Course on Analytical Chemistry
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Module 8
Lecture No 38
Thermal Methods of Analysis – II (Contd.)

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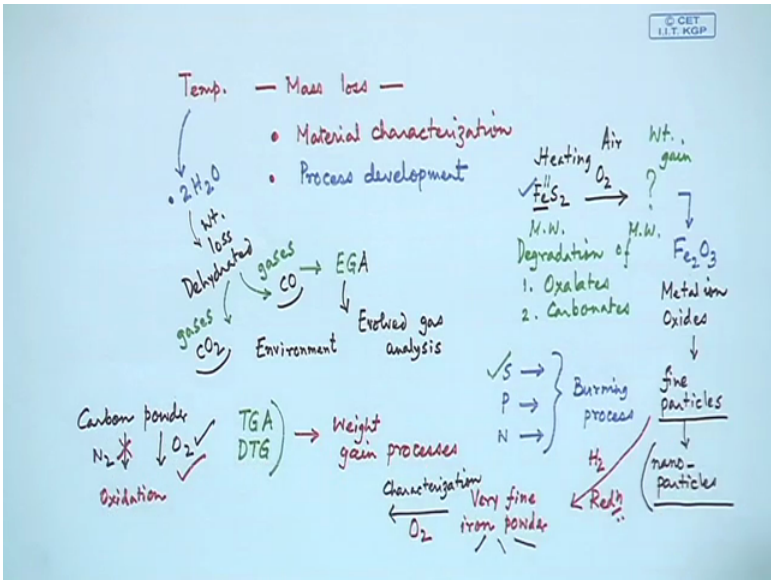

Hello welcome to this class of thermoanalytical method where we are talking about a simple thing which was the mass loss and this mass loss we are trying to monitor with respect to temperature increase and that is very simple and a very straight cut way of knowing the thing that how much stable this compound is or the material is, so one important thing is that it is very much useful for material characterisation and also sometimes we can use this particular technique if we know nicely at what particular temperature of the amount of mass loss is taking place and that mass loss can be very much useful for some process development also and so far we have seen that there will be something that means that you can have the water of crystallisations searchers that what we have discussed in case of calcium oxalate that 2 of the water molecules which is present in the crystal lattice and nicely network in terms of hydrogen bonding or trapping inside the void of the crystal lattice.

What we find that the removal of this thing we accompany the weight loss or the mass loss such that we can have the corresponding dehydrated sample. So after knowing this thing that means the dehydration process and take place and if we have more number of water molecules say 5, 6, 7 up to 10 water molecules we have seen the example of sodium carbonate, so at the same time if we see that if something is happening such as we have seen in the case of heating FeS_2, so what is happening when we go for heating this particular FeS_2 species because we know now very well that if there is a loss that means the loss of this thing or we have seen that in case of your magnesium oxalate or calcium oxalate, the gases which are evolved.

So these gases these are carbon monoxide or carbon dioxide and that basically give birth of a typical another analytical technique related to mass, mass loss as well as the temperature change or this species so which can be termed as evolved gases what we can consider, so what gases which are coming out from these samples that means the degradation of your oxalate species or the carbonates. So we can study nicely the degradation of oxalates number two carbonates or any other species, even sometimes we can go for the corresponding degradation of nitrates et cetera but in other cases when we see that this evolved gas if we go for its corresponding analysis it can be termed as the evolved gas analysis, so evolved gas analysis and we have also seen the 2 different types of this particular type of mass loss when we consider that typical environment.

So when gases are coming out such as your carbon monoxide or carbon dioxide which are coming out from the solid thing which we are heating so this thing will go and these 2 gases which are coming out, so above the solid we have this particular gas so these 2 gases basically than maintain the corresponding environment. Similarly when we heat something that means we heat this in presence of O_2 or in presence of air we all know that we are looking for something where some high-temperature reaction can be feasible such that you can have the corresponding iron base sulphate formation that mean sulphur is getting oxidised.

So when sulphur which is present as the anionic form of this metal iron salt is getting oxidised, so degradation of any other non-metallic species like the sulphur burning, phosphorus burning, nitrogen burning the gas burning also the nitrogen gas burning, so we can consider one after another for the typical burning process. So in this particular burning process if we consider that something is happening and ultimately what we have seen that it goes ultimately to the corresponding oxide formation that means Fe_2O_3 formation from this iron.

So quantitatively what we can do is that the quantitatively the amount of iron which are present in this unknown sample, so any other sample containing these metal iron species can be converted to its corresponding metal oxides and sometimes if we are able to make or able to produce or able to prepare these metal iron oxides or metal oxides course originally these are present in some oxidation state or plus 2 plus 3 so metal oxides or metal iron oxides can produce there fine particles so it is possible to prepare those fine particles and if they are in the very small size area or the nanometre area you can consider that we will be able to prepare corresponding nano particles which have very good application tremendous application in terms of their other property other physical property if we have corresponding semiconducting behaviour we can use these particles as the semiconducting material in the sensor process or any other thing.

So in between after getting this in between when we see we are talking about the corresponding burning of the sulphur proton the sulphide part or S2 2 minus part which is present with this iron in the ferrous state, iron is in the ferrous state, so the corresponding conversion of the sulphate and if we consider simply the molecule weight of the sample what has been taken that of the molecule weight of these species is being formed duty the oxidation by O2 we see that this particular step there will be some weight gain at high temperature heating. So we will see this particular sample that not only we have the weight loss or mass loss in some cases but we can have something where we can see the corresponding weight gain also.

So this particular technique the thermogravimetric analysis and its corresponding derivative one the derivative thermogravimetry can also eat very much useful to monitor, to identify and to check corresponding amount of weight gain. So nicely we can monitor the weight gain classes, so that we will see that how we can have and how much you have the corresponding weight gain. So what you see here that the example of some chemical reaction what we can have an increase in mass that means you can have this particular one.

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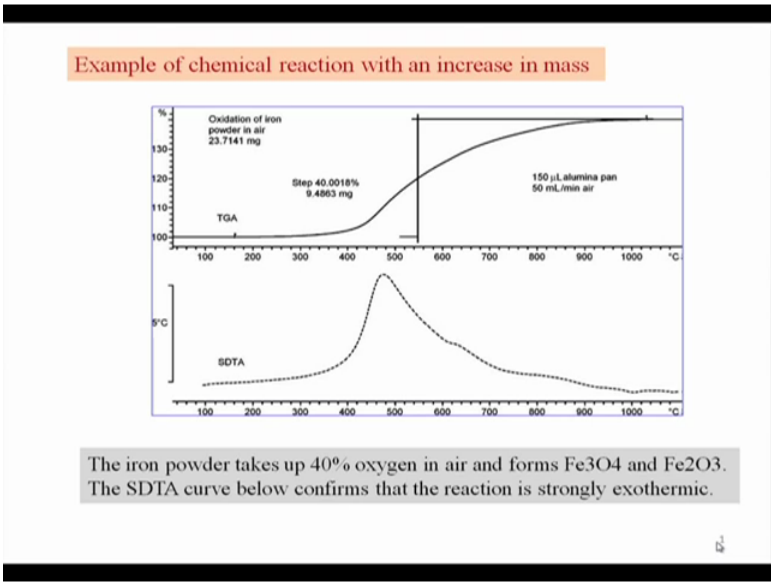

Example of chemical reaction with an increase in mass

The iron powder takes up 40% oxygen in air and forms Fe3O4 and Fe2O3.
The SDTA curve below confirms that the reaction is strongly exothermic.

That this particular reaction which is a thermochemical reaction will consider to any such reaction when it is utilised any transformation it can be decomposition or it can be conversion related to that of our oxidation with an increase in mass so like that of our FeS2 burning in air is similar to that we have a corresponding increase in mass. So instead of taking your FeS2 sample we can also take a typical example again taken from your book so the oxidation of iron we are taking that oxidation of iron powder in air so what we have seen just now that we are talking something related to semiconducting oxide material. Your FeS2 is your oxide material but if your environmentalist is such that, that Fe2O3 can be converted to very fine iron metallic iron powder.

So what we should do, we should do something that at high temperature so at high temperature can go for its reaction with hydrogen gas or any other source what this H2 can go for the typical reduction reaction. So after the deduction means we start from here have the sulphate as the intermediate, then we go to the corresponding oxide and some of the time we can also get the other variety that means Fe3O4 the mixed oxide of the iron can also able to make from there and the fine particles of Fe2O3 is also there and if we go for the corresponding deduction of this Fe2O3 can go for fine iron powder.

So now we just try to monitor corresponding these iron particles because these iron particles also again be your fine particles you can function this as the nano particles but again in terms of say simple characterisation, how good they are? Because sometime these particles if they are very fine immediately react with the O2 present in air and this fine particle will be pyrophoric in nature, so they can be pyrophoric, they can be catalytic and they can have other good examples.

So taking this particular information what we have seen previously also in terms of your carbon powder the carbon particles, the carbon powder when you burn in presence of nitrogen and in presence of oxygen we see that the complete burning of carbon as carbon monoxide as well as carbon dioxide is only possible when the environment is your O2 environment but when the environment is a gen we will not be able to go or its corresponding oxidation, so your oxidation will not take place your nitrogen is there but in case of O2 this oxidation is possible to happen.

So if you get this fine iron powder particle there, they if they are so pyrophoric that even other room temperature when it is exposed to your O2, it can immediately react, so in air or O2 environment if we go for the corresponding oxidation of iron in air, so this is a typical characterisation service and how the corresponding mass gain profile or mass gain plot can be available to ask that we can see from the corresponding TGA plots that means what we see that in case of your oxidation of iron in air so we have taken roughly about 23 milligram of this particular sample and we go for the corresponding heating of the sample, heating of the sample on some alumina pan.

So this particular part we just see that how much we get that is the corresponding to that that means this particular change, so this weight loss basically we are considering it from almost this is almost this particular percentage that means you have the 100% of the samples so what weight we have taken we have taken 23.7141 milligram you see such a sensitive balance we use thus that we can take the weight up to fourth place of decimal, so this fourth place of decimal will immediately tell us that if we heat the sample at say 550 degree centigrade or 600 degree centigrade or 700 degree centigrade we have a continuous mass gain is particular sample and which is complete around say 950 degree centigrade, so at 950 degree centigrade we have a corresponding weight gain is almost 140%, so 100% was your iron powder and by taking its corresponding oxygen it is converted to your oxide so iron oxide what is form which is more than that at means weight gain is 240%, so this particular step means considering this point which is a part of thousand.

So above 1000 degree temperature so above thousand 40 or 50 degree centigrade see that the gain is about 40% so you mass which was originally that percent regard to your 23.7141 milligram of your iron powder is gaining weight of 9.4863 milligrams, so this particular weight will also tell you what is forming over here that means the corresponding composition of the oxide we can we know and this composition of oxide will immediately tell us that whether your species is forming what we have seen just now that whether it is Fe_2O_3 or Fe_3O_4 for this particular process costs the weight of iron is known and the weight of the corresponding oxide is known and the percentage gain is also known.

So this particular thermogravimetric analysis is very useful one what we know due to the corresponding mass conservation and the mass gain for a particular process and we have seen a particular type of the corresponding SDTA technique that if we go for the corresponding derivative one and this derivative one is not also very much monotonous at means if we go and if we supply such and air passage that means 50 ml of air per minute is passed on the sample and we heat the sample and the derivative plot is actually giving rise to the corresponding change of this temperature.

So it is the corresponding temperature change for this derivative one is 5 degree centigrade and this temperature change with respect to the corresponding temperature for the sample if you are derivative plot and when we do not go for that means we have the variable temperature rise depending upon your weight of mass loss because when the mass loss is more the furnace temperature change should be slowed down and we get a typical plot of this type.

So as a result what information we get that information will tell us that you cannot restrict a thing to Fe_2O_3 only the can also have the Fe_3O_4 because this is only the corresponding one for the oxidation of complete oxidation that means in the ferric form. Fe_2O_3 is a ferric oxide but this we consider as Fe_3O_4 is a ferrosoferric oxide, so ferrosoferric oxide means you can have certain percentage in the ratio of 2 is to 1, 2 of the iron centres are present in the trivalent state that means in the ferric state and one will be in the ferrous state.

So this is in the lower range that means this will form part and when you have complete oxidation the Fe_3O_4 will be converted to a Fe_2O_3. So this 40% weight gain at this particular time at means around say 800 to 900 and up to 1000 degree centigrade is due to the formation of both and was we can find that if we are the typical formula of this thing we can find out this particular transformation the amount of Fe_2O_3 and amount of Fe_3O_4 formation.

In this particular plot that the derivative plot is also showing because we will see now in this particular class or the next class that what is known as the corresponding differential thermal analysis and we can have for this particular thing that means whether we have a typically plot of upper in upper direction or in the downward direction what we see that particular weight gain process is also a exothermic process so oxidation and most of this oxidations are giving rise to the corresponding temperature rise of the sample so we have corresponding temperature rise of the corresponding sample what is heated, so is a typically exothermic reaction so most of the oxidations are considered as they are very much exothermic in nature.

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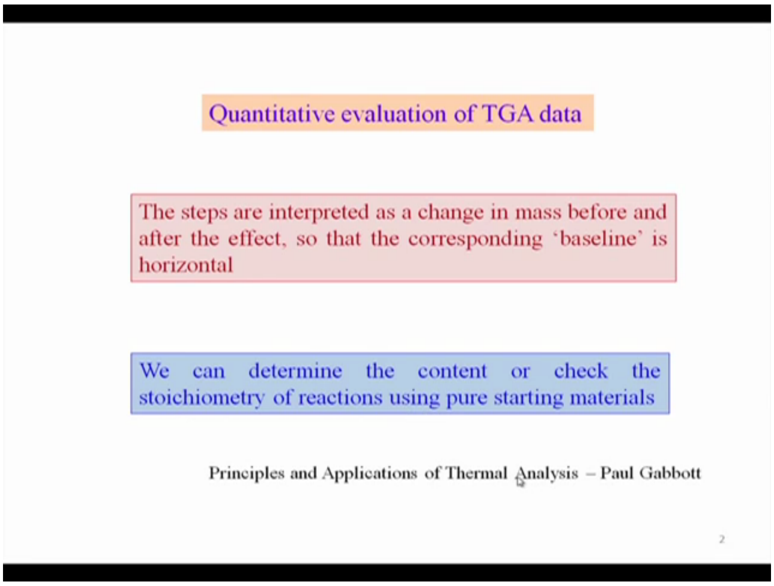

Quantitative evaluation of TGA data

The steps are interpreted as a change in mass before and after the effect, so that the corresponding 'baseline' is horizontal

We can determine the content or check the stoichiometry of reactions using pure starting materials

Principles and Applications of Thermal Analysis – Paul Gabbott

So how we use the corresponding data what we get that means the at what temperature we have the corresponding change in the corresponding mass and such that we can have different data points or temperature versus mass of the sample we plot and now we try to evaluate the information what we can gather which is qualitative in nature is known as the corresponding quantitative evaluation of your data what we can get your thermogravimetric analysis. So we can have different steps and those steps can be considered can be evaluated as a change in mass before and after the effect.

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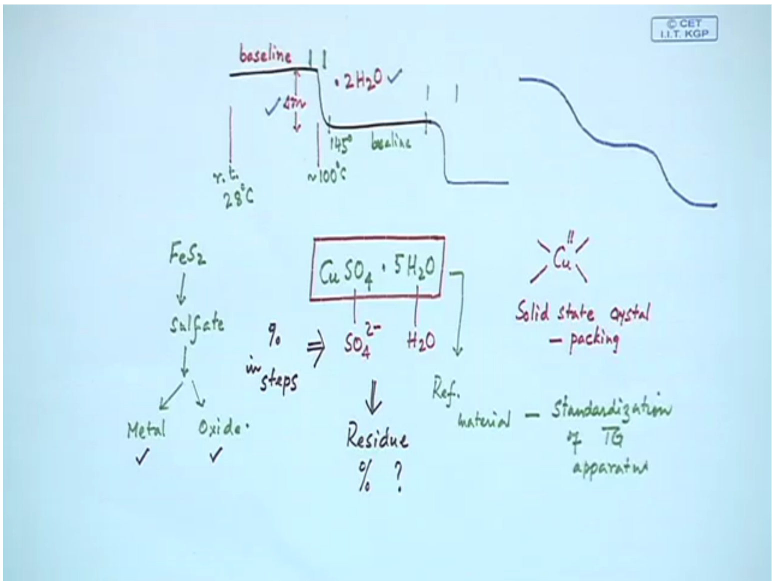

So the corresponding baseline is horizontal so that we are seeing from the very first day of this thermometric analysis that if we can have mass loss like this and we know that one is the corresponding temperature axis and another is your corresponding mass loss axis and we see that this particular magnitude of these is the corresponding mass loss.

So we see that this particular one is also a horizontal plot and this is also a horizontal plot and restart basically consider that our weight loss is taking place a baseline that means from a temperature range of say these to these very we see that the water of crystallisations are going out in case of heating your oxalates samples of calcium and magnesium and this water loss from this particular point is that, that with a very small temperature range, this range is very small, so within a very small temperature range our elimination of water of the crystal lattice is taking place.

So before that that means this is the room temperature starting and this can be around 100 degree centigrade, so if your room temperature is 28 degree centigrade or 30 degree centigrade, so within this range from 28 to 100 degree centigrade, we have a typical baseline and when the mass loss is completed also say around 140 or 145 degree Centigrade if you consider it and after that online is again horizontal, so this is baseline for the first weight loss for the first mass loss step.

Then the second one where particular range is also a typical baseline, so this can also be considered as another baseline for the second step if it is there at all, second step of your mass loss or weight loss in this particular fashion so the quantitative data that means if we get a very sharp change that means it is almost a very small temperature range so this is also a very small temperature range but instead of this we have a process like this or a process like this for these 2 steps that means a continuous one not very (())(21:56) step, is very difficult to find out what particular temperature you have the corresponding baseline because it is continuously degrading, so in that particular case the delta M value for the removal of water of crystallisation is very difficult to identify.

So the very important criteria what we should have or the quantitative analysis of the DTA data is that, you should have a typical baseline and the beginning and at the end such that in a very small temperature change window we had a typical delta M value and within this particular range on this axis we found out the M delta M value in milligrams such that we can find out this and we should try to co-related that whether this mass loss will correspond to the corresponding amount of water which is being lost from the sample taken or your analysis.

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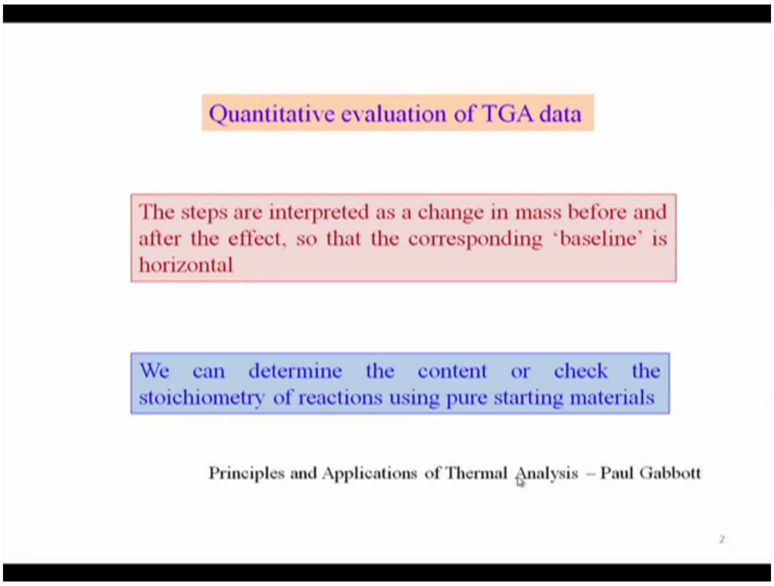

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So this baseline thing that means we should have so before and after we should have the baseline and which should be horizontal in nature. Then what we can do you can do that the content or check the stoichiometry of the reaction using pure starting materials, so sometime whatever precipitate we can have as I told you that in case of your precipitation of your calcium oxalate or magnesium oxalate.

Externally we add oxalates salts or the sodium salts and we add all these to the corresponding beaker and we get the corresponding precipitate of these as the corresponding precipitate of calcium oxalate or magnesium oxalate but remember at that particular point or at that particular time that in case of your or calcium present in the sample of your magnesium present in the sample we get quantitatively corresponding amount of your oxalates or the real samples are not so pure we have certain percentages of calcium as well as certain percentages of magnesium present in it, but there are other (())(24:05) samples it can be your other bivalent metal ions and those bivalent metal ions can give or may not give also the corresponding oxalate at the insoluble precipitate but if they give the corresponding oxalate at the precipitates.

So your precipitate what you are expecting to be of calcium oxalate is for the contaminated with that of the bivalent metal ions. So how we checked this particular plot for your quantitative thing that means the real plot for any weight loss process we should have the pure sample of or satisfied sample of your calcium oxalate or magnesium oxalate, we take that particular sample and heat that and we take the corresponding weight loss at those particular temperatures. So this basically is taken from the one good book is principles and applications of thermal analysis by Paul Gabbott and we have adapted some of these things that means the plots and all this from this particular book.

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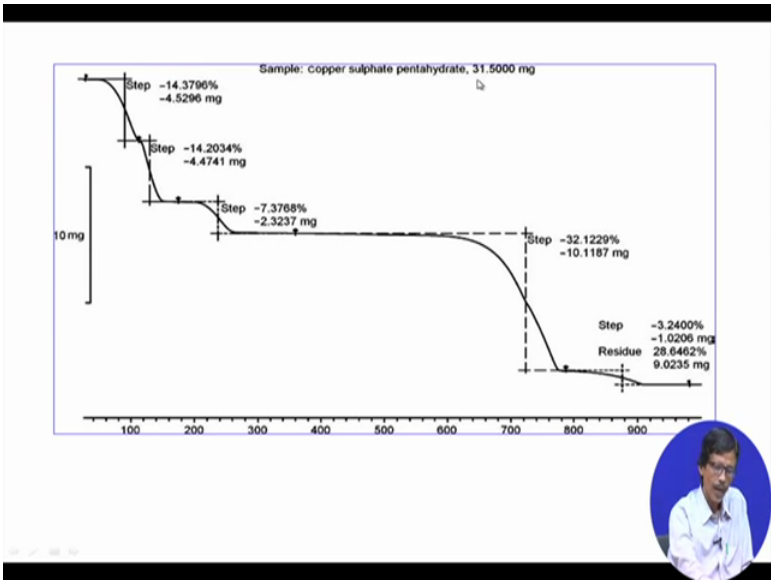

So if we take now, we simple example what we are studying from our school days that a good reference you can have for handling your instruments is copper sulphate which is having 5 of water of crystallisations. So copper sulphate pentahydrate we call this, so this water sulphate pentahydrate what we find and we try to see the copper environmental whether your this water molecules are bound to it or you can have some sulphate bound to it and all these things how sulphate.

So two things that means you have the anionic SO4 2 minus and the water molecules which are surrounding your bivalent copper two center and in the solid-state packing basically, solid state crystal you have and the packing is therefore very important and when it is packed equally we are writing this particular hydrate salt within the crystal lattice and when we heat it and what we are looking for the corresponding loss of water of crystallisations.

So you are all so we are looking for this loss as well as we will be looking for something very can consider whether your sulphate is also getting lost from the species or not at we will also see because we have a very good example always we should try to keep in mind that and we immediately we get the corresponding sulphate of it and then we can get 2 things together that means we can have the corresponding oxides or we can have the corresponding your metal that means the iron powder stopped so these are the things basically what we can consider.

So heating a particular sample which can be a very good reference material for any instrumental in which can be standardise so it is your reference material also or standardising the instrument, for standardisation of TG apparatus. So if we want to standardise a corresponding TG patters we must take a very pure sample of your copper sulphate pentahydrate, so if we take about 31.5 milligrams of this particular sample what we find at this 31.5 milligram of this sample, if we heat it so we have one step of loss then the second step of loss and the third step of loss, then we have a very big loss and then we have the corresponding residue.

So this basically tells us that typical quantitative analysis of your TG plot and this quantitative analysis of this TG plot will give us the corresponding information that in a step wise manner because we know that this steps if we find if your eyes are very well-trained and you know that this is a very good baseline but here to detect this particular baseline is very difficult sometimes.

So it is difficult we should go for the corresponding derivative plot, otherwise we have this and then any we have a very broad or a very on baseline so look at this things that means this is the access for your weight loss that means the 10 milligram scale, so this is the 10 milligram scale so this step that means we step 1 is not even 10 milligram is close to 5 milligram, it is 4.5 milligram second one is also that third one is still less but the fourth one is a very big one so which is 10 milligram, 10.1187 milligram weight loss and ultimately we have the residue and most of the time what we have because we are ending were here where the temperature we have reach this 1000 degree centigrade, so this 1000 degree centigrade temperature will tell us that what is your corresponding residue what remains there.

So analysing this thing that whatever sample you have if you know that a pure sample of copper sulphate pentahydrate is given to you and what I just told you can have the corresponding weight losses these weight losses so these 2 that means the loss of sulphate as well as the loss of a molecules can be your choice and what are the corresponding residue that also we should think.

So if we think for a while before we go for the next class that we should have some residue because is that, the percentage of residue if we are able to determine because the detail analysis of this TG plot will tell us what should be your residue and what should be the corresponding mass loss in steps that means different steps you have, so if you consider that you have 5 water molecules and one sulphate anion.

So 5 plus 6 species are there so we may not get 6 steps for this water loss but we can have less number of those steps but meaningfully and chemical meaningful also because we must have something which is your residue which should have a good formula for that the way we have seen in case of your heating of your FeS2 or your heating of your mind powdered to get the corresponding oxides of your iron. So in your next class we will see how we can analyse and how we can quantify basically the corresponding thermal degradation of or copper sulphate pentahydrate sample, okay. Thank you very much.