Course on Analytical Chemistry
Professor Debashis Ray
Department of Chemistry
Indian Institute of Technology Kharagpur
Module 7
Lecture No 34
Thermal Methods of Analysis – I (Contd.)

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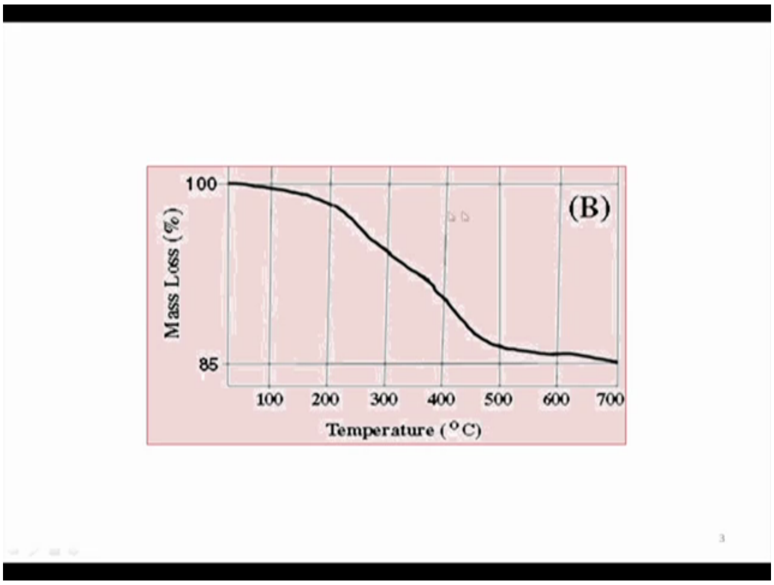

Hello welcome back, so we are discussing about the degradation process of calcium oxalate and we are thinking that how the corresponding weight loss can take place so this is a very simple plot of all these TG experiment you can have the corresponding samples only thing that you have to make the corresponding samples of calcium oxalate and put that particular sample in the instrument and nowadays the automatic instruments can record this particular type of plot where we find that as I told you in one of our previous classes that whatever amount of sample it can be 15 milligram or it can be 10 milligram sample of calcium oxalate so we go for the corresponding heating processed depending upon the crucible what you can have.

So the small crucible which can have the 15 milligram or the 10 milligram of sample is heated within the furnace but when you plot, the plot is the corresponding mass loss in percentage. So whatever amount of sample you take it is independent of the amount of sample whether in one single run you take 15 milligram of sample in another run you take 10 milligram of sample a when you divide the weight of the sample to this particular one of the scale goes to 100 so we can go for 100 so we start from the 100% of that particular sample and we keep on heating the sample.

So this is the furnace heating scale the temperature that heating rate of the sample if it is synchronised with time you can plot this that means X axis can be plotted in terms of the time also. So you see for a particular sample from room temperature to 100 to 200 to 300 to 400 to up to 700 and the nature of the sample is known by the typical trace of that particular sample so is basically very much characteristics of that particular sample. You do not find 2 samples can have exactly same thermogravimetric plot.

So the plot is very much characteristic for that particular sample and you see that up to 100 degree centigrade you have a negligible weight loss then 200 then 300 and all these things basically goes if we go for a 700 degree case but above 100 what we find what we have seen and we will again discuss about the corresponding one for calcium oxalate and magnesium oxalate, that in this particular case the typical staircase like plot we do not see because these are some real samples sometimes we get this for metal complexes, the polymeric samples or any other solid samples where you find that beyond 100 degree centigrade.

That means about 100 degree centigrade a monotonic change or monotonic decrease or the weight loss is monotonously going down and it is basically only the slope is changing so after 100 degree centigrade we get continues with laws of all these things till 500, after 500 it is again slowing down to till we reach 700. So during this whole period of process of heating from 100 degree to 700 degree centigrade what information we get from this particular type of plot is that the percentage of weight loss it is only 100 is going down to 85% so 15% weight loss till a very broad temperature range is a very high temperature range of 700 degree centigrade.

The material is no doubt is very stable material because 85% mass is still remaining at 700 degree centigrade that means the 15% of these that 15% can be your trapped solvent molecules, trapped water molecules or some water of crystallisation or some gaseous species like that of our carbon monoxide, carbon dioxide is or even if we heat some sulphate or the sulphur dioxide or sulphur trioxide can come out from that the color medium, so these gaseous samples of all these products can only contribute to the 15% to the actual weight of the sample which is undergoing the thermal degradation process.

So until and unless you have a very discreet and very good horizontal lines not say that the sample as stable till 100 degree centigrade at least here we can say that is sample is little bit stable means it is 1% or less than 1% loss till 100 degree centigrade that is stable till 100 degree and it is more or less stable at this particular weight loss or must change is between

600 to 700 degree centigrade, so between 600 and 700 degree centigrade because it is a is a quite a bit wide range of temperatures, so if we want to dry the sample at this particular temperature range of 600 to 700 degree centigrade what we find that the sample corresponding to this mass loss and the remaining sample what we can have we must have a formulation for that and we can say that sample stable in that formulation within this particular temperature range.

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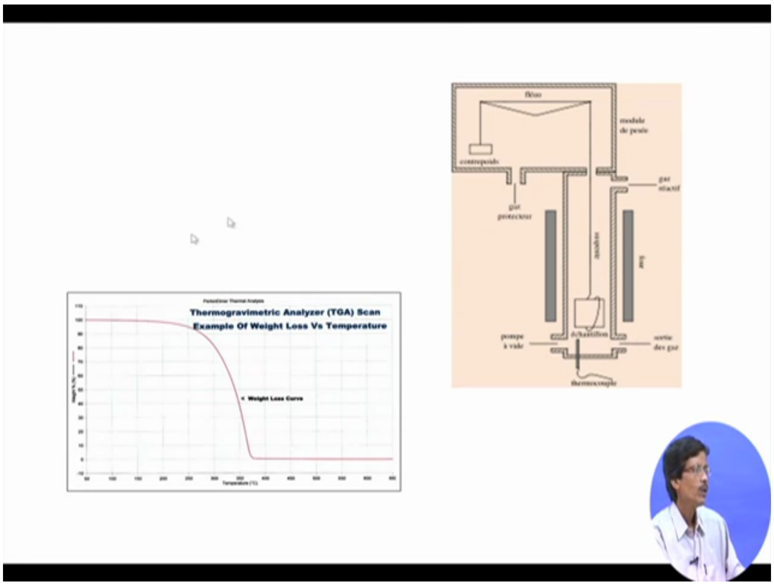

So what particular instrument we can use to record this particular thermogravimetric plot that we will see and in our 1st 2 classes what we have discussed is that, that we can have a thermobalance what K Honda introduced the 1st and historically important thermobalance and these all will only the corresponding extension of these things, so this is the thing that means we will have the corresponding beam, the corresponding balance beam and this balance beam is there at one hand you have corresponding weight and the sample is going inside and this particular sample is kept within a corresponding furnace and furnace is basically (())(6:46) heated, so this particular arrangement and in the sample inside the furnace will be useful for recording your corresponding thermogravimetric trace.

So just now what we have seen it is another one which is a typical example again percentage starting from 100, so it is thermogravimetric analyzer or the analysis basically it is the analysis, so analyser the instrument what is doing the particular analysis is the corresponding analyser but is the analysis is TGA analysis thermogravimetric analysis plot and weight loss versus temperature plot is like this so you are also not very discreet or very sharp staircase like of arrangement but from year basically we can have a again some continuous weight loss curve we see but at this particular temperature which is 350 degree centigrade beyond that is 375 degree centigrade or if we consider at 400 degree centigrade, 400, 500, 600 and 650 degree centigrade so from 400 to 650 degree centigrade we do not see any weight change over there.

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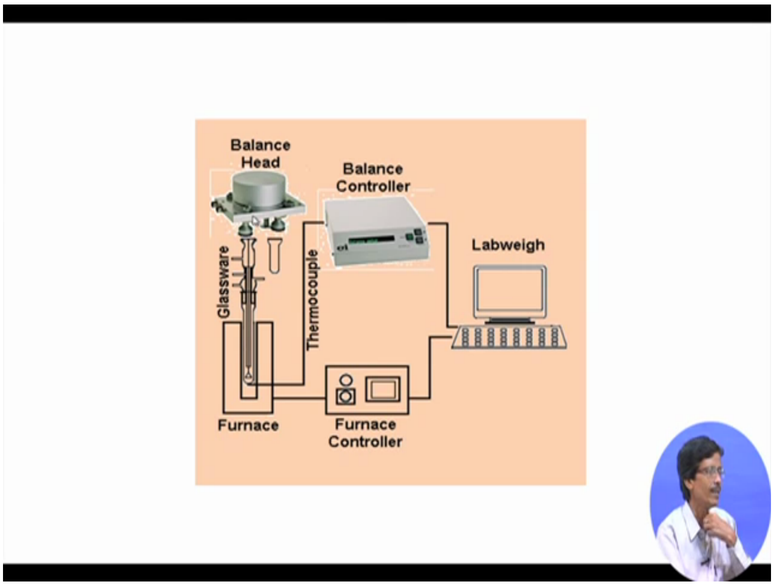

So we use the instrument would get the particular plot and how we analyse this particular plot we use that a board advanced one that means the instruments which is coupled with that of your balance head. So we have the balance had then the coupled with this glass wires and all these things and we have the sense that means a temperature sensing unit means what particular temperature is being sense by the sample itself, so we have the thermocouple and this particular one is a controlling unit which can control not only the temperature also the weight in their balance.

So this furnace controller and this is the balance controller so this thermal controller to control the balance unit and the furnace controller and balance the responding controlling of the corresponding temperature rise and when these 2 are connected we go for a corresponding (())(8:55) thing. So the information of the data what we get from this particular one is recorded and is ultimately plotted in the form of the corresponding TG thermogram what we can analyse nicely another different type of thermogram.

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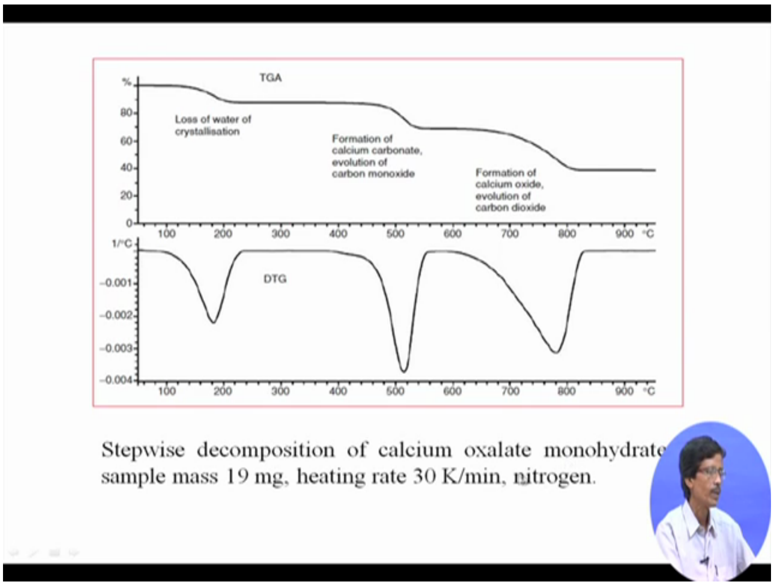

So one such thing is like this so what we have seen so far is the corresponding calcium oxalate monohydrate sample size is also known, sample size is if we take 90 milligram of the sample and heating rate is also 30 K/minute and in nitrogen atmosphere. So in the nitrogen atmosphere what we find just now what we are discussing about the same sample and the apparent is what we use for thermogravimetric analysis means the TGA trace can also be coupled with the corresponding derivative one or it is nothing but the corresponding one is that simply you plot the corresponding derivative one means the derivative of the corresponding mass change with respect to the corresponding temperature.

So this one basically we go for this corresponding change will be give you a corresponding derivative plot, so derivative plot have some good correlation with the TG plot. So as we have seen in soft calcium oxalate a weight loss of water of crystallisation so this is the 1st step we get that is a weight loss of corresponding water of crystallisation which will be around 200 so it is stable up to 200 degree centigrade.

Than what we see that at the particular temperature of 500 degree or so we can have the corresponding formation of calcium carbonate with the evolution of carbon monoxide, so evolution of carbon monoxide is not is not exactly 500 but it is less than 500, so the formation of calcium carbonate and evolution of carbon monoxide and what we are talking about so far that is very important and 2 things we are discussing that you heat the sample or any other sample any other analyte can go for either you created in air or oxygen or you heat it in nitrogen.

So in the atmosphere is nitrogen that is why when we are discussing the sample characteristics as well as the environment of the sample because all these cases are very important cases for a high-temperature reaction because all these thermal conversions are taking place at a very high temperature and in some cases gases are coming out and some inert gases like nitrogen or any other that means argon the sample at that particular high-temperature should not react with this nitrogen because if we need that and we all know that the metallic calcium or any other thing if you heat at a particular temperature it can also give you the corresponding calcium nitrites.

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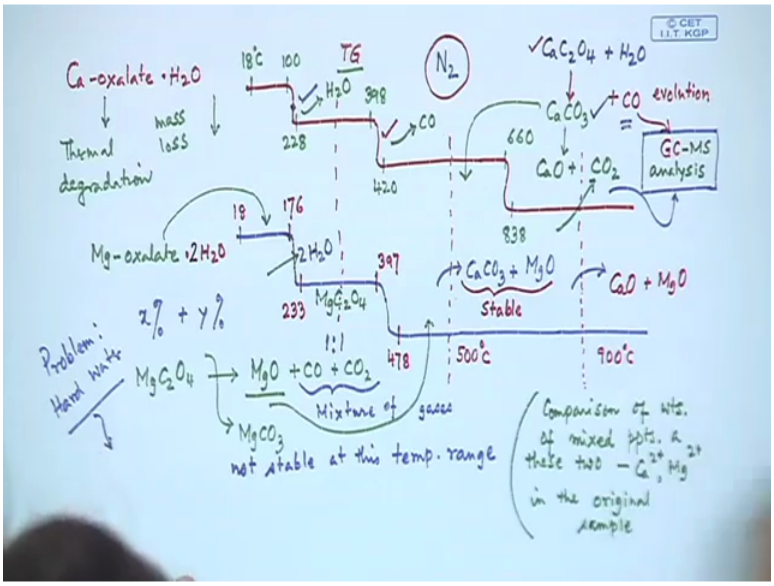

So we should be careful about all these formation that mean the reaction with that of your nitrogen so in nitrogen atmosphere that means in inert atmosphere this particular calcium oxalate what we have and we give it in some inert atmosphere and what we expect over there that you have the corresponding calcium oxalate monohydrate, then monohydrate is giving rise to simple CA C2 04 that means they are dehydrated one plus water. So this is the thing that means at this particular temperature range and if that is a very sharp one, so at this particular temperature we can try the sample we get this as the corresponding one of anhydrous calcium oxalate.

Then what we get that at nitrogen atmosphere no water no sorry no air present and no dioxygen is present so this particular one in some inert atmosphere that means it is neither in oxidising environment nor in some reducing environment, but at this point when we have the anhydrous calcium oxalate which is stable in this particular range of 228 to 298 but above 298 when we hit it what we get at this particular temperature range of 398 to 420 degree centigrade this particular one will decompose in a state which can give rise to the elimination of carbon monoxide. So carbon monoxide evolution can take place over here and in some of our future class we time permits we will discuss the corresponding gas analysis of this processes.

So if some suitable technique is available that means the corresponding chromatographic separation if you can do then the gas chromatography we can do on the sample and if it is attached with some mass spectrometric analysis, so we can go for GC-MS analysis for these gases which is coming out from the sample. So which is very important information that some part on which is also not very useful gas is a carbon monoxide which is coming out from this calcium oxalate and we get the remaining one as your calcium carbonate.

So here we have this that means your calcium oxalate anhydrous calcium oxalate is slowly decomposing to calcium carbonate and at this point or carbon monoxide evolution is taking place. At this point water vapor was coming out and we have the stable calcium carbonate at this point. So within this temperature range of 420 to 660 degree centigrade we have stable calcium carbonate and if possible we can analyse this for your CO.

Then in the last step this is getting degraded so calcium carbonate in a straight way is getting degraded to calcium oxide plus carbon dioxide. So now this gas is coming out in this particular step of a temperature range which is how 838 degree centigrade. so about 838 degree centigrade what we see what we find is beyond stability of your only calcium oxalate so this particular metal iron carbonate like other metal iron carbonate we can have magnesium carbonate, we can have barium carbonate, we can have strontium carbonate because all these are also very useful samples for the standardisation of the thermogravimetric analysers.

So you are also again what we find that there is CO2 can also be analysed by GC-MS analysis, so identification or the scope is there identifiable carbon monoxide in one step and carbon dioxide in any other step. So anything any biological process or any other thing where gas is coming out from the sample you can analyse those gases and the remaining sample or the solid what we can have, we can analyse. So the furnace what is heating is going for the corresponding conversion but the balance what is present this thermogravimetric analyser is that they are taking the weight in one case it is the weight of this or the weight of dehydrated form so hydrated form your sample A, this is sample B, this is sample C and this is your sample D.

So that is a very useful and a very good example of the conversion of a calcium bearing compound one from A to B, B to C and C to D. So what will happen now to migration oxalate dihydrate? So this is the corresponding now once you know this for calcium oxalate very minutely or very useful way. Now what we can see that in case of this particular sample what we find over here for magnesium oxalate immediately you know that the elimination of these 2 water molecules, so 2 H2O will be eliminated at this particular step.

So this particular step is therefore giving rise to the elimination of 2 water molecules, so the corresponding magnesium will be forming over here so this is the step where the magnesium oxalate stable from 233 degree centigrade to 397 degree centigrade, so this is our magnesium oxalate MG C2 O4 which is anhydrous. This is your dihydrate than water losses taking place, this is your anhydrous form, then anhydrous form is going to something like this but what happens depending upon its different nature that means the magnesium iron is different.

So what thermal reaction what we can write is MG C2 O4 which is anhydrous one which has been formed from the elimination of 2 water molecules are so the previous information we can have in our knowledge is that we can give rise to something which is a separate state for the carbon monoxide evaluation and in another case it is evolution of carbon dioxide but in this particular case straight away this magnesium oxalate is giving rise to magnesium oxide that means here we do not have the corresponding presence of magnesium carbonate because the magnesium carbonate not be that much stable this particular temperature range which is above 397 degree centigrade. So 397 degree centigrade is such a high-temperature and at that particular temperature we see that you or magnesium oxalate is stable.

So at this particular temperature so we can have like this or calcium oxalate thing at and can have a separate state that means one more state where magnesium carbonate should be stable at this is not happening so this is not stable at this temperature range. So what we see and what we get is that the magnesium oxide plus carbon monoxide plus carbon dioxide, so in a single step this is solid residue what we will have in this particular whole range of this particular stability starting from 478 degree centigrade so we have the solid residue.

So this solid residue will be here and these 2 gases so mixture of gases now. The situation is getting little bit complicated so we have the mixture of gases will come out are so there also we can apply same technique of this particular GC-MS analysis because we gas chromatography, the terminology for chromatographic analysis is we all know that the chromatographic technique is a separation technique.

So is a gas chromatography technique is the corresponding separation technique of the mixture of different gases, so initially it separates or the corresponding distribution of the different gases you can have, then the mass spectrometric analysis we can do on the amount of gas, so if we have the mixture of gases also that can be injected in the GC-MS instrument, so that can initially separate into these 2 gases that can find the corresponding amount of carbon monoxide and carbon dioxide and what interesting information why you can get from their is that a mixture of gas which is in the ratio of one is to one.

So one is to one mixture of carbon monoxide and carbon dioxide is coming out due to the instability of magnesium carbonate at this particular temperature range is a very useful information for the analysis of both calcium oxalate and magnesium oxalate and this particular stability of this temperature ranges if we find that at this particular 500 degree centigrade so when the temperature is 500 degree centigrade, so at this particular temperature so at 500 degree centigrade here and at 900 degree centigrade if we do the thing that means if we have a mixture of these 2 since magnesium carbonate is not formed over there is not stable at this temperature range.

So if we have a mixture of calcium oxalate and magnesium oxalate which is our original problem because our problem what was there is your hard water and that particular hard water can have both calcium as well as magnesium in your thing that when we have this hard water so it precipitated out these 2 as the magnesium and the calcium but now solely what we can do we can analyse these 2 compounds that the presence of both calcium and magnesium only thing that what we can have the X percentage of calcium oxalate plus Y percentage of magnesium carbonate.

We have to find out from there depending upon the corresponding particular formula and the molecule weight of the sample what we weight out in the balance for the normal gravimetric analysis you can find out the percentage of calcium and the percentage of magnesium present in the sample of your hard water. So what we find over there is a very simple information that if we have a mixture and if we see the mixture without going into all these thing that means all these detail analysis and all these detail identification and characteristics of the sample what we find that this particular one that means at 500 degree centigrade free heat this mixture of this to oxalate we get that at 500 degree centigrade because we have seen that here it is the calcium carbonate.

So only calcium we will take get the weight of calcium carbonate and magnesium oxalate because these 2 are stable at this particular temperature. So this calcium carbonate and magnesium oxide are stable at this temperature and if we take the weight that means whatever precipitate you got, you heat it at 500 degree centigrade in some oven and you take the weight, what do you expect?

This particular knowledge or this particular information must have active ad step range here you will only get the weight of calcium carbonate and weight of magnesium oxide and to check the particular percentage terms of the amount of magnesium and calcium present in the hard water, we take the another help of heating the sample at 900 degree centigrade. So heating that particular sample at 900 degree centigrade is also give rise to another information because both of them can exist in simple oxide that means as she will be present as calcium oxide as well as your magnesium will be present as magnesium oxide.

So this give rise to the immediate information and from the analysis of the amount of calcium oxide and the magnesium oxide of all these things and the comparison of the weights of the mix precipitating, so if we go for comparison of weights of mixed precipitates at these 2 temperatures that means 500 degree centigrade and 900 degree centigrade at those 2 temperatures will permit to determine the content of both that means a calcium 2 plus as well as magnesium 2 plus content in the original sample.

So this is the real example of your analytical technique but we can use to determine calcium 2 plus and magnesium 2 plus in the sample of analysis where we get this for you analysis that by heating the sample to 500 degree centigrade and by heating the sample to 900 degree centigrade only is the amount of calcium and magnesium strength in our original sample that means the sample which is present in our hard water.

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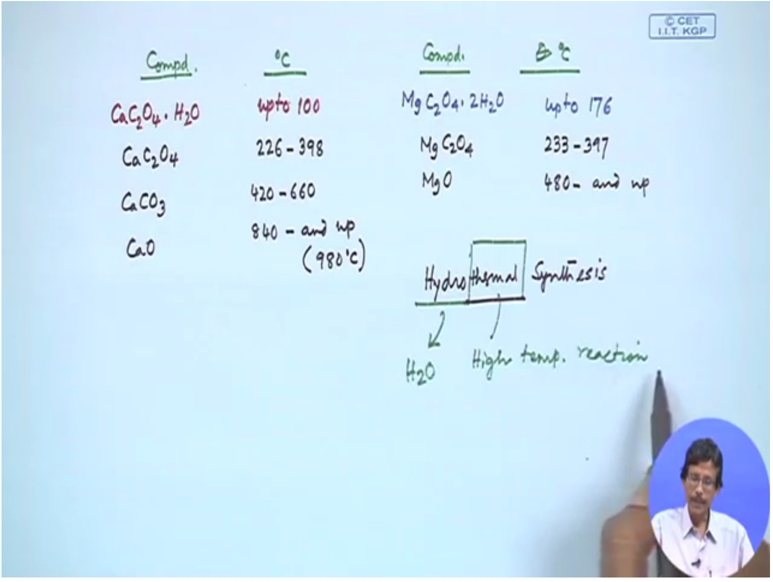

So that hard water sample handling is a very important thing and the nature of these plots are also very much important because once we have this information or the different species that their Thermal stability so any compound you can have and the temperature we can write, this can be your useful drying temperature for the precipitate like that of your magnesia oxalate, calcium oxalate or nickel DNG or aluminium oxalate, so here we have from the plot what we can extract as data that you have the calcium oxalate monohydrate stable up to 100 degree centigrade. Similarly if we have on the right hand side if we think like that other compound degree centigrade.

So other compound is your magnesium oxalate dihydrate now which is stable more stable up to 176 degree centigrade, so if we just compare these so thermal stability of these 2 species you can compare by knowing the temperature of these 2 and we have the degradation that means we get the anhydrous calcium oxalate what is going out which is within the range of 226 to 398. Similarly anhydrous magnesium oxalate is also stable within the range of 233 to 397 degree centigrade.

So what we find then a degradation of this and degradation of this is different so you have calcium carbonate in your hand which is stable in the range of 422 to 660 degree centigrade, so this also give rise to another horizontal space but which is 480 little bit higher because you see most of the time your temperature range for the magnesium is little bit higher at this particular one is 850 is basically the temperature where we do not get the calcium carbonate but we immediately go for the corresponding magnesium oxalate or oxide.

So the formation of this magnesium oxide which takes place at 480 degree centigrade so and up that means and above, but where this particular calcium carbonate is stable so you do not get the corresponding automation of magnesium carbonate over here, so for calcium oxide formation which is taking place at 480 and up say up to 980 degree centigrade. So these particular so these are all the corresponding data if we do not have the corresponding plot as the thermogram.

So we should know the corresponding analysis this way and you see that not only a single compound which is undergoing the corresponding thermal degradation but it is transforming some useful species which is also a very useful technique or the thermal analysis and sometimes we go for some technique where thermally we can go for some synthesis, synthesis of some new compound, synthesis of some catalyst which basically a useful technique nowadays the researchers are also using which is known as hydrothermal synthesis just name you just know it that since we have this process of thermal thing so thermal thing is there then hydro is your water.

So what we know any chemical reaction we can do or perform in making a sample of 2 analyte A and B which independently we can analyse for it their content but if we mix this together then we can just simply makes and star it magnetically we get a new compound C with along with some other by product D but if you go for heating at a very high temperature in a closed vessel, so this will give rise to some information about high temperature reaction what you can have.

At this high temperature reaction can give rise to the immediately that in solution of corresponding degradation pattern and all these things and the reactivity pattern will be different if we simply heat the compound like making the thing for the industrially important compound like cement formation or the cement products or these cement synthesis in a industry that several oxides carbonates and some useful materials which can be heated to a high temperature. So if we get some time in our future classes sometime particularly during the application service will find that how useful this reactions or this thermal reactivated compound formation is useful or synthesis of new and useful compounds. Thank you very much.