Course on Analytical Chemistry
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Module 7
Lecture No 32
Thermal Methods of Analysis – I (Contd.)

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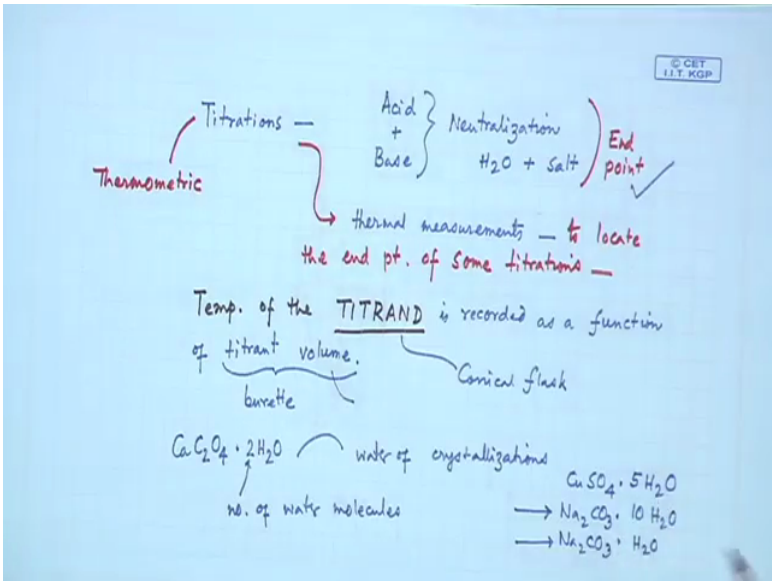

Hello, welcome back to this class of thermal analysis where we are talking about corresponding titrations because we all know the simple titrations where some acid is utilised with that of our base and we go for the corresponding neutralisation reaction and how we can monitor thermally this particular titration. So we will just simply put something which is the thermal term so it will be thermometric titrations so in that thermometric titration what we can measure now goes in a normal titrations all these things we use indicators and the color change of that indicator will tell you that all the acids as being consumed by the base and the product is only water as well as the salt.

So we can detect the endpoint by knowing the corresponding color change for the indicator added that reaction but in this case we go for thermal measurements, so thermal measurements would do, why we do that thermal measurements because to locate this particular endpoints so this is the endpoint, so to locate the endpoint of some titrations which can be detected nicely so for some titrations we can go for, so what we can do there at this we all know that you can have some analyte and the titrant so temperature so again a calorimeter type of arrangement we can have so temperature of the titrant, remember it nicely that what we are monitoring?

The temperature of the titrand can be monitored or is recorded as a function of titrant volume. So what we all know that we just go for this addition or this particular edition of volume from the burette and we take something in your conical flask, so now we can yourself tell that if we can have some arrangement such that we can measure or we can monitor the temperature of the reaction flask or the conical flask where we add certain reagent or certain assets so this titrant we are adding and we this particular volume is giving (())(3:57) to detect the corresponding endpoint.

So we get some change in the particular temperature so at the neutralisation point so there will be some sudden change in that particular temperature change so we can monitor this to temperature change so one monotonous change in again sudden break and the slope of this particular straight line beyond the endpoint will also be changing so that way we can locate the corresponding endpoint by doing the corresponding thermometric titration.

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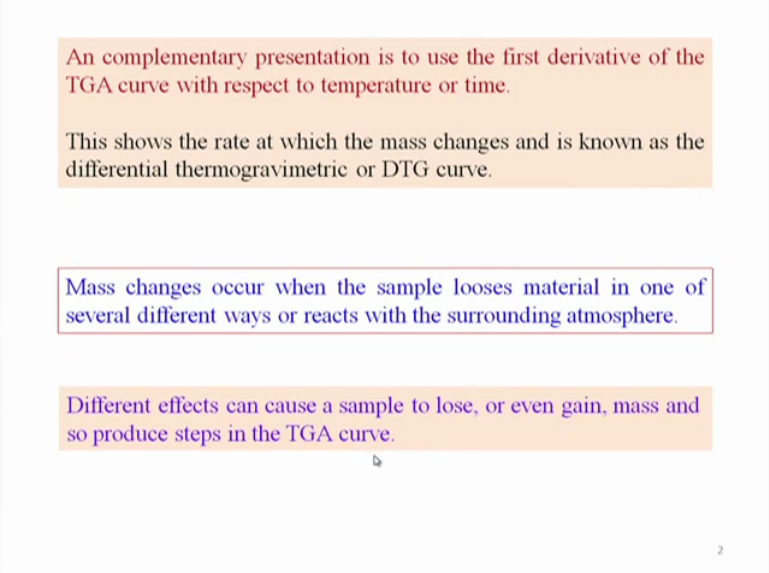

So what we see that so far that the DTG curve we have then the mass changes in that particular case, why it goes for the corresponding mass change is that the sample loses some amount of material in one of several different ways or it reacts with the surrounding atmosphere. So it loses the mass as I told you just now that if you have calcium carbonate sample or a corresponding magnesium carbonate sample so the carbon dioxide elimination or sometimes carbon monoxide elimination also can take place.

If there is elimination of carbon monoxide we get the corresponding oxides of the metal iron or if directly the responding CO plus CO2 is removed what we get we get the corresponding

oxides in one form but the sometimes we directly get that particular one with the intermediate formation without intermediate formation of the corresponding carbonate species. So a different effect can cause a sample to lose or even gain mass and so produce steps in the TGA curve, so TGA curve the stepwise change what we see is due to the corresponding loss in the weight or in the opposite direction if we go for that is the corresponding gain in weight.

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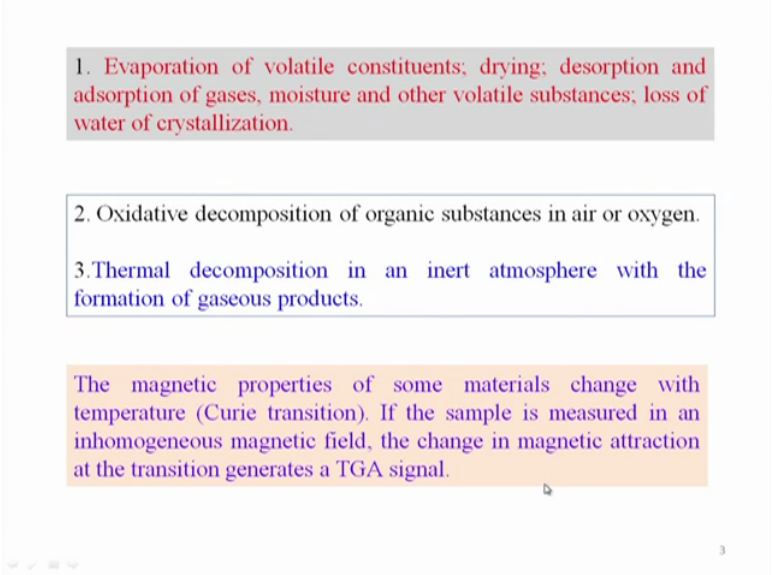

So how we do all these thing because a particular sample so what are the different processes or different pathway basically we go for these materials is the evaporation of volatile constituents. So while we dry so while we dry basically and this particular drying process when we dry the sample of nickel DNG as I told you or the desorption of some material or adsorption of gases.

So when the adsorption of gases are there they will be a gain in weight or the moisture loss or the moisture gain and other volatile substances and loss of water of crystallisation. That means if we have the water of crystallisation just now I told you that will consider in some of our classes that very good or the very useful reference material for calcium or any other thermobalance because how we standardise a thermobalance.

So thermobalance can be standardise by using a corresponding sample of calcium oxalate, it can be monohydrate or dihydrate so we should be very much careful about knowing the number of water molecules so the number of water molecules which are trapped as water of crystallisation or crystallisations. So these water of crystallisations we can monitor and we can measure the number of water of crystallisations because we all know that all these

samples because copper sulphate is nothing but pentahydrate we all know that sodium carbonate had 10 water of crystallisations when it is specifically prepared and in some point it is only monohydrate, so how we can differentiate these 2 samples whether it is a decahydrate or a monohydrate that we can do simply by doing the corresponding analysis where we measure the temperature change for all these.

Then we can have some oxidative decomposition of any organic substance in air or oxygen that means we are simply burning something so we can go for the typical decomposition of organic substance, if the organic substance is the solid one and in presence of air or some oxygen means excess oxygen or in pure oxygen your compound is typically burning because most of these organic compounds we know they are forming from carbon, hydrogen, nitrogen, oxygen, sulphur and all this so they will basically give rise to the corresponding water molecules, the carbon dioxide or the nitrogen oxides and all these.

Then we can have the thermal decomposition if we go for this in an inert atmosphere with the formation of gaseous products. So what are the differences between these two that decomposition of organic substance in air that means we are deliberately looking for oxidative decomposition but in presence of oxygen we are burning the material but when you put this in inert atmosphere like that of your nitrogen atmosphere or argon atmosphere because in preference sometimes we should take only argon atmosphere in lieu of nitrogen atmosphere because the temperature which is quite a very high and at that temperature we can have reaction with the nitrogen was all know the metal ions can form nitrites or sometimes in presence of more oxygen it can go for the nitrates or nitrites also.

So if the inert atmosphere is maintained by that nitrogen (())(9:53) this nitrogen at high temperature can react with material then that particular material is converted by forming the corresponding nitrates or nitrites will gain some weight but if the inert atmosphere is maintained by argon or any other inert gas it will not give rise to that sort of reaction or if you find that there is some gaseous product is eliminating like that of our carbonate material.

So immediately conclude at your sample is having some carbonate salt and that carbonate is giving rise to carbon monoxide as well as carbon dioxide. And one more interesting property of this TGA measurement because we are talking about all this in relation to the TGA measurement and we have introduced that you can have the corresponding thermobalance, so how we can monitor the magnetic properties so in relation to this magnetic properties.

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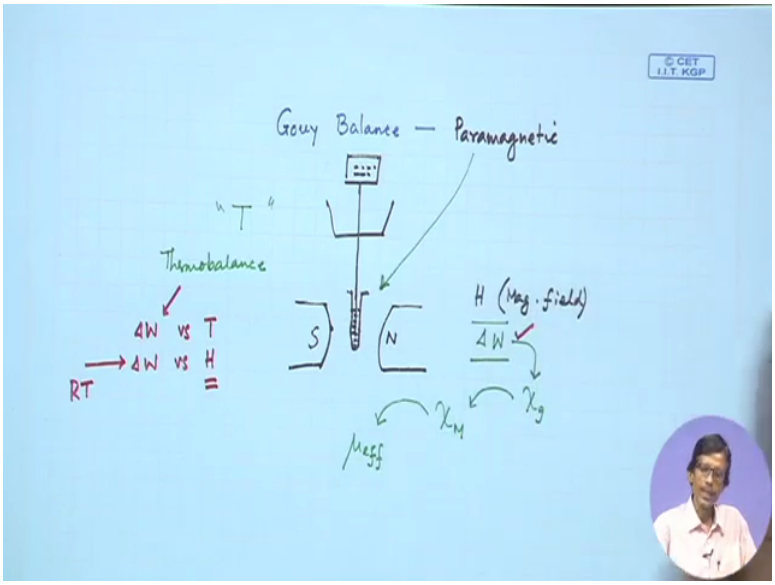

So just briefly we can see or know the thing that we can have some balance which is known as Gouy balance which is being utilised for knowing a material whether the material is paramagnetic or not. How it works? Because if the corresponding tube which we put on that balance is paramagnetic and the balance pan basically or we take the weight, so we have the pan of this things, so where we put the weight or digitally we can measure the weight and you have the corresponding tube so (())(11:43) tube is there.

So (())(11:45) tube is basically hanging over here and we take the weight and the sample is filled with this tube but if we place this particular one with (())(12:04) some magnetic so this basically the record digital recording of the weight change so in absence of magnetic field the H is the magnetic field. We take the weight of that particular sample and if these sample is paramagnetic one your this sample is paramagnetic one and in presence of a magnetic field there will be a weight gain so we are corresponding change in the corresponding weight so delta W.

So delta W will be therefore the corresponding paramagnetic property of this and which can be converted to the corresponding kai g value and the ground susceptibility value and then it can be converted to kai m value and then to new effective. So it is nothing but a very simple thing that instead of doing the temperature effect we measure the thing in presence of a magnet so now if we go or if we make this one a typical arrangement where we can also see the temperature effect that means you have the thermobalance.

So if we have the thermobalance and in that thermobalance what we see, we see again a corresponding change that means this delta W with regard to temperature and here we are talking the delta W versus magnetic field in terms of the magnetic field because this measurement we are doing at room temperature but here the temperature is varying. Now if we mix all these 3 that means we bring some thermobalance in a magnetic field, what is the effect? So different magnetic materials and we characterised in that way and one such characterisation is the ferro magnetic behavior.

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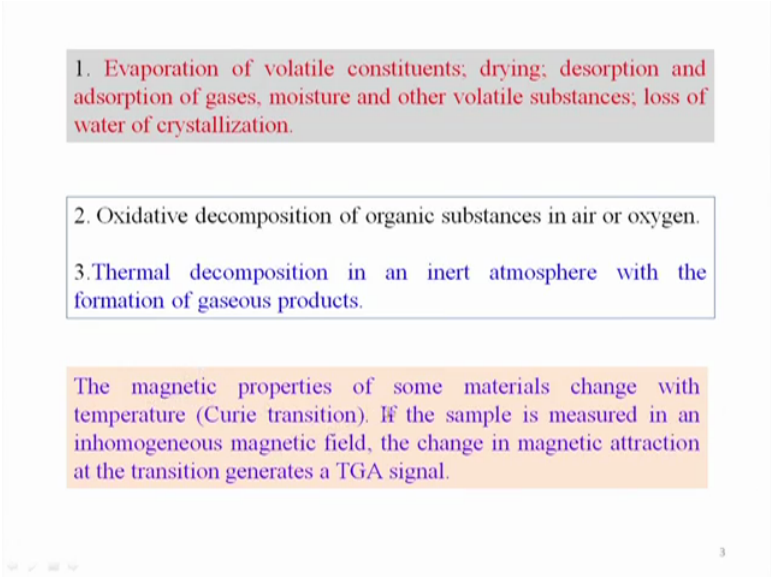

So the magnetic properties of some of these materials what we want to see with the temperature change so is the curie transition we all know the temperature change that is why some of these measurements we do at a very low temperature because the temperature effect is always there on the magnetic samples. So if the measurement of the weight change is done in an inhomogeneous magnetic field, the change in the magnetic attraction at the transition generates a TGA signal. So the presence of inhomogeneous magnetic field (col) can cause the magnetic attraction for the sample which is paramagnetic in nature or sometimes it can be a ferromagnetic sample also, so we get a corresponding TGA signal due to that particular effect.

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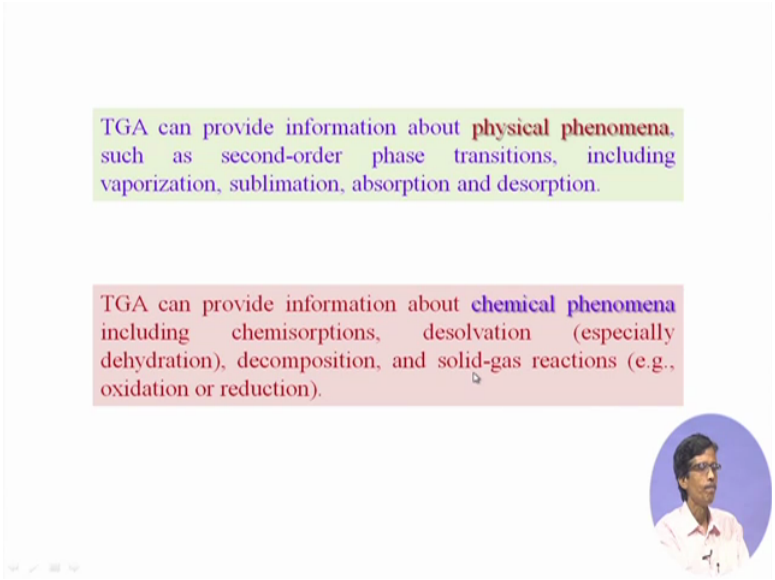

So these things therefore we find that this TGA gives all those good information and can provide information about the physical phenomena or the physical changes so what are those physical phenomena what we can see because even if you do not have any chemical change we can monitor in terms of the corresponding physical characterisation it can be metallurgical sample, it can be a material sample, it can be any other ore or minerals which can be characterised for their physical characterisation, such as you can have phase transition.

So if you have a second order phase transition which includes vaporisation, sublimation, absorption and desorption, so all these things that certain materials is not decomposing but it is vaporising but it is going for sublimation. We can monitor the particular change by your TGA. Then TGA can also provide information about the chemical phenomena, chemical phenomena is related chemisorption, chemisorption we all know so chemisorption are there then specially desolvation or the dehydration or we are removing the responding water from the solvent of crystallisation, so this can be a chemical phenomenon because the solvent of crystallisation is removed and if the water molecules are trapped within the crystal lattice, what we know that we get the regular crystal and the crystal form will change if we remove those water of crystallisation.

Then the organic compounds as we know or inorganic salts can go undergo decomposition and interestingly some solid can go for some solid gas reaction because you will know that the solids are reacting with some solutions or it is reacting or solubilizing in water molecules but directly we see some reaction with the gas molecules. It can go for oxidation or reduction or you can go for some gas sensing material, so the gas sensor we can develop if solid sensor

you can have and that can go for some sensing behavior by trapping the corresponding gas molecules we can have certain change so TGA analysis that material whether that material is useful for making a gas sensor we can analyse for that also.

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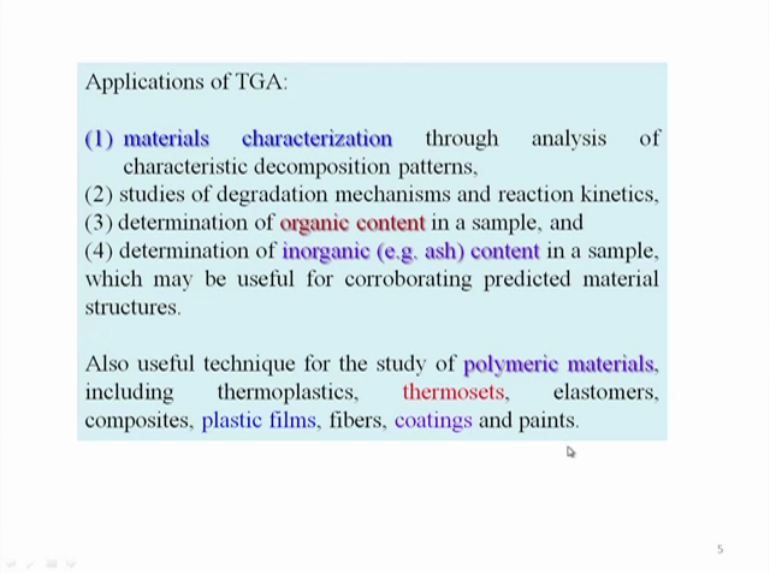

So altogether if we see that a huge number of applications we can have with this TGA so the huge number of applications first will come under our mind is the material characterisation, so far we are talking about the corresponding materials so any materials including your organic sample or organic molecules, inorganic salts we can characterise very nicely for its thermal stability also, so it can be characterised for its different decomposition pattern like that of your calcium oxalate or magnesium oxalate who will see.

Then degradation mechanism or the reaction kinetics those are very tricky process but you can also monitor those that what sort of degradation mechanism is happening over there and the reaction kinetics and high-temperature reaction kinetics the same time and if certain compound has some organic volatile material trapped inside, so the organic content or the organic matter present in some mud or in any other solid material, so volatile organic matter or volatile organic compound we call it VOC. So volatile organic compound can be estimated or calculated by doing this sort of thermogravimetric analysis.

Then determination of inorganic content that if the inorganic content is there it can be converted into some oxide or ash formation in a sample that can be analyse by TGA and it can also conclude about or it can predict about the corresponding materials structure because all these things will be related to the material structures. And apart from all these one useful

importance of the TGA is the polymeric materials characterisation so it comes under this material characterisation but in under the polymeric materials characterisation.

So anything of any sort of this polymer we can characterise such as thermoplastics, thermostats thermosetting plastics also, elastomers, composites, plastic films, fibers, coatings and sometimes even paints also that how far it is stable or how much it is stable in terms of the corresponding temperature rise. So what we see that the use of the thermobalance in such a way that we can see the first introduction of that particular thermobalance.

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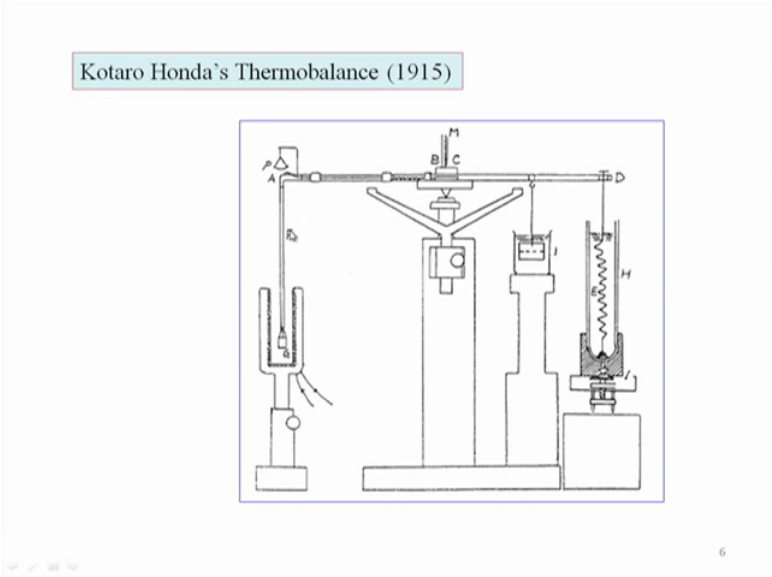

What we see for the example what we have seen or what we have told you that is Kotaro Honda's thermobalance it has been introduced as I told you in 1915 and the schematic of that thermobalance is not a complicated one it was his own original drawing which has been given so it has also some historical importance and historical perspective.

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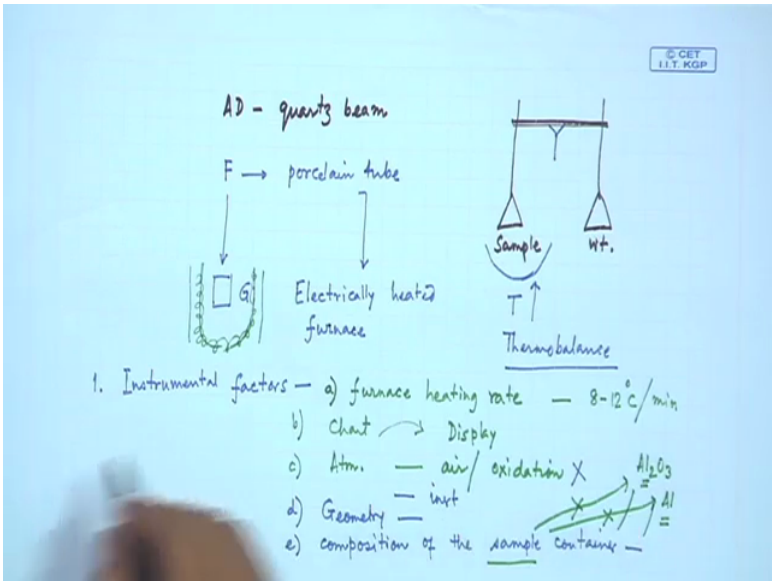

So the beam what we get this A and AD, AD is the beam so we have a AD quartz beam as we all know that a typical balance what is known that is this is can one arm and this is one arm another arm also so what we do we put sample in one arm and the weight on the other so that basic idea we here also will follow to take this and this is the balancing unit. So you have a AD as quartz arm and the interesting thing is that we have a porcelain tube F.

So if we see this F, F is a typical porcelain tube so this F is porcelain tube and this porcelain tube is goes inside so where we keep the sample because we have to have something that means we want to see the temperature effect on that particular sample so this porcelain tube goes into the furnace which is nothing but an electrically heated furnace. So is electrically heated furnace, so this electrically heated furnace useful to go for this particular measurement and this F is there for them connected to the sample holder or the sample which is nothing but your G.

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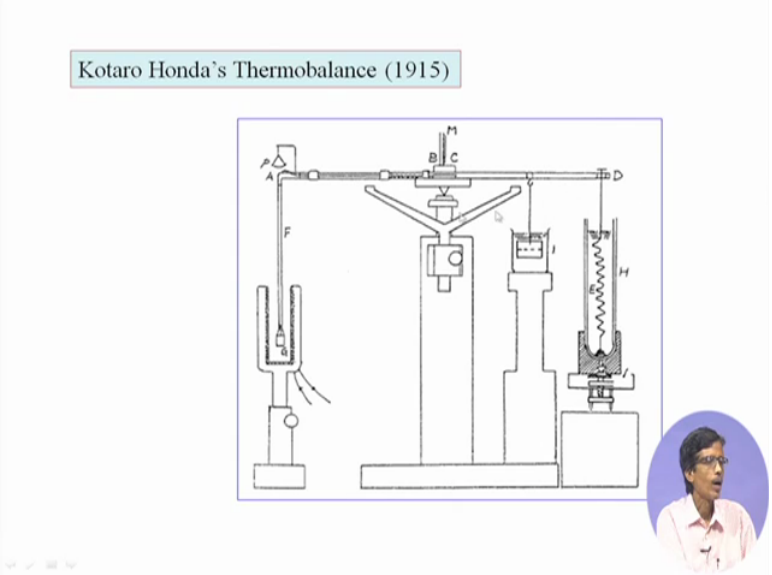

So this porcelain tube so from this quartz beam F is there and this is your G, so what we see that it is particular thing that if you have some mechanism such that we can measure this thing and G is the sample holder and you see that this is the 2 wire that is the electrical coiling is there such that this particular part is your furnace. So first it was developed in that way so furnace just simply heated so your sample will be heated and we want to see the temperature sorry the weight change. So if there is a weight change that means the weight is slow by slowly weight is reducing so that can be monitored over here.

So some damping arrangement some other damping processed is over here, so this is the entire thing such that on the right-hand side how much it is just tilting from this original position so that is basically monitored for your weight change and nowadays the digital balances are introduced and the digital balances are basically going for the corresponding modification of this thermobalance so historically this important thermobalance has been modified to nowadays or the modern thermobalance what we use for TGA or DTA measurements.

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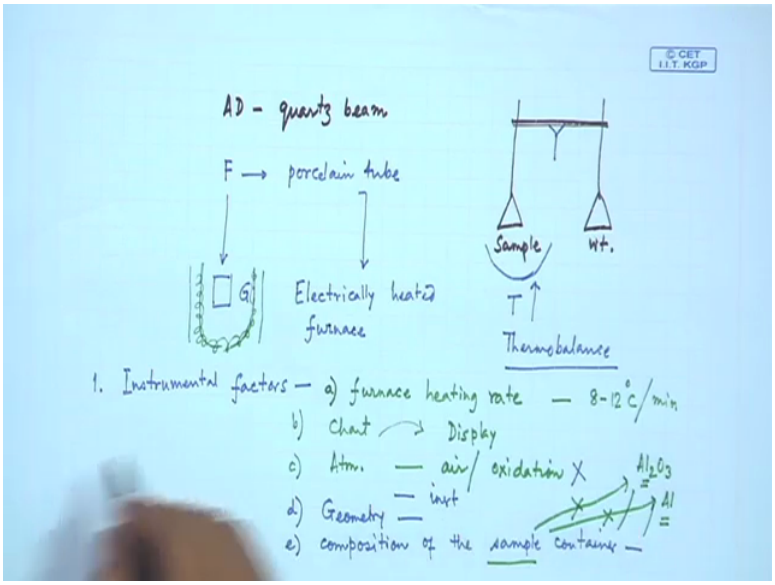

So in all these cases what we see that this instrument and so this is a very simple and basic instrument what we see is your thermobalance and we should see something related to its corresponding instrumental factors, so instrumental factors we should see those instrumental factors are very important to understand because we are handling something where the sample G is kept inside the furnace, so and the furnace we have seen just now that it will be electrically coiled up for the heating process, so this instrumental factor is the corresponding furnace heating rate.

So this furnace heating rate is important and in most of the time even from the Honda's time that it is in the range of 8 to 12 degree centigrade per minute so we should adjust this particular rate otherwise if we go for very fast heating so your trace or the plot the corresponding thermogravimetric analysis would be different. Then immediately we go for the recording chart or the chart speed because that time we were using the recording chart nowadays it is directly going to the computer monitor so but the handling of those data points and their accumulation and ultimate the display, so now it has been changed to the display unit.

Then is dependent on the furnace atmosphere as we have seen just now and if it is air we can expect that there is some oxidation of the material, so we can have air or the can have some inert atmosphere where we can we do not expect any kind of oxidation or sometimes the typical decomposition. Then the corresponding geometry or the sample holder and the furnace geometry also, so the geometry of these materials can also plays some important role and then composition of these sample containers which is important.

So composition of the sample container, where we keep that particular sample that means the crucible nowadays we use aluminium crucible sometimes we can use only aluminium crucible. So these things so these materials that means if we use some aluminium-based crucible aluminium or aluminium metal foil, so this sample should not react those materials otherwise there will be some other reaction we cannot monitor and which we are not want to see for this particular process.

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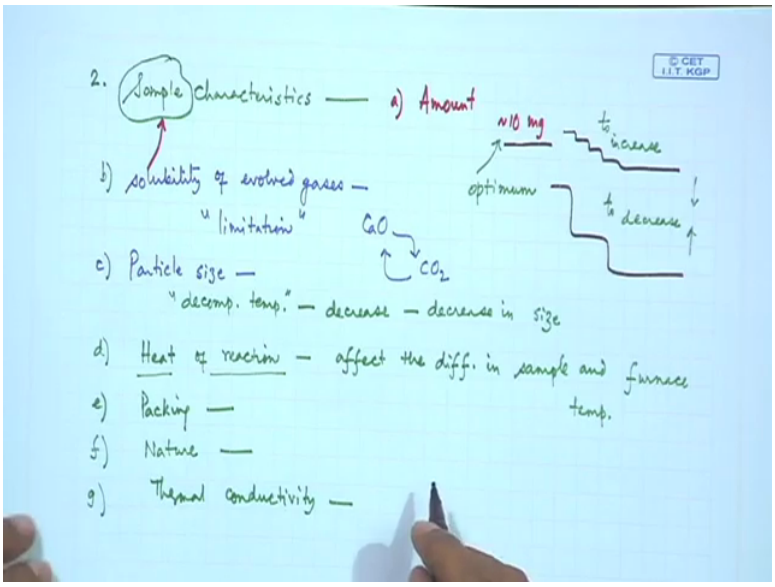

Then these are all instrumental factors so after all these instrumental factors can have the sample characteristics. Number 2 is sample characteristics what we can see it is very important because this will not change from the history old thermobalance to the modern-day thermobalance because sample we have to monitor by yourself so the corresponding one the first thing is the amount so you have to have some optimized amount within the range of say 10 milligram we usually take for with the modern thermobalance or modern thermal analysis apparatus so if the amount of sample is less what we see this staircase type of thing are very close by.

So what we should do for this and what we should do if a plot is like this that means your weight loss is more over here and your weight loss is less depending upon the amount of sample you have taken. So if the plot is like this you have to increase the amount of sample to be taken and if the plot is like this we have to decrease the amount of sample to be utilised. So this optimum amount is therefore important to get a reasonable so that corresponding plot which will be in between this neither this nor this, so in between plot we should get.

Then in the next step of precaution what we can see is the solubility of evolved gases of evolved gases what we can have because that is the serious problem if the gas what is coming out which is soluble in the melt or the product what we are getting so it is basically a limitation for the process and we should be very much careful to see that the whatever gas is coming out. Suppose your calcium oxide is forming by the elimination of carbon dioxide from calcium carbonate but if this calcium oxide is soluble in in this particular gas we get something different form that means the calcium oxide will still be there and we will not be able to see the weight change.

Then we have the corresponding particle size because we should have good powder sample because the corresponding decomposition temperature will decrease with the decrease in size so we should be very much careful about handling the powder sample and should be not be very quartz sample, so what sample will have higher temperature so the decomposition temperature which is very right one depending upon the nature of the other physical characteristics of the sample.

Then someone more important property that is the heat of the reaction we do not know anything about the heat of the reaction when we first do it, so heat of reaction can also play some important role so it can affect the difference in sample and furnace temperature. So we should be careful about the heat of the reaction for a particular reaction what we are monitoring, so then the packing we should also see how closely packed within the crucible and definitely the nature of the sample.

And lastly we should have some idea about the thermal conductivity so you see the situation is getting much more complex for only the sample characteristics so all these things and all these precautions we should take and we should know about the corresponding structure of the material where we want to see that how the size, the packing, the nature of the thing and the thermal conductivity because of thermal conductivity can also change when we go for the corresponding centering and swelling of the sample, so all these things will be very much required to monitor to take the corresponding rights sample all these thermal measurements, okay. Thank you very much.