Course on Analytical Chemistry
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Module 8
Lecture No 40
Thermal Methods of Analysis – II (Contd.)

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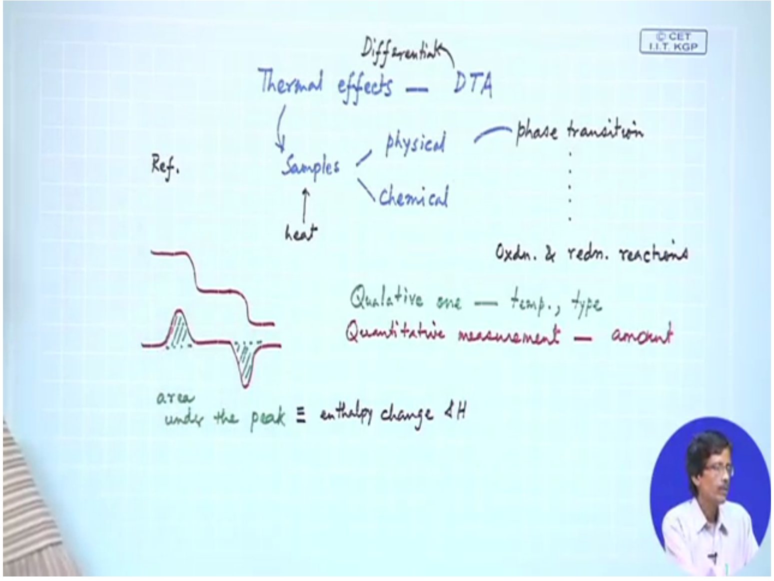

Hello good morning to everybody so we are just looking for the thermal effects on some samples and we have started our discussion in this regard by looking at a particular technique which is differential thermal analysis. So this particular again we are talking terms of the corresponding thermal analysis of the samples and how we can record this and what are the different DTA plots we can see, so that we will see now because the different thermal effect or the heat effect on some sample can give rise to the different changes which can be your physical one that means the changes can be physical changes or those can be chemical in nature that means the chemical changes.

Starting from a simple phase transition what we all know that a solid sample can go for phase transition very well, so starting from phase transition to many such processes where we can also monitor the oxidation and reduction reactions including dehydration, vaporisation and disassociation all. So this particular technique so this d is not a derivative one it is a differential one so is a differential technique so we will see how this particular technique will be useful when we can have something that means we heat the sample.

So in a furnace we heat the sample and that can be continuously compared with some reference material as we all know that when we do spectrophotometric estimation we have some reference sample such as your solvent itself, so compared to this particular reference material we heat the sample then we try to record the corresponding trace what we get due to the corresponding heating of the sample as well as the reference material inside one particular furnace.

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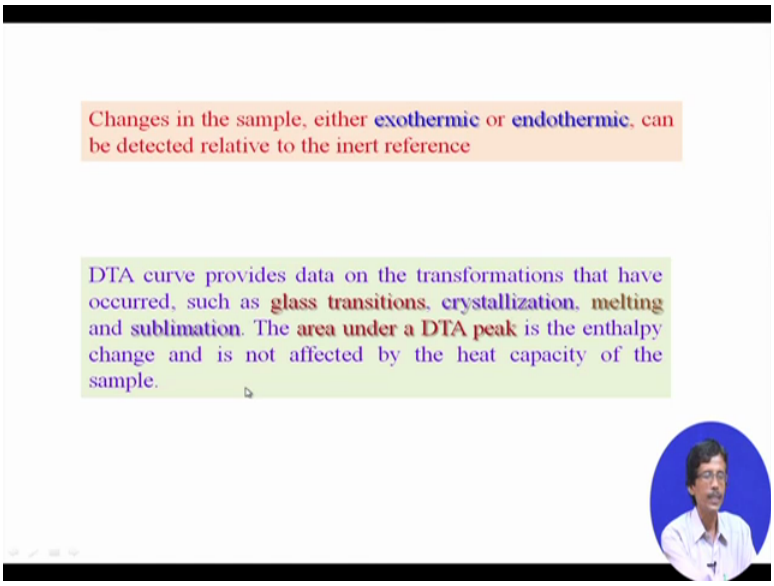

Changes in the sample, either **exothermic** or **endothermic**, can be detected relative to the inert reference

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.

So what we see that (())(2:50) looking for 2 types of changes or your delta H one can be your exothermic change and another can be your endothermic changes, so these 2 changes are very nicely, can be recorded, can be monitored and can be compared with any such sample because the diverse type of samples can be used to analyse these things and along with the phase transition and the oxidation reduction reactions that we can see also the melting as well as sublimation and if we can go for some quantitative estimation that means when you look for these 2 things that means you qualitative one.

That means the qualitative aspects what we can see that the temperature as well as the type of reaction whether you have the endothermic or exothermic reaction that we can monitor but if we go for a typical quantitative measurement using DTA, quantitative measurement, so amount of heat or amount of the particular energy, the thermal energy to be supplied or removed from the sample can be monitored.

So what we see that since this particular plot is a dedicative one and we have seen that a corresponding Tg curve is something like this only and if we get some other type of plot is where some area can be bound or both this 2 different types of thing, one can be your exothermic one another can be endothermic one. So what we can see here that the area under the curve because the mass loss and it is not related to mass loss, it is the corresponding effect, the temperature effect relative to that of your reference, so this area particularly this area under the curve or area under a peak because always we know if there is any peak, the peak area is always very much important to monitor.

So qualitatively what we can do, quantitatively we can go for the corresponding estimation that means this can be equivalent to the enthalpy change and this we can write in this fashion that it is enthalpy change or delta H and we can see also that this particular thing that when we go for the quantitative measurements that area under the peak or under the curve we monitor but this not affected by the heat capacity of the sample, so if there is a difference in the heat capacity from one sample to the other we will not see that is reflected to the corresponding peak under the DTA plot.

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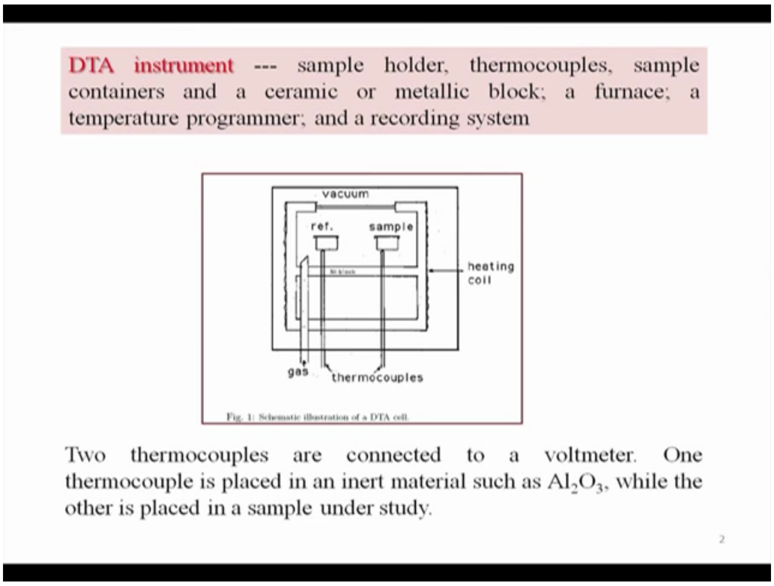

DTA instrument --- sample holder, thermocouples, sample containers and a ceramic or metallic block; a furnace; a temperature programmer; and a recording system

Fig. 1: Schematic illustration of a DTA cell.

Two thermocouples are connected to a voltmeter. One thermocouple is placed in an inert material such as Al_2O_3, while the other is placed in a sample under study.

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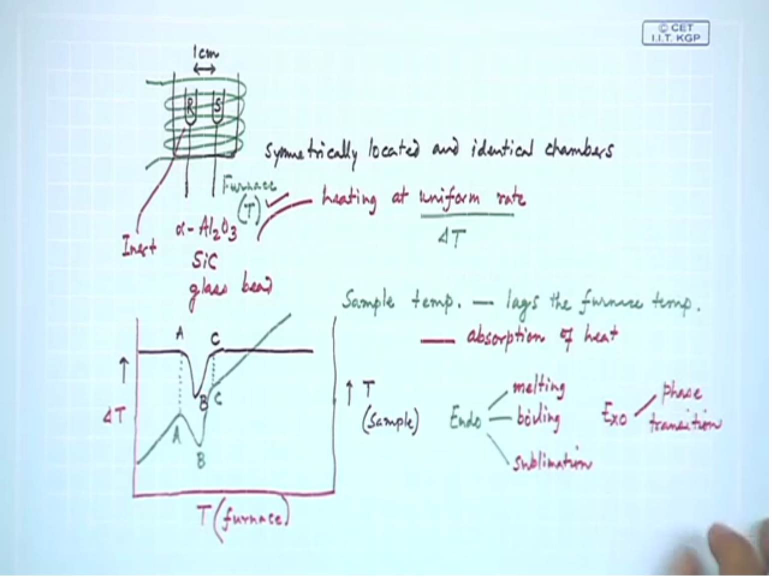

So what we look for a typical instrument, so what type of instrument we can have so a particular DTA instrument can have these particular components starting from your sample holder. So how your sample holder will be that we can see and earlier we have seen that our main interest is that we have to keep or we have to heat both the sample as well as the reference material together, so if you have this is reference material and this is the sample material, which we should enclose inside a typical furnace and this particular furnace what we see then that so can be electrically heated if it is bound to the coils and these 2 are pretty close because you can have some uniform heating rate as well as the environment, these 2 can be very close with then a distance of 1 centimetre.

So 2 symmetrically located because these 2 chambers, this is a crucible or whatever, so 2 symmetrically located and identical chambers, these 2 can be separated also, so because we have some connectivity from here for recording the corresponding heat effect and sometime a instrument can be common because we can record both Tg plot and the DTA plot over there, so what we find then that 2 symmetrically located symmetrically located and identical chambers we have to use and when you have this particular reference material or the reference sample, so what are those references because the references should be some inert sample.

It can be your alpha alumina simply Al2O3 or it can be a solid silicon carbide which is also very inert and can have some good or very high temperature withstand or sometimes a typical or a simple glass bead, so these are the sample, both sample and the reference can be heated at a uniform rate, so what we do the heating will be done at uniform rate, so we go for the typical heating then we see the corresponding temperature change or the temperature what one can be increasing and another cannot be increasing in that fashion or is not linear.

So when we heat this particular at a uniform rate and we monitor the delta T, delta T between these 2 and this delta T can be plotted as a function of the furnace temperature, so this is your furnace, so this furnace if the furnace is kept at a temperature T, so delta T can be plotted against T, so what we have then that this particular one can be recorded, can be heated and all with the help of some thermocouple and some electrical connectivity. So what we have the sample holder, so uniform sample holder we have.

Then thermocouples, the thermocouple is the recording device we all know that there is a corresponding resistant change, if there is a temperature change and there is a voltage difference, so that voltage difference can be monitored. It is not only true for this particular instrument but it is also true for the next type of thing what we will be talking about is the DSc, the differential scanning calorimetry. Though there we use basically the scanning calorimetry so a calorimeter will be used instead of the furnace what we are using over here, so there can be good similarity between these 2 instruments so that we will discuss.

Then we have the sample container, where we keep the sample and ceramic or metallic block because we have put that inside that particular ceramic or metallic block. Then a furnace, a temperature programmer because western bridge type of arrangement can be there and finally the recording system it can be your chart recording system, it can be of computer recording system or it can be your some oscilloscope.

So typically what we see that a schematic for that for a DTH chamber is that you have the enclosed one, that particular one is the typically enclosed one. Then we have some heating coil, so heating coil is covering your this whole furnace and this reference and the sample material what I just showed you that R and S, so R and S is the also connected to some thermocouple because thermocouples will be recording the corresponding temperature change and the difference in temperature between your reference and the sample material.

So that is very important the use of that thermocouple and the connectivity because these 2 thermocouples will then be connected to the voltmeter, so one thermocouple is placed in an inert material that is the thing that means the reference material such as alumina while the other is placed in a sample under study, so this is a reference material which is your AL2O3, so we put that inside that AL2O3 while the other is placed in the sample under study so other thermocouple will be under the sample.

So these 2 thermocouples will now use and we just try to record this thing, so the when we see that there will be the temperature that means the reference temperature you have, we have the sample temperature and you have the furnace temperature. So that we typically monitor for their, so when we have that this that when we record the sample temperature, so recording of thermal temperature is very important, sample temperature and when it is behind that means when it is lags, the furnace temperature what does it mean then?

If the temperature of the sample is less compared to your furnace temperature and furnace is trying to heat the sample in uniform manner but the sample is absorbing some amount of heat, that is why your sample temperature is less, so there will be some adsorption of heat, so absorption of heat so that we will try to monitor. So during these 2 cases that means the number, shape and position what we can identify as well as the area under that peak that I told you just now that for your quantitative measurements, the area under the peak is very important.

So now if we see that what your recording device can give rise to the corresponding plot, so T is your temperature this furnace temperature, so T is your furnace temperature, if we have this furnace temperature and we will plotted against your delta T that means the difference between the sample and the reference material. So what we see that the corresponding one so this delta T is there and if we plot on the other axis which is your simple the corresponding T of the sample, the temperature of the sample.

So when it is delta T what we see that we have a plot like this and which is also have a deep and then it goes again to the horizontal line, so what we have it starts giving rise to a lower value of delta T that means the change and then he goes to the minimum B and then again it is going up and giving you C. So if we get this that in terms of the corresponding sample temperature, the plot will be a different one and that particular plot will be because the sample temperature as the furnace temperature is increasing, the sample temperature will also increase like this and it will go and cut like this, so here also you have the corresponding A point and the corresponding C point and this is definitely your B.

So these are the 2 different types of plots we can have, so this is your sample so this is the sample temperature and this is the corresponding one as the reference as in the delta T, so we can have 2 different types of these, so 2 processes, so the when we go for the qualitative analysis, so the qualitative analysis will tell us that either we have the endothermic activity for those samples can show different types of behaviour or we can have the exothermic behaviour.

So that we just typically try to monitor and we examine and we then co-relate with the corresponding area of the curve because this area is (call) will quantify the corresponding temperature effect. So exothermic one is a typical example for phase transition, so it can be typically the phase transition and endothermic one is for melting, it can be for boiling, it can be for sublimation. So we are not talking anything in terms of the corresponding sample mass, so it does not require any change in mass.

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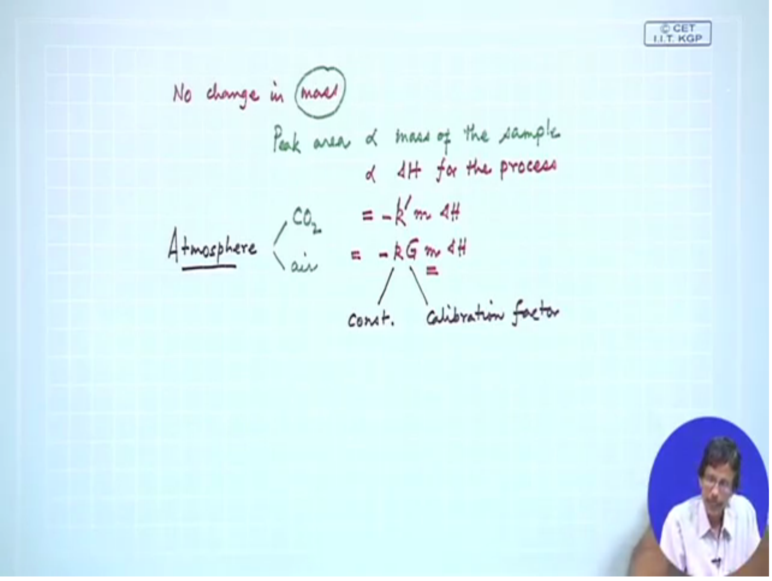

No change in mass

Peak area $\propto$ mass of the sample

$\propto \Delta H$ for the process

Atmosphere $\left\langle \begin{array}{l} CO_2 \\ \text{air} \end{array} \right.$

$= -k' m \Delta H$

$= -\underbrace{k}_{\text{Const.}}\,\underbrace{G}_{\text{Calibration factor}}\, m\, \Delta H$

So no change in mass unlike your TG measurement, so in case of your thermogravimetric measurement we are looking for a change in the corresponding mass but here we are talking in terms of the corresponding temperature change. So in order to obtain meaningful information by quantitative analysis which is your corresponding peak area, so peak area obviously will be dependent on the mass but we are not looking for the change in the mass but it will be proportional to the mass of the sample, mass of the sample.

Then it will be proportional to the most important quantity we are looking for the delta H for the process what we are trying to identify. So if we bring the proportionality constant as small k prime will be mass and delta H, so this will be the very simple relationship or it can be simply minus it will be minus if it is a endothermic process minus k and G m delta H.

So if we know the corresponding mass, what has been taken for this particular measurement, we can co-relate that and this particular one can be your constant because for more number of sample analysis we can have a constant for the regular arrangements or the regular measurements and G what can be converted from your k prime is your calibration factor. What we can use for this particular study.

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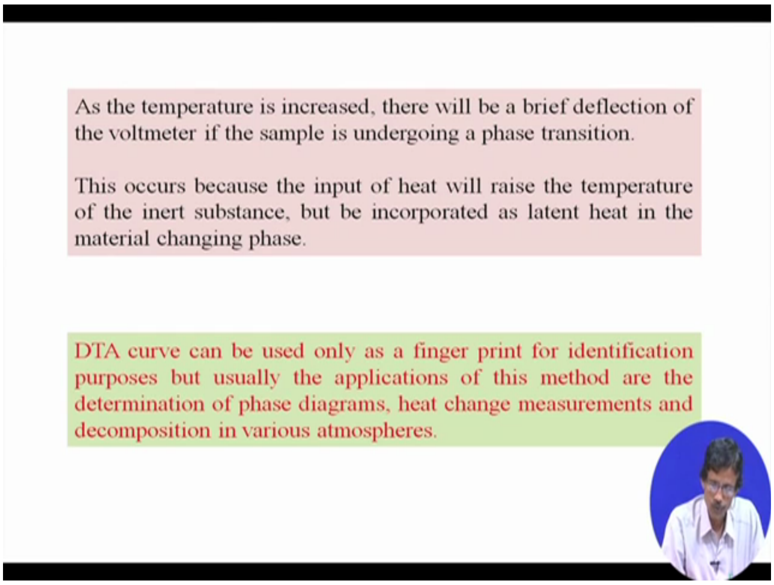

As the temperature is increased, there will be a brief deflection of the voltmeter if the sample is undergoing a phase transition.

This occurs because the input of heat will raise the temperature of the inert substance, but be incorporated as latent heat in the material changing phase.

DTA curve can be used only as a finger print for identification purposes but usually the applications of this method are the determination of phase diagrams, heat change measurements and decomposition in various atmospheres.

So what we see that due to that particular examination as a temperature we try to increase, there is a brief deflection of the voltmeter if the sample is undergoing the phase transition. As I mentioned just now that phase transition is exothermic process, so that exothermic process can be recorded very nicely due to that particular thermocouple, thermocouple to voltmeter and the response is being recorded in the voltmeter and the voltmeter can give rise to the corresponding plot because the input of heat will raise the temperature of the inert substance.

So the inert substance temperature is rising what the latent heat in the material for changing the corresponding face is required so that is absorbing some amount of heat, so which is stored as a latent heat for the phase transition that is why temperature is lagging behind. So what we get, we get a typical DTA curve and it can be used as a fingerprint for identification purposes like our IR spectroscopic analysis, we have seen that different number of that stretching frequencies can give rise to the corresponding fingerprint type of analysis that is you have to match the thing that means for a particular sample you have a DTA curve and you can measure the DTA curve with the pure version of that particular sample such as that of your calcium oxalate or magnesium oxalate what we have seen earlier.

So this particular type of fingerprint identification or calibration for different calibrations, usually the application of these methods for the determination of phase diagrams. Ultimately what we get is the phase diagram and heat change measurements and decomposition in various atmospheres. So what are those various atmospheres? So the effect of the atmosphere is very important and that particular atmosphere if we just simply compare the 2 things that means that carbon dioxide atmosphere and the air atmosphere, how it will look like?

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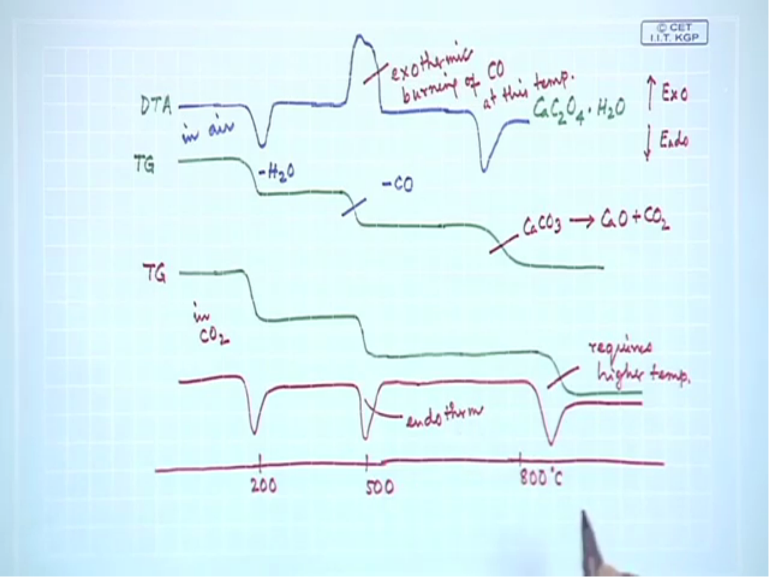

So the corresponding plot what we have seen earlier that the TG plot we know and that particular TG plot will just convert it to the corresponding DTA plot, so what we have seen the TGA plots for decomposition of calcium oxalate is like this. So this is your TG plot for calcium oxalate monohydrate CAC2O4 monohydrate, so we will be talking all these in air and when it is in air, so what will be your corresponding DTA plot, we are interested to know that particular plot, so the DTA plot because this loss we all know that the water of crystallisation is being lost over here, so if your evaporation process which is this is going like this and for the second plot, what would be that?

So we know that this particular point it is the elimination of carbon monoxide and when we do this thing that means we are doing this in air, we are making this measurement in air. So this particular one will go up, up up up and it has not a very symmetrical one but is like this. Then it is again moving and this particular one will again give rise to a plot like this, so this is your corresponding DTA plot what we get for these measurements.

So this upward and downward so these DTA plots if we get something that means if it is upward plot so it will be your exothermic process, which we all know that corresponding process we can have, the sample temperature and the corresponding reference temperature will lack behind and some amount of voltage is develop and the opposite one will be for your or endothermic processes is a downward, so upward is exothermic process and the downward is your endothermic process.

So since this is your exothermic one, so definitely this one is a exothermic process for what because we all know from your TG plot at the CO is eliminating, so this is at a particular temperature because this is your temperature axis what we know, so is your temperature axis, so this temperature axis so the first point is close to 200 degree centigrade the second one is close to 500 degree centigrade and the third one is around 800 degree centigrade. So when we heat that that means at this temperature which is close to 500 degree centigrade, we have the corresponding CO elimination as we know forming calcium carbonate plus carbon monoxide and this is your therefore exothermic burning of CO.

So exothermic burning of CO where it is burning because its burning is only taking place in air and in presence of your O2 of that air, so of CO at this temperature which is very important. That means we will have the elimination of CO and that is being confirmed by your DTA analysis that your CO is coming out and that CO is being burned in air forming again CO2, so you just simply compare, we will be able to compare it for the next one that means your corresponding one for what we get in CO2.

So the corresponding plot because we are looking for the corresponding effect or the change means your that particular one in CO2 environment and this water elimination step is more or less same but in CO2 environment some certain amount of change you can have, so this particular one is very similar to that but what we find that the 3rd step that means the step where we have the elimination of your CO2, it will be at a very high temperature compared to the previous one. So that is the effect what we try to see in CO2 when we do, when we go for the measurement in CO2 environment.

So your TG plot will be this where we have this temperature is this one and this temperature is little bit higher. So at this point what we have seen that your CaCO3 is getting decomposed to calcium oxide plus CO2. So this elimination of CO2 which is the corresponding environmental so according to the corresponding (())(27:04) we know that we are giving a corresponding concentration of this, so the decomposition temperature of calcium carbonate will be increasing, so this decomposition temperature of calcium carbonate that is why showing a high decomposition temperature or your this one, so the decomposition of CO2 requires a higher temperature.

So now it requires higher temperature, so this is then known to us so what about your then the corresponding DTA plot, DTA plot in CO2, so we will have a plot is like this here but now the second plot is also endothermic in CO2 and we have the third one at here is like this, so you have the corresponding one that means your corresponding plot for it would be endothermic one because the CO burning in CO2 environment is not exothermic process, now you find an endotherm.

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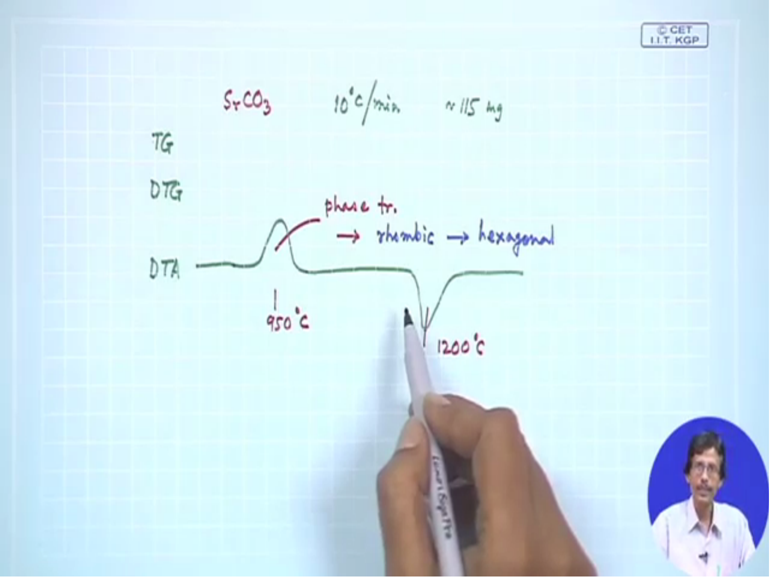

So these are the very important comparison and important in studies what we can make for your DTA analysis and what we see that a simple another carbonate if we take, if your sample is simply strontium carbonate like that of your calcium carbonate and if we heat it and the corresponding TG plot, DTG plot we all have, so we have the TG plot, you have the DTG plot and then we just look at DTA plot.

Will it be same compared to that of your calcium carbonate? No it is not that. If we take strontium carbonate and we heat it at 10 degree centigrade per minute at the rate and if we take around 115 milligram of the sample, so we require a little bit higher amount of sample because it depends on that particular sample, it depends on the corresponding sensitivity but again we get some plot, exothermic plot and then we have the corresponding decomposition of the carbonate is like this.

So this particular plot this case it has to be identified is a very high temperature not a very small one so 950 degree centigrade temperature and it is 1200 degree centigrade where we find a new things for this simple strontium carbonate also unlike your magnesium or calcium carbonate. So it is due to corresponding phase transition, we all know that the phase transition is exothermic process and in this particular case even the strontium carbonate and show the corresponding space transition behaviour and this space transition behaviour is exothermic in nature and is due to the corresponding change of the form which is from rhombic to hexagonal one.

So that is why we see that DTA thing is not only giving rise to a different types of gases what is coming out from the sample and how it is burning and most interestingly this phase transition from any material, any inorganic glass sample or inorganic solid material or the rubber like polymer material we can identify particularly for this phase transition because we know that the polymer analysis we can have the corresponding glass transition temperature TG, then we can have the crystallisation temperature, all we can study by this particular useful technique, okay. Thank you very much.