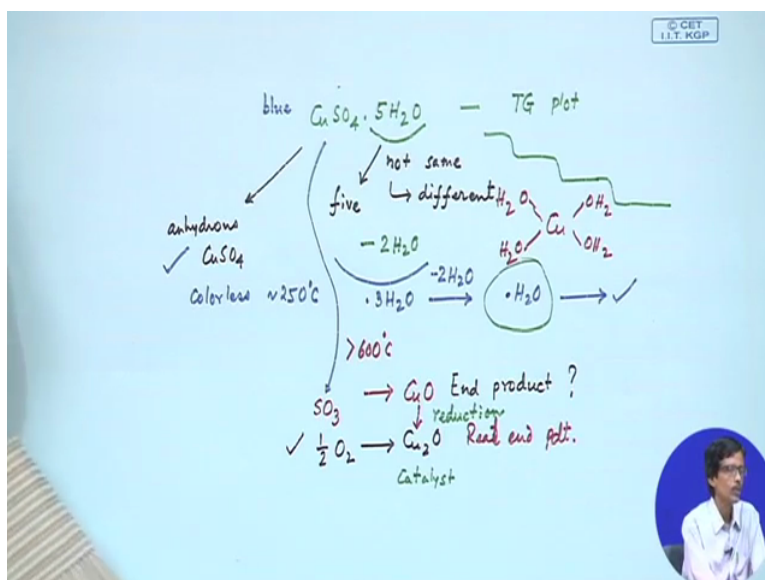


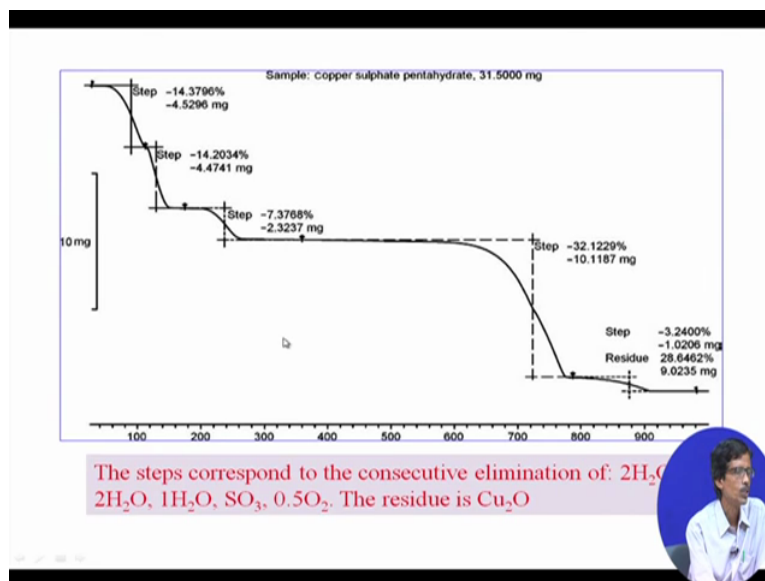
Course on Analytical Chemistry
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Department of Chemistry
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Module 8
Lecture No 37
Thermal Methods of Analysis – II (Contd.)

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Hello, welcome back to this class where we are discussing about corresponding thermal degradation of a very simple salt what we know and what we used from our school days which is your copper sulphate pentahydrate and we want to see the corresponding plot that means TG plot we want to see. So if we know nicely this particular TG plot and if you can analyse this thing very correctly you should be able to a mass loss characteristics like this what we have seen most of the time we draw like this and is a very simple one as we have seen in case of and we have analysed that for also your calcium oxalate and your magnesium oxalate sample.

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So what we have seen that we have the different steps and these steps are for corresponding elimination of the different number of your water molecules, so if we have this particular copper sulphate pentahydrate so what we find that we have step number 1, step number 2, step number 3, step number 4 and step number 5 so 1, 2, 3, 4, 5 so what is the corresponding steps so if your sample is very pure and if we go for the corresponding elimination in this fashion that means when the temperature is just about 100, so it is just above 100 so you have this corresponding 120 then 40 then 60, 80 and 120 degree centigrade.

So when we have this particular one that means when you have just 100 degree or 120 degree centigrade we get the corresponding first weight loss and so we have the corresponding weight losses and these weight losses are such that we can have 2 equal steps that means you have this that means you have this particular 1st step is that that you have initially we just go for loss of 2 water molecules, so 1st will correspond to the 2 water molecules so what we should know now for these particular information that in a step wise manner your all the 6 things that means you have 5 water molecules as we have seen that you have 5 but all these 5 water molecules are not same that means they are entrapment within the crystal lattice is different.

So that connectivity within the solid lattice is different so that is why all 5 are not going away immediately at a particular temperature and also it is not of your typical lattice water what we know that the dehydrated sample because what you expect at if we go like this like your calcium oxalate or magnesium oxalate means if we go for as typical anhydrous copper

sulphate so at some point we should (3:40) if all 5 water molecules are eliminated in a single step we should go for the corresponding one as your copper sulphate pentahydrate species but the 1st step we have the corresponding loss of 2 water molecules so what we get at that particular point and if there is a good baseline but we do not have that baseline good baseline that means the stability of that particular step is very less that means the stability of the corresponding species what is formed over there, what is there?

Which is nothing but after removal of the 2 water molecules we remain with only copper sulphate trihydrate, so this water sulphate trihydrate has not much stability, so it immediately go for its loss again or another 2 water molecules so these 2 are almost consecutive but at 2 different temperatures so this is being completed. So is starting from say around in the so it is starting basically the loss is starting around 80 degree centigrade and it is basically lead at 120 or 140 degree centigrade where 4 of the water molecules are going away and dose loss of 4 water molecules is also correspond to a loss of minus 14.3796% and minus 14.2034%, so is a 14% of loss in these 2 steps will correspond to this particular that means by weight it is 4.5296 and 4.4741 milligram.

So these 2 are you are losing then what we get you have the corresponding one for your loss that means the next step, the next step will definitely be your corresponding percentage in terms of half of the same. So if 1st one is 14% 2nd one is 14% the 3rd one will be 7%, so you have in the 1st step the 14% weight loss then the another 14% weight loss so what we get at this step we monohydrate copper sulphate monohydrate then you have the anhydrous copper sulphate, so at this point when you reach here we get the corresponding anhydrous copper sulphate and this anhydrous copper sulphate what we get basically about 250 degree centigrade.

So if we want to make a sample of copper sulphate which is anhydrous in nature because it is blue in color this particular in the solid state also but anhydrous thing of this copper sulphate is colourless so which we get around 250 degree centigrade so at 250 degree centigrade what we get as the colourless copper sulphate which can be considered as a anhydrous one. So if we take this anhydrous copper sulphate and keep in again in in some moist environment or in a moisture containing some an environment of air it will again trap was water molecules and will again go back to your pentahydrate sample.

So what we see now the stability of this copper sulphate that means anhydrous copper sulphate which is not so easy to get because in most other cases I cure anhydrous calcium

oxalate or anhydrous magnesium oxalate most of the time we get that around 140 or 150 degree centigrade we get the anhydrous one but here we have to reach around 180 degree to lose for water molecules and to get typically anhydrous one which is above 260 degree centigrade, so only above 260 degree centigrade we get the corresponding anhydrous copper sulphate sample and this anhydrous copper sulphate sample is pretty stable this temperature to say about 600 degree centigrade. So till 600 degree centigrade you do not see any loss of mass from the copper sulphate sample but when we heat the sample at 600 degree centigrade we see a little bit of monotonous weight degrees from here and which is little bit broad also and we go up to say 780 degree centigrade so this is your 780 degree centigrade.

So till 780 degree centigrade we have some reasonable mass loss which is corresponding to 32% of the weight what has been taken and in terms of milligrams it is 10 point some amount 10.1187 milligram of weight loss almost $\frac{1}{3}^{\text{rd}}$ of the sample what we have taken for the measurement. So this particular one if we co-relate nicely with that of our sample and we have seen that we have SO_4^{2-} as $(\text{O})_8(36)$ but when we go for the solid State heating so this solid State heating of the sample of this copper sulphate pentahydrate basically giving us the loss of SO_3 .

Now SO_3 will be losing from here as we have seen in one of our previous example of your ferrous sulphate heating that is SO_3 is the most useful component what we get that means sulphur dioxide elimination from all sulphate samples are very easy particularly at a very high temperature which is above 600 degree centigrade. So if we get that means this is the case of loss of this SO_3 then once we get SO_3 loss from their copper sulphate we immediately think of that, okay this SO_3 is going out from one copper so we must have copper oxide over there. So end product can be your simple copper oxide in your hand but is not like that, so what is your end product for this particular type of thermal degradation.

So whether cupric oxide will be your end product or not, so we keep on heating the sample from your this 68 780 degree centigrade because it started from 582 to 680 this span basically over 200 degree centigrade so throughout this 200 degree temperature rise your is SO_3 elimination is complete. So if we go beyond that temperature so around 900 that means around (80) 80 degree centigrade there is a very small weight loss which is roughly about 3%. So 3% weight loss and the amount is also only 1 milligram in the range and then the amount what is remaining at their at 1000 degree centigrade we can go relate that, that what

is the remaining sample. By looking at the weight left on the pan, what is they have taken for the heating?

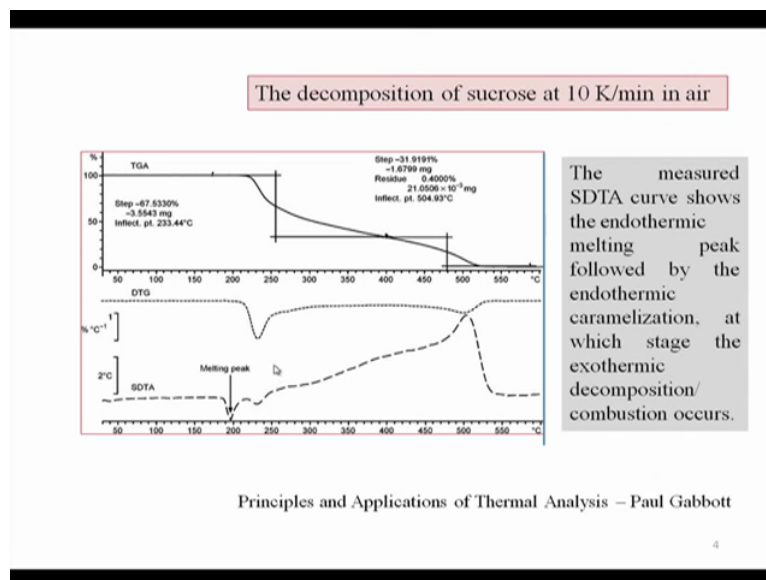
So the weight of that particular thing that means the empty and weight and the residue of the sample what is formed over there by this particular heating process will tell us the residue weight is 9.0235 milligrams corresponding a percentage of around 28% are stop so that 28% weight remaining as residue on the visible is not due to your CuO but is due to your Cu₂O that means is during this particular heating process the sample has (in) inherent tendency to give you the corresponding form as the cuprous oxide and this Cu₂O basically going for itself reduction process with the elimination of half of the oxygen, so if we consider so that particular step can also be very nicely detected in this particular plot and O₂ elimination from CuO if it is formed as a very (O)(11:56) species because we are unable to detect formation of CuO as the end product of heating of copper sulphate pentahydrate.

So it is your Cu₂O which is your real end product what we get from this particular heating process so this real end product, so this real and product is going for so the conversion means this conversion from cupric oxide to cuprous oxide is basically a reduction process so at high temperature we go for this typical reduction, so no reducing agent is require it is only the elimination of O₂ gas. O₂ itself is going out from your sample giving rise to your Cu₂O because this particular Cu₂O is also a very good and useful species it can be a catalyst also.

So from copper sulphate pentahydrate we know all the different steps and we can also some good idea how this particular one means how this particular one that means the monohydrate has some stability and this monohydrate can be prepared also and this monohydrate is water binding is completely different with the involvement of the sulphate so that is why we get this particular one that means this water molecule is completely different from that of the 4 other copper which is present and which is going away from this.

So what we can consider that we know that the copper is a typical coordination number of 4 so if 4 of them are of same type we put for water molecules around this copper which are of one type so we put this as a one type water molecule over there. Then we have to put and we put it also that another water molecule and the sulphate anion and which are also entangled with the sulphate that means some close association of this water molecule with that of your sulphate will give rise to the extra stability to the particular water which is lost in the third step. So this gives us a very good idea about the corresponding thermogravimetric analysis or identification as well as the characterisation of sample which is well known to us.

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So any other sample such as your food materials also be very nicely analysed this this particular technique so the decomposition of your sucrose sample, so the decomposition of your sucrose sample at 10 kelvin per minute and air will give rise to a plot like this. So your TGA plots will see or say that it is basically stable till 220 degree centigrade where we have so the sucrose can be dried enough for this particular one case. So and beyond that have a continuous mass loss for a typical weight loss of this thing and we can have a corresponding residue after this complete burning.

So you have this that means this particular part we can separate out with these 2 horizontal lines we can extend so this is one horizontal line so but you have the basically this sort of inflection point actual plot is like that and we can break into this as the horizontal line and this steps basically, so we can pinpoint this temperature we can pinpoint this temperature also for this particular inflection point. What is your 504 degrees centigrade at this particular point above 500 degree centigrade?

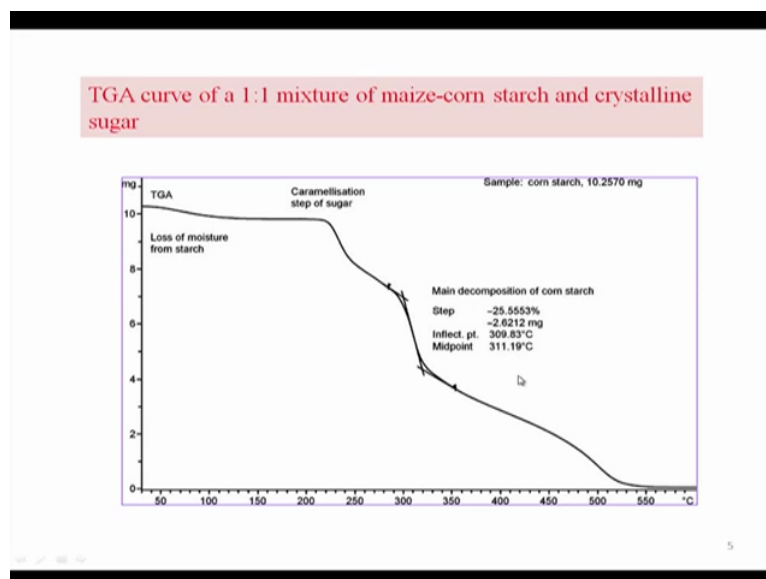
So this particular step which is basically a 63% weight loss is starting from 233 degrees centigrade so this is a typical loss of your sucrose burning process but what sort of this burning whether it is exothermic or endothermic just now we have seen in some other example at one we have the plot which is in the upper election the derivative plot we call it as exothermic, heat is being released energy is being released but if we consider that corresponding derivative plot of this so this particular change of this is typically

corresponding thing that means your endothermic melting process or we sometimes call it as a typically the food engineers basically say that the food chemistry for that which is caramelization.

So this caramelization process is being taking place you to the melting process when sucrose has the melting the melt condition so the melt the sucrose melt basically give us the corresponding caramel or we use for making cake making pastries and all these things so which are very useful process at which stage the exothermic decomposition and commercial also occurs.

So after that also so this is your endothermic peak and when we try to detect this particular one that means at around 500 degree centigrade so followed by and endothermic caramelization peak at which is the exothermic decomposition or combustion occurs. So what we get again from that same book we get this plot that means your sucrose can be characterised in terms of its endothermic or exothermic peaks are depending upon its corresponding melting process.

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So what we see now that if we have another material that means maize and corn starch so it is a mixture. So not only the pure sample the sample quality, the sample purity also can be checked if we find that this temperature for this mass loss what we know that the corresponding determination of melting point is also a very good technique for identifying the purity of the sample. Similarly the boiling point also is a very good technique to

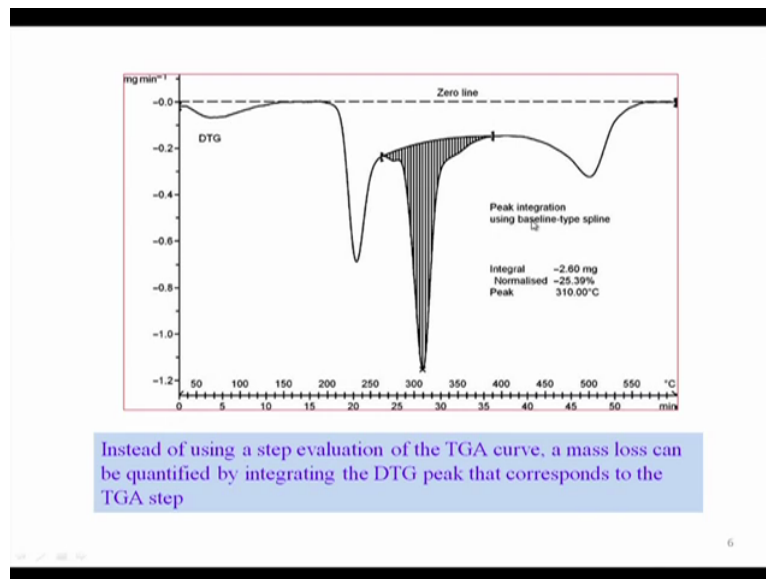
determine the corresponding purity of the sample in such a way that we now see that the TGA Lord the TGA curve of a mixture of maize and corn starch and crystalline sugar.

So you have this starch and the sugar, so if we have the corresponding mixture of these that means you have this as we have seen that about 200 we have the caramelization step for sugar initially we have the loss of moisture from starch, so starch has huge amount of moisture. So when the mixture is being heated basically all these 3 all the corresponding component of the food material so the corresponding TGA plots the characteristic TGA plots is also tells us that what sort of thing is happening and what sort of mixture we have?

So 1st is the moisture loss then the caramelization process then this particular step what has been also deconvoluted in terms of some straight line slopes of these so one straight line then 2nd one is a very direct one which is the perpendicular one and then some slope corresponding to the baseline thing, so baseline as been drawn over here so which is the basic main decomposition step of corn starch and which is also about 25% of the decomposition starting from your 309 degree centigrade is the midpoint inflection point as well as the corresponding midpoint is here so midpoint temperature or your decomposition of starch.

So not only the burning of the carbon particles or the carbon paste or any other carbon powder but we can also analyse the corresponding food samples very nice food samples sometimes the powdered samples of all these can be analysed and since we are processing for these things making cake, making biscuits making pastries and all these things will require to have some temperature that means oven temperature. We set some oven temperature and most of these things around 200 or 300 degree centigrade but if we go beyond that what sort of other things can happen during the corresponding making of the cookies the home-made cookies or the biscuits that we can find out from your TGA plot of the food samples.

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So the quantitative analysis now if we can go that the typical quantitative analysis if we see that the derivative or will then be useful. So the derivative plot whether it is a exothermic plot or endothermic plot what we see that this typical one so if you have that from 0 and is the when it is derivative plot that means it is milligrams per minute that means if we go for in the time axis, this is your now time axis so if you are derivative plot the instrument directly records the thing, so the DTG plot is like this so from 0.0 the negative direction that means the mass loss is taking place for this particular process and if we go for its corresponding integration using the baseline of this particular point so if we have the first step then you have the 2nd step around 300 degree centigrade.

So this is the temperature above this axis is the temperature axis and then the time axis. So it is almost the monotonous increase means whether you go for the time axis or the temperature axis, so around 300 you have this particular peak and this peak is being shaded and how you draw the baseline because originally you have this 0 baseline and this 0 baseline was like that when we have started our process that means when we start our according the thing from 0 degree centigrade so we go for this but this particular plot that means this particular (()) (22:24) the top this one that means the depression is this particular point of say temperature we see that when it is going up it is not reaching to your original 0 line.

That means sometimes it is not so easy to get that your plot is touching the baseline before the start of the plot and at the end also it is going down again to the same one. It is not happening to any kind of plot what is happening over there in the real sense is that in you go

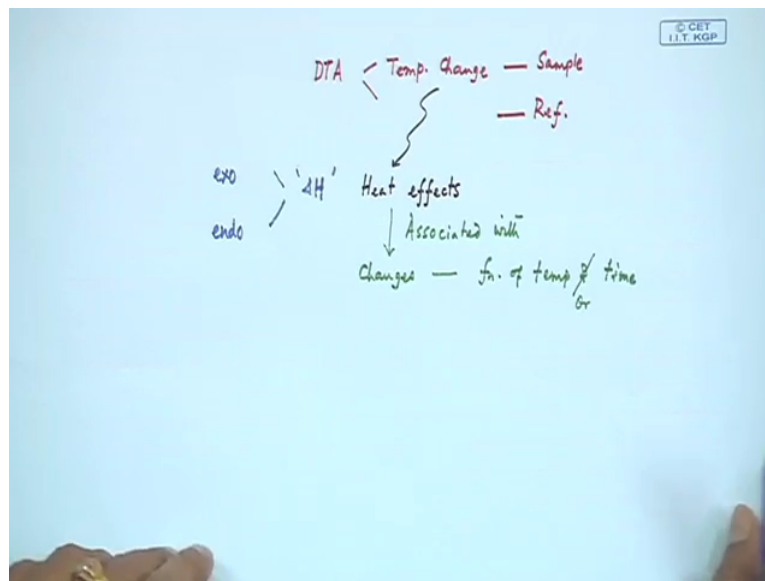
for this thing because when we reach this when it try to go back to your baseline, what is happening that your this temperature is nearby, this temperature is why so this temperature will be (0)(23:15) so you recording for the 2nd peak is also commencing.

So the commencement of the 2nd peak immediately after the 1st one will not allow the baseline is the 0 line it will be like this, so when after this also again a very sharp line it is reaching over here but at this point also it will not again go and go back to your 0 line because you have a 3rd point. So if you have the 3rd point so this will go so when you go for the baseline type (0)(23:53) we get so is a not this particular exact slide but instead of that we smoothen the plot that is as if this plot is not there, so if we smoothen the plot and we see the line so this if we make this as a (0)(24:09) also and sometimes the computer software can take care this thing to draw it in this particular form.

So if we go like this and this particular plot is basically this and then the shaded area, the shaded area is because of this corresponding area you to the particular thermal process. So instead of using the step evaluation of TGA curve because we know that the TGA curve can have the different step. A mass loss can be quantified because we are looking for the quantification that means the actual amount of mass loss what is being taking place from your derivative plot.

By integrating the DTG peak that corresponds to the TGA steps, so your TGA step was there so you have the original TGA step and correspond to that TGA step we have the corresponding derivative one and the area under this derivative plot is then quantified for this responding mass loss and which I to co-relate with your TG plot. So your data are you have your hand and this data you can also quantify in terms of its corresponding area determination, so this area determination will also tell us in such a way that if we go for this for this derivative plot so this derivative plot will give us the information in this regard how you get this derivative plot and how we can co-relate this with that of your thermogravimetric plot.

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So the next case we will just go for your corresponding another technique is your not a differential thermogravimetric analysis but a derivative one is also not is a differential thermal analysis is a another type of analysis where we will concern or we will focus our attention on the temperature change. So if we can monitor the corresponding temperature change of the sample as well as the reference we can have some plot for that and as a result what we are just basically looking for this temperature change is the corresponding heat effects because we are heating the sample as well as the reference within the same furnace. So we will now try to monitor corresponding heat effect and how the heat effect means how much heat we give to the sample or the reference is responsible for the corresponding change in the temperature.

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Differential Thermal Analysis (DTA)

- DTA involves heating or cooling a test sample and an inert reference under identical conditions, while recording any temperature difference between the sample and reference.
- This differential temperature is then plotted against time, or against temperature.
- Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference.

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So what we find here for the differential thermal analysis, it involves the heating or the cooling test of the sample and the inert reference material both of them we place inside the furnace because both of them are nearby within a difference of say 1 cm only so they will remain in identical conditions and while recording any temperature difference between the sample and reference we will try to monitor. Then this differential temperature is then now this temperature we call as the difference these differential temperature when we keep sample as reference in the furnace which is different from your differential TG plot.

So this differential in temperature is when plotted against the time or against the temperature because in DTG plot we are talking in terms of corresponding mass loss but here we will be talking in terms of the corresponding difference in temperature between the sample and the reference, So now if there is any change in the sample which led to the absorption or evolution of heat between these 2 that means the sample and the reference.

So if you have the changes there he would can be that the corresponding absorption whether you have the exothermic process or an endothermic process can be detected relative to an inert reference that you have the inert reference and that reference sample is also being heated you have the simple reference material it can be your like that of your Crucible material like alumina it can be your Alpha alumina also and that alumina is so heated so how the temperature rise can take place for alumina sample as well as your sample under test.

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Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference

DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak is the enthalpy change and is not affected by the heat capacity of the sample.

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So we get these 2 things that means the heat effect what we find this basic heat effects and these heat effects are basically associated with several chemical and physical changes. So there are changes which can be chemical or physical and we have to plot as a function of temperature and time or temperature or time, okay not and it is or time. So function of temperature or time we plot this and these temperatures are there, so what we try to find is that the heat effects, so what we basically look for any reaction we now have some idea about the delta H values because we know that if there is equilibrium we always talk in terms of the corresponding ΔH (29:53) energy change of the reaction.

That means the delta G value now will talk in terms of the corresponding delta H value and this delta H value can be both way that means it can be exothermic or it can be endothermic. So basically what we now look for that the heat effects are there sample is taking heat for a particular type of process means it can be of crystallisation, it can be your decomposition, it can be your oxidation or it can be your deduction, but what sort of this heat effect we can see for these processes. So any change of this sample can either be exothermic or endothermic can be detected related to an inert reference material.

So what we see that this TGA curves can provide data on the transformations, several transformation these transformations can be exothermic transformations or endothermic transformations and such as you have the glass transitions, you can have the crystallisation, you can have the melting, you can have the sublimation. So all these processes can be monitored by DTA that means (diff) the corresponding thermal analysis differential thermal

analysis and like that of your DTG plot the DTA also can give rise to some area under the plot that means it is also peak type of thing.

We can monitor the corresponding enthalpy change and not effected by the heat capacity of the sample, the sample capacity will be ignoring that will not consider the corresponding (()) (31:33) heat capacity but we are looking for this particular processes and we basically it is in terms of the corresponding differential method and sample temperature now what temperature change, it is the temperature change of the sample will be continuously compared with some reference material or the reference material sample as the corresponding reference temperature. So the reference temperature is being monitor that of our reference temperature with that of our sample temperature if we heat both of them together inside the furnace, okay. Thank you very much so next day we will continue again from here.