oxalates like your corresponding calcium oxalate and the magnesium oxalate.

So we find that in a particular time when you have this particular slope of the corresponding interaction for a particular weight loss and this is also your weight loss and we get the corresponding temperature where this corresponding temperature you all know that if we have both a mixture of calcium and magnesium oxalate what we find from there is your corresponding one where we get that this will be decompose but at some point where this particular point we have the corresponding mixture of magnesium oxide and calcium carbonate because you know that at this temperature which is 700 degree centigrade and at the temperature of say 870 degree centigrade we will have a mixture of magnesium oxide plus calcium oxide.

So to get this very useful inflection point all these things because the weight of these things means if this is W1 and if this is W2, we can find out the individual content or individual contribution of the magnesium present in it or calcium present in it at one more important thing is that, that if we have this particular weight loss at this point it can be sometimes such that it is very basically a continuous one with some shoulder. So we have only the shoulder if it is a continuous one and it is a shoulder so it is a difficult one to locate, difficult to locate.

So it will be difficult to locate this particular point particularly the temperature so that is why from TG we go its DTG plot and we get all these information and not only this to magnesium and the calcium but sometimes we get a general compound of this type it can be a mixture with certain number of water crystallisation for different other oxalates like calcium oxalates or barium oxalate or strontium oxalate of these and their decomposition pattern or degradation pattern and sometimes what we do that if we do not know that this is unknown quantity of X, unknown quantity of why and unknown quantity of Z sometimes we can add some your sample of calcium oxalate because that is a good reference sample we always make that reference sample for the standardisation of the TG instruments TG DTA instruments.

So some we run the thing where unknown calcium, barium and strontium is there. Then in the 2nd run we add certain amount of calcium that will immediately tell you at what temperature the known calcium along with the unknown calcium will break or will decompose so that will give rise to the corresponding amount of calcium with reference to that of your added sample, then with respect to the corresponding calcium compound because we know that what amount of original sample we are thinking we can find out the barium amount or the strontium amount.

So these are the very good examples, only thing is that there are temperatures will be different depending upon their loss of whether they loss like that of your magnesium and calcium that carbon monoxide or carbon dioxide or altogether for this particular purpose. So the heating rate if we come back to the discussion of heating rate that influence of heating rate, how heating rate can change the nature of these plots and particularly we are interested to know about the corresponding lot where we find that is TG and DTG plots will be little bit different and we basically go for the corresponding pin pointing of the corresponding elimination of the material.

So if your sample undergoes a chemical reaction what we find that the temperature region in which the reaction occurs is very much dependent on the heating rate. Now we are bringing the rate of heating or the furnace because so far we are talking about is there will be a mass loss and that mass loss will correspond to any physical change and that physical change also can sometimes be co-related to your chemical degradation.

But in this particular case what we see now the effect of the corresponding heating rate and that give rise to something where a particular technique what we can consider as sample controlled TGA. What does it mean? Because the depending upon the corresponding nature of your amount of weight loss we see that if the weight loss is pretty more that means your corresponding step height is very high, so the rate of heating should be reduced so we should not have a very fast heating rate when the mass loss is more.

So is a quite different approach unlike your simple TGA for separating the overlapping reactions makes use of rate of change in sample weight to automatically control the heating rate. So if we can control automatically the heating rate that means instruments can take care nowadays everything is computer-controlled so depending upon the rate what we know for its corresponding mask loss we can also vary the corresponding heating rate of the instrument. So what we see that the faster the change in mass that means the corresponding step height is more, the slower should be the heating rate, we slow down the heating rate such that he slowly record the corresponding mask loss at that particular temperature.

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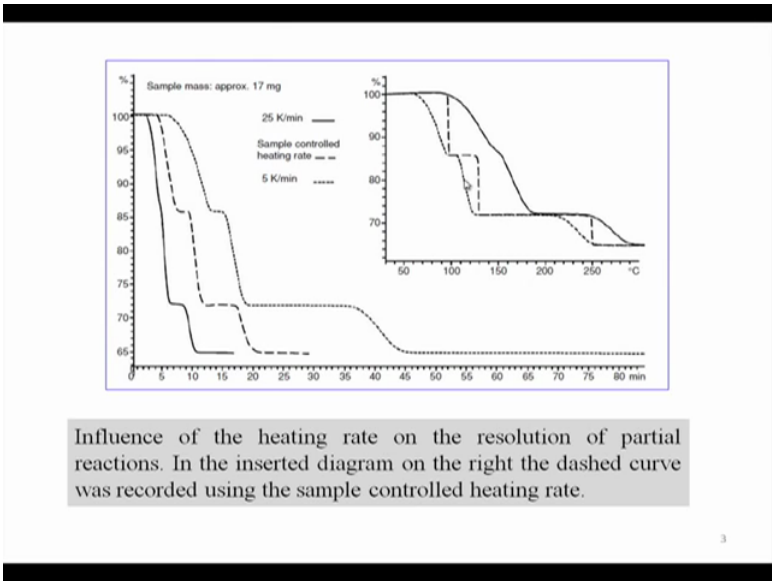

Influence of the heating rate on the resolution of partial reactions. In the inserted diagram on the right the dashed curve was recorded using the sample controlled heating rate.

So if this is the thing so we have we can see that what are the differences can have, so in the 1st case what we see that this particular thing has been plotted against the time not the temperature. So what we see that in a particular case that means in this particular sample what we have taken that we will see that what is that particular sample that heating rate for a sample of approximately 17 milligram only so in the range of again 15 milligram 15 to 20 milligram, so the amount of that heating rate for the solid line is 25K per minute to the slowest one is the corresponding dotted line and intermediate you have the (())(8:23) line so intermediate one is your (())(8:26) line.

So what we see that if we go from 25 kelvin per minute heating rate to 5 kelvin per minute heating rate we see the nature of this corresponding plot is different is not that the temperature is changing temperature of the decomposition is changing because in this particular case we are plotting against the time that means when the corresponding one is slow one we take more time to see the corresponding change or to observe the responding mass losses at these points.

So when the rate is very fast means the solid line you see we can finish the experiment within 17 minutes, so within 17 minutes we finish the whole experiment whereas in case of the 5 Kelvin per minute rate of heating is you can finish the corresponding one at 80 minutes. So it has some definitely have some advantage so how we get that particular type of advantage, so if we have this particular one and if we slowly co-relate these things in between something which is the dash line, so dash line is something which is known as sample controlled heating rate. Sample controlled heating rate, the sample will dictate what is your weight loss and

depending upon the amount of weight loss for the sample the heating rate should be variable and it will be controlled by the instruments.

So influence of the heating rate on the resolution of partial reactions, so if we see that if we change the heating rate so we will have the more resolve case of the corresponding reaction someone is also overlapping if we get that these 2 are overlapping we can find 2 different steps for this one but it is not there but we can have that particular one if we have some overlapping steps at a particular or very close space temperature. So what we have this inset, inset tells us that the diagram on the right is dashed curve was recorded using the sample controlled heating rate, so what we have, we have the corresponding one when we plot it in terms of the temperature because this was against time.

Now that can be plotted in terms of the corresponding degrees centigrade so the same temperature we should have but in one case where you get that where the rate is high that means the solid line which is 25 kelvin per minute, so now this is going like this. When it is with time it is the this plot, so this plot when plotted in terms of the corresponding temperature it will go like this so in both these 2 cases solid line is 25 Kelvin per minute rate so it is going like this and will finish by say around 25 degree centigrade. So at this particular point the maximum weight loss has been observed because it will be close to 60 percent or 65 percent of the weight loss is taking place and we are looking for these weight losses at these 2 points.

So what we see that this is for the solid line and the dotted line, where you have the slow steps that means the 5 Kelvin per minute we get these as the corresponding one but the advantage in these 2 cases are not clearly visible neither the solid line one nor the dotted line one because you do not have the very good steps for this point. Similarly we do not have a very good step for the 2nd one also but if we go for the technique why this is a special one which is known as the corresponding sample controlled heating for your TG analysis that when we recorded with sample controlled heating rate will be in between that neither the slowest one nor the highest fastest one, where we get that so when it reaches a particular temperature of the heating rate is such that which will be in between and your thing is that the heating rate is slowing down slowing down slowing down, so almost vertical step can get.

Similarly for the 2nd one is also like that for the 2nd one this particular one 2nd one is almost vertical down, so almost vertically down step we can have and also the 3rd one. So you see how clearly we get this point as a temperature which is very close to 95, 2nd one is also pretty

close to 140 and 3rd one is also the close to 250 degree centigrade. So these are the typical advantages of going for a sample controlled heating rate which basically changes the shape of these things, so how we can modify the shape of this plot the TG plot steps can be modified by simply changing the heating rate so that is the typical advantage of this particular technique and nowadays the automatic instruments can automatically take care of this thing to give you this particular data where we can change the corresponding temperature and the heating rate.

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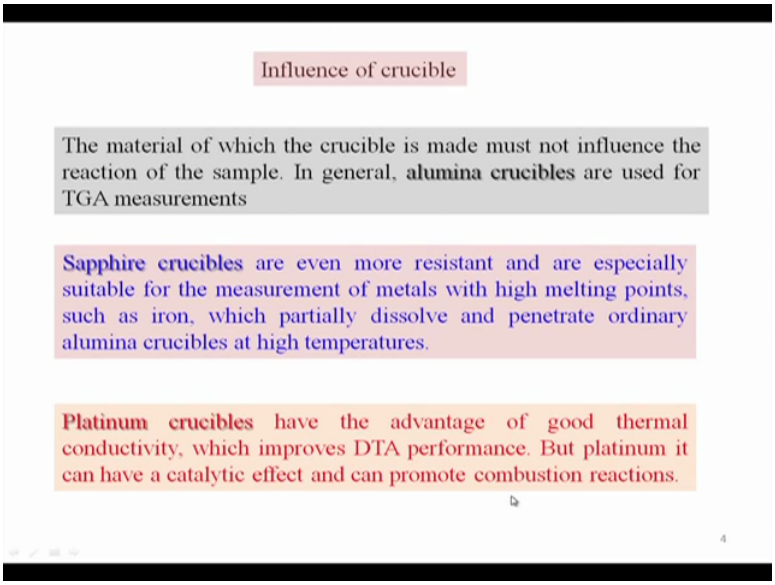

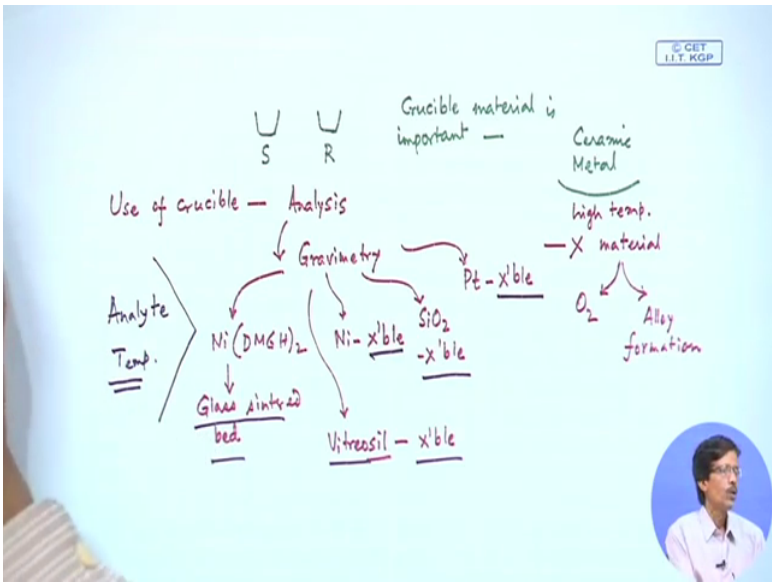

Now we will see what are the corresponding crucibles what we are using in within the furnace, so we have the very small crucible units one we have seen that we can use this as the sample and the side by is a reference one and both of them are within the furnace, so the

crucible material is important crucible material is important, why so? Because it can be some ceramic type of material, it can be metal containing material or some other material so this particular material can withstand a very high temperature and should not react with the material under investigation that means at a high temperature some materials we are using and sometimes in presence of air and oxygen we heat it.

But if the particular sample of that particular crucible and react with this material it can give you complex oxide or sometimes it can give rise to alloy formation. All these things you should avoid for this particular use of this crucible, so how we can change the corresponding nature of this crucible and the choice of those decibels. So what material we are analysing for your TG or DTG analysis is taken in the crucible and it should not influence the reaction of the sample that means it should not react with sample material at high temperature.

Most of the time we take AL2 O3 which is Alumina in one particular form we call…mostly it is alpha alumina because we know that there are beta alumina and the gamma alumina because the chemical compositions of those are all same, those are all AL2 O3 but the solid straight structure the solid straight nature are all different, so we call some alumina samples which can be your alpha alumina are used for your TG a measurements, so it can go up to a 1200 or 1300 degree centigrade temperature. Then you know that the sapphire is the material which is a very good material which can be naturally occurring or synthetically prepare we know sapphire is a gemstone also, so this particular material which is definitely costly one is even more resistant compared to your Alumina crucible.

So if there are some materials or some oxides which can react with Alumina, which may not react with your sapphire crucibles cause the use of this crucibles are also very important when we do simple analysis laboratory analysis such as in gravimetric analysis or in gravimetry that we have seen that in some cases where we are precipitating nickel DMGH we use a glass sintered bed containing crucible, then we can have some materials some fusion reaction we can do on some nickel crucible, so nickel crucible can also useful.

Then we can have silica crucible, then we can have another special quality of silica crucible because Sil is there because there is a vitreous silica is a vitreosil crucibles are there and also for some very sophisticated measurement we use platinum crucible, so you see for the very simple gravimetric estimation of some of these analyte or some of these samples, so depending upon the analyte what you take you have to choose accordingly the different types

of crucibles, so these are the different types of crucibles so all are different types of your crucibles.

Similarly for this thermogravimetric analysis where analyte is being heated at a high temperature, so it must be very much stable at that particular nature and the material what is being heated within that particular crucible should not react. So this sapphire goes in a high level than that of your Alumina and especially suitable for measurement of metals so when we go for metals particularly the metallurgies.

In the metallurgies engineering people, what they do they it do something what the see that ceramic formation the alloy formation or they are handling of all this metals and heating that particular thing at around 1000 degree centigrade, but we are the chemist what we do emotionally to some reactions starting from room temperature to boiling water temperature to boiling solvent temperature and sometimes we can do also some solid-state reaction on some sand (())(19:56) or some reaction on see any other furnace or sum muffle furnace which is giving you a temperature of 600 to 700 degree centigrade at when we use a typical metallurgic process metallurgical process ore extraction or mineral identification.

So we require some high melting point so such as iron such as we are treating something for iron to analysing something with iron or we are going for iron as the component for alloy formation, we should analyse the corresponding draft that means the TG curve or that DTG curve taking that particular iron sample in sapphire crucibles because which particular case they partially dissolved or penetrate ordinary Alumina crucibles at high temperatures because if we take iron, some amount of Alumina and being consumed that means after sometimes of use the Alumina crucible is will be corroded out and they sometimes they penetrate also these Alumina crucibles at high temperature because iron, if the material has not been made nicely because the surface texture and all these things are very important not reacting or the surface should be resistant to react with the iron sample.

So this is one form of crucible what we can use in reference to of your alumina crucibles. Then as we have seen just now in case of your gravimetric estimation what we can see the typical platinum crucible for some of the samples, so here also platinum crucibles can be used for a good thermal conductivity because it can past temperature very quickly which improves or your DTA performances, so next thing what we can discuss after going for all the DTG techniques, the DTA differential thermal analysis so in this differential thermal analysis the DTA performances in the card if we used the corresponding platinum crucibles.

So platinum can have a catalytic effect the same time we should also be careful if you monitor some reaction in that particular crucible at high temperature should not use that particular platinum because platinum surfaces are very much reactive and sometimes it is catalytically reactive also and sometimes it promote combustion reactions, because the gases what is forming can be degraded. So because we know that the catalytic converter the cars and all these things so when we round the corresponding internal combustion engines we burn the fuel or running the engine in the motor vehicles. So this particular combustion and give rise to the nitrogen oxides and platinum can also initiate some decomposition of those nitrogen oxides in terms of gases nitrogen and gashes oxygen, okay.

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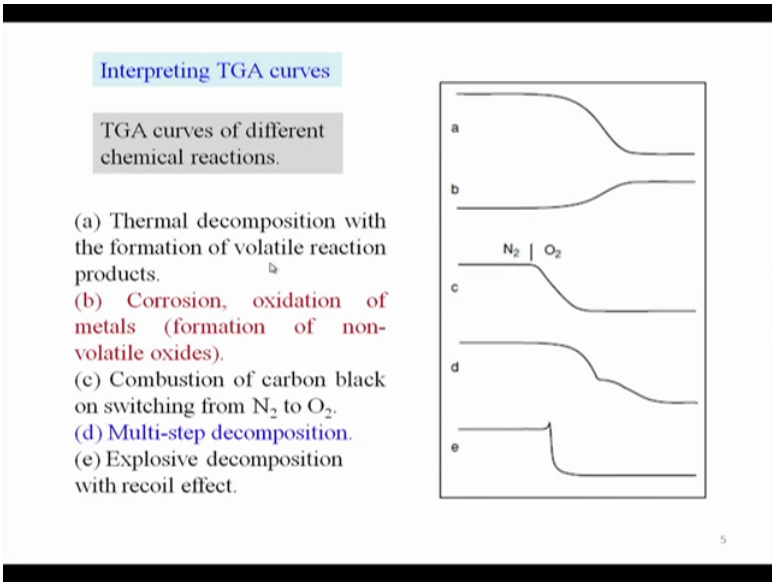

So this particular one that means taking the advantage of different types of these crucibles, how we can interpret the different types of TGA curves? Once we get the TGA curve then our challenge is that how we can read that particular TGA curve and what other data we can extract out or in the reverse way if we have the data only in our hand how we applaud those data for meaningful TGA curve or the DTG curve. So the TGA curve the simple thermogravimetric curve only and have different shapes depending upon its physical characteristics or physical change or sometimes for your chemical reactions.

So what are those chemical reactions we can see? That we can have different types of shapes, so basically what we can see that in one case you have a shape like this in another case you have shaped by the 2nd one or we can have the corresponding one that means the C, D and E. You see this all this things we are only looking at 2 axis one is the corresponding time or temperature axis and another one is your corresponding mass loss axis.

So if we consider that for one is for the mass loss so after some time at particular temperature we have a very monotonous or a monotonically decreasing mass and which is again stabilise after sometime and which is getting horizontal at some point but the 2nd one the B curve is completely different ages running in the opposite direction that means at some point of time at some time or some temperature your thing is gaining weight at means some reaction is happening where we should see the gain in weight so.

So not only the TG plot or the TGA plots are useful for mass loss, it can also monitor the corresponding mass gain for a particular type of chemical reaction what we can monitor. 3rd one is also with a vertical line on the left-hand side you have N2 and on the right-hand side we have the O2 that means what we can monitor is that on similar type of sample or the same sample we can monitor up to this point of temperature in an atmosphere of nitrogen because we have discussed in so many times at the environmental place some important role for all these thermal degradations.

So up to this point use nitrogen for your weight loss change so what we see that when you cave this as nitrogen we do not see any weight loss up to this temperature but when you change the temperature sorry the environment from N2 to O2 what change we see that immediately by moving the environment from N2 to O2, there is a immediate start of the corresponding weight loss, so weight loss in place till we reach is particular temperature where the material what is coming out due to this decomposition is stable even in your O2 environment.

D is a little bit pretty complex one where we have a immediate or a very sharp decrease then sudden some point of flat range that means horizontal line then again another decrease and the last one the E curve we have a kink that means a very small or a very brief gaining weight then a very sharp decrease and a very steep one like that of a typical staircase type of plot of this particular case. So slowly or one by one if we feel that the 1st one will be for your thermal decomposition with the formation of volatile reaction products.

That we already seen in different cases but if we give you this particular plot you should be able to tell what is happening over there and if the different options are giving you should be able to tell that this is or something that means this weight loss is there and why we say that the volatile reaction products because for a particular type of reaction in our previous class we have seen the decomposition of Mercurous chromate that mercurous oxide is forming which is volatile in nature so in this particular chemical action and what we find that in this

chemical reaction when some volatile matter is found in which is your mercurous oxide and that mercurous oxide will be removed from that particular material as a corresponding volatile sample and weight loss is due to a corresponding loss of your HG2O.

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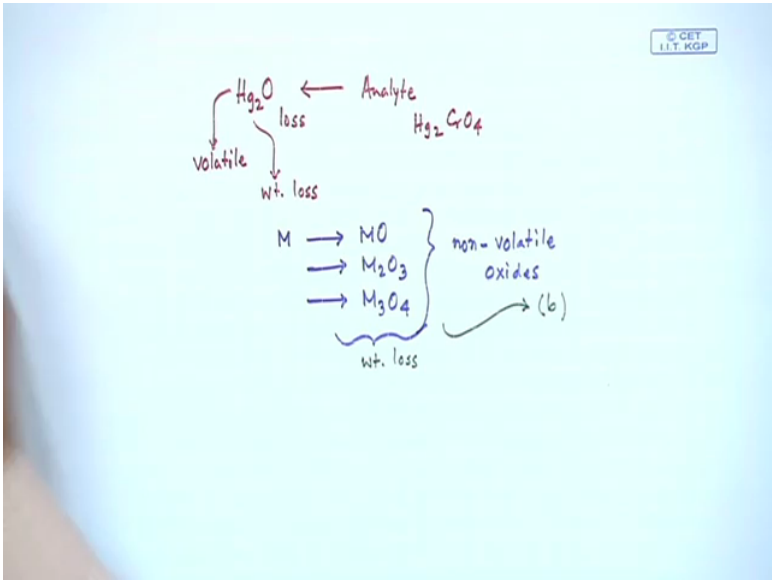

So we can monitor HG2O loss and one important thing we should also remember we should know as a typical knowledge that this sample is volatile and which is coming out from your analyte or the sample, so the corresponding weight loss is due to removal of HGO from the crucible and from the crucible is in the furnace and furnace is taking its corresponding weight either balance, so this is your corresponding weight loss so the volatility of one component of the sample is therefore important.

So one of the reaction products at means when we heat Mercurous chromate we see that Mercurous oxide is forming, so in solid-state that is why all these reactions are very important because sometimes we find that 2 components A and B can be reacted to give you a complex species and which can only take place on a solid mixture on say on sand bath, so sand bath has a particular temperature of 300 to 350 degree centigrade and that particular temperature you basically keep the corresponding reaction which is the corresponding complex formation reaction by solid-state fusion reaction but we should not have any of volatile component of that particular part of the complex which can go out from the medium.

2nd one what we have seen is a typically weight gain process after sometime that means after certain temperature so what we see it can be corrosion study, so metallurgist or metallurgist engineers do study the corrosion experiment on some sample at that particular sample

particular environmental or it getting corroded at some temperature because the temperature (())(29:56) corrosion can be studied for some sample say some iron (())(30:00) or iron sheet or iron slab.

Then oxidation of metals and due to that particular oxidation instead of getting this particular one what we have just seen as the volatile metal iron oxide, but if we see at this particular oxidation in presence of typical dioxygen or typical dioxygen which is present in air and be useful for the formation of some metal iron oxides and those metal iron oxides are nonvolatile in nature. If they are nonvolatile in nature so there will be some weight gain because something is forming that means oxidation so M will be converted to MO.

So this is forming from your HG2 CrO4. Now in another way what we see that if we have M, M is forming to MO or forming to M2 O3 or forming to M3 O4 and if all of them are nonvolatile oxides, what we find for all these we should get a weight loss and a curve like that of our b, so we get the corresponding curve b when we have a metal iron or the metal sheet or any other sample which can give rise to the corresponding oxidation of some oxide which is nonvolatile in nature.

Then C we have seen that 2 gaseous environment one is nitrogen environment and the other is your O2 environment so in case of see the combustion of carbon black you see that the combustion of carbon black when it is in the nitrogen environment all we know that the carbon black we produce because these carbon black is a very useful material, useful product.

Different companies are producing carbon black so it is a very active ingredient and mostly used for making different types of tires. To increase the responding thermal conductivity of these tires the automobile tires, so until and unless you have this particular O2 environment, so nitrogen environment is no such weight loss so when we move to oxygen environment in place of your nitrogen environment.

so immediately we will have the corresponding weight loss to the formation or corresponding degradation of all these carbon particles with your CO2 formation so this is a very useful technique for that. Then this one which one is very sharp one then another one is a very slow step and slow degradation step for the 2nd one which is due to your multistep decomposition action.

So this is the 1st step and the 2nd step should also be able to detect in terms of a very small horizontal line and which is the stability within this particular temperature range only then it

again start degrading and lastly why we get this particular kink is due to a explosive nature of the corresponding degradation process and this particular one is explosive decomposition with some recoil effect that will basically give rise to a shape which is known as the kink shape of this then it basically goes for your corresponding degradation process. So looking at all these different shapes and the curve for your TGA analysis should be able to at least comment on what sort of curve and what sort of plot we can have and what sort of degradation we can have for a particular type of analysis, okay. Thank you very much.