Nanotechnology Science and Applications
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Lecture - 07
Calorimetry

Hello, in this class we are going to look at Calorimetry the past few classes, we have been trying to bring information together to look at the thermodynamics associated with the nanoscale or any aspects that you need to look at little bit more carefully with respect to the nanoscale and how thermodynamics can be used to get some useful information once you go down to the nanoscale.

So, in the context of thermodynamics I mean you are used to seeing a lot of equations in your textbooks and working with problems and so on. Experimentally with respect to thermodynamics, the technique that is most important I would say or used extensively is this technique called calorimetry and so that is the technique that we will look at briefly through this class today and in particular, we will look at some variations of it and so. So, this is what we will do today.

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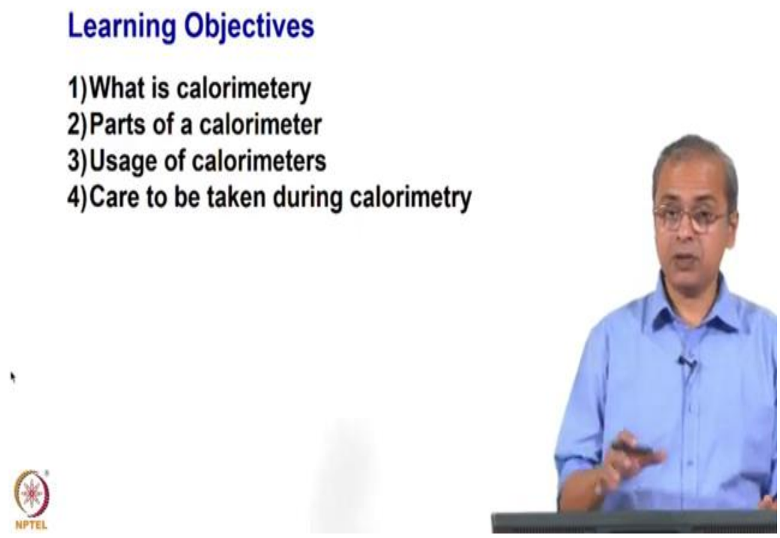

Learning Objectives

1) What is calorimetery
2) Parts of a calorimeter
3) Usage of calorimeters
4) Care to be taken during calorimetry

So, our learning objectives for todays for this particular class, what is calorimetric. So, we will look briefly at what it is that is in this context of calorimetry, what all are the things that come together. What are the parts of the calorimeter and what are the critical parts and what exactly they do? usage of calorimeters in what way we are using them and any kind of care that needs to be taken during calorimetry.

Of course, if you look at courses in chemistry and so on, you will have or even a full-scale course on thermodynamics you may have much more detailed information on calorimeters. We will look at it in the context of our discussion in this core in this course and so, we will the level of detail will be a put together accordingly. So, we will begin by looking at this first point, what is calorimetry.

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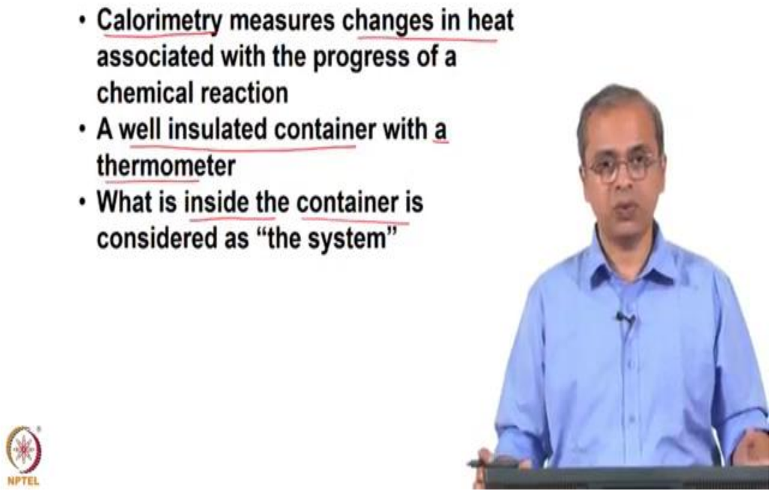

- Calorimetry measures changes in heat associated with the progress of a chemical reaction
- A well insulated container with a thermometer
- What is inside the container is considered as "the system"

So, in fact, calorimetry simply measures changes in heat associated with progress of a reaction. So, typically we are associating it with chemical reactions of different forms, you can also have phase transformations and things like that which are maybe relevant in say in the metallurgical context or a material science context, but at some fundamental level they are all chemical changes of some nature.

And so, calorimetry measures changes in heat associated with the progress of a chemical reaction, it is kind of important because that heat is what you once you get a sense of what is that heat chain that is involved, you can extract different thermodynamic parameters out of it and that is what you see as thermodynamic data. So, when you see thermodynamic data when you, look up the specific heat and many other pieces of information in manuals or tables of a different sort.

They are all typically coming out of data from a calorimeter where you are essentially measuring changes in heat. So, what is a calorimeter? A calorimeter is at some fundamental level it is primarily well-insulated container of some sort in which there is a thermometer. So, you have a well-insulated container and there is a thermometer, it has a thermometer. So, this is at some fundamental level this is a calorimeter, you can make inexpensive calorimeters, you can even make one at your home we will discuss that briefly which will in principle do this job and it's very likely that that is how they started out making calorimeters.

So, in principle, you can do this job with essentially in an inexpensive calorimeter at home, but in general, you need much more sophisticated calorimeters primarily with to look at highly sensitive changes which maybe with small sample sizes and still you are trying to measure some specific changes in the process. So, this is the idea of a calorimeter and whatever is inside this container whatever is inside this insulated container is considered as the system and of course, you always hear this thing in thermodynamic context of the system and the surroundings.

So, essentially whatever is inside is the system and it is a well-insulated system, it stays inside it at this point inside a calorimeter it is not really in direct communication with what is outside which is the surroundings. So, this is the system that we are interested in.

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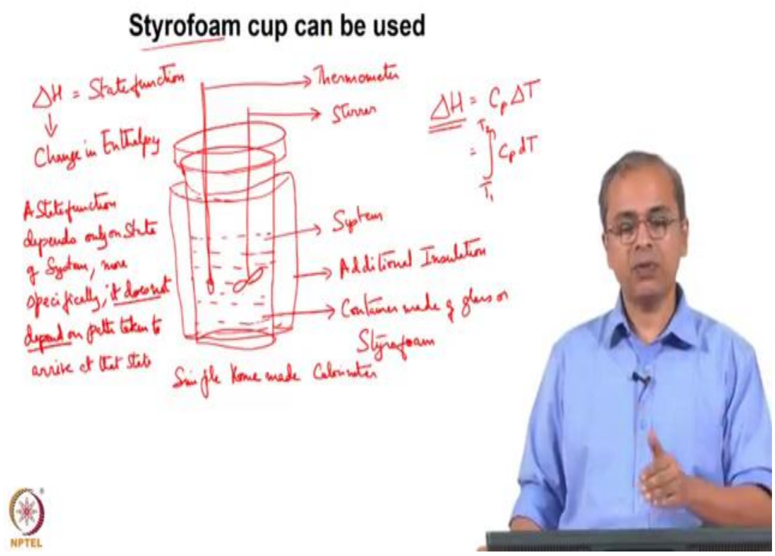

Styrofoam cup can be used

ΔH = State function
↓
Change in Enthalpy

A State function depends only on State of System, more specifically, it doesn't depend on path taken to arrive at that state

$\Delta H = C_p \Delta T$
$= \int_{T_1}^{T_2} C_p dT$

So, as I mentioned the, you can actually make a calorimeter at your home and it is a very straightforward construction and a good example of that is any insulated container so, for example, you can take a Styrofoam cup, you can also take a flask of some sort which is well insulated or even a say a glass tumbler over which a glass tumbler of some sort over which you put some additional insulation.

So, primarily you have some kind of a tumbler or a glass and we add some other insulation on top of it. So, you can wrap some other insulation all around. So, you have some insulation going around. So, there is some insulation that is wrapped around this glass so that you have additional insulation in the system and it is very difficult for the heat outside to go in, very difficult for heat inside to go out. So, that is basically what you have, you have to naturally then you have to have some kind of a lid on top which also adds to the insulation and in this, you have to have a primarily two things going into it.

So, one would be a thermometer and so, this is some insulation and what you have ins here, container made of glass or in this case, for example, we have mentioned Styrofoam, something that is inherently insulating. So, this is what we have one additional thing that we usually have is a stirrer. So, you can have a stirrer and the stirrer it can be of different aspect physical shapes, but essentially the idea is that you should be able to do something outside the chamber which will help stir something inside the chamber.

So, inside it, you have some liquid for example, and so, you have some liquid here. So, you can do a number of different things so, you have this liquid here you have a water, for example, you can just add some salt to it and then you can see if there is any change in temperature. So, you can do that kind of measurement.

So, you basically have some liquid here and this is essentially your system. So, you essentially have an insulated setup which inside which you have some substance, in this case, I have just use the example of water and in that water so, you put this thermometer into this water, you put this stirrer in the water you stir it gently for some few minutes and then you check the temperature, you check the temperature and you see that it is stable there is no changes in temperature.

At that point, you can perhaps add some salt to it or you can add you can have two different liquids which you can mix there and so on and then again you close this container, you measure the temperature so, you wait for some time and then you see what the temperature is. So, you will get that you will find that if there has been a change in temperature and it is simply some temperature associated with say the specific heat of that system being.

So, if you have a specific heat of the system involved and then on that basis, you have some change in temperature. So, you will have,

$$\Delta H = Cp \times dT$$

$$\Delta H = \int_{T1}^{T2} CpdT$$

so, this is basically what we have coming in a calorimeter.

So, this is as I said a very fundamental measurement because once this change in heat that is involved, you can get various other pieces of information about the thermodynamic activity that is present in the system and you can get some fundamental quantities out of this process.

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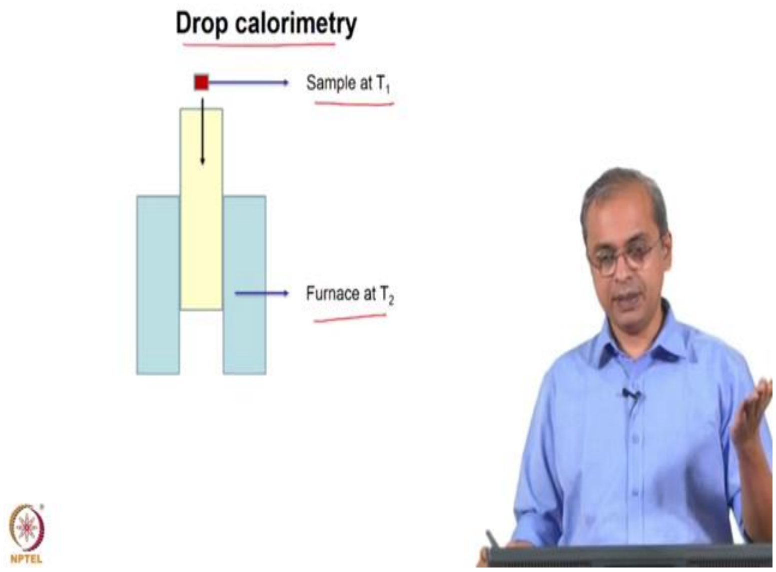

Drop calorimetry

So, if you look at the calorimeter you should you can also see that there are various variations on it. So, if you for example, if you look at what we just saw here, this is like a very simple homemade calorimeter so, and you have a very expensive one. So, they primarily differ in how sensitive they are in terms of being able to measure changes in temperature and any other control controllers that you have, the whole idea of calorimetry is based on this fact that the ΔH that we measure is called a state function, it behaves as something called as a state function.

So, ΔH is a state function in ΔH is also the change in enthalpy. So, this is basically the heat involved in a process is referred to as the change in enthalpy associated with that process and it turns out that it is a state function that is how nature seems to behave and that is what they have discovered about nature that it is a state function. What is the meaning of it being a state function, the meaning of something being a state function is that the value that it takes depends only on the state at which it is?

So, at first glass maybe that does not seem like much, but it is very critical. A state function has a value that depends only on the state of the system more specifically; it does not depend on the path taken to arrive at the state. So, this is a state function, a state function depends only on the state so, it only depends on the state of the system specifically more specifically; it does not depend on path taken to arrive on that state.

So, it does not depend on the path taken to arrive at the state that is the important thing and that is very fundamental to how the calorimeter works because you are not because it the enthalpy behaves in this manner this the fact that it is a state function, it does not matter whether you start at room temperature and you are trying to find the change in enthalpy for some material going from associated with some material going from say room temperature to say 80ºC.

Let us say you want to find out the change in enthalpy associated with this material going from room temperature which may be 30ºC to a temperature of 80ºC so, that is 50ºs change in temperature. So, this 50ºs, you can accomplish in hundred different ways instead of going only to 80º C, you can go to 150º C and then come back to 80º C, you can sit at 60º C for 2 hours before you move up to 80º C, you can go gradually from 50º C to 80º C.

It just does not matter which path you take you started at 50º C I am sorry, you started at 30º C and you arrive at 80º C as long as your starting point is 30º C and your finishing point is 80ºC.

The enthalpy change will be exactly the same and that is very fundamental to how the thermodynamics of the system works and that is how nature behaves. So, this ΔH is a state function and calorimeter is a process, calorimetry is a process by which we look at heat exchanges and therefore, the temperature and associated temperature changes and from that we extract this enthalpy information and because it is a state function, we do not worry about how it arrived at that location, we are not concerned about how it arrived at that location as long as it arrives at that location, whatever is the difference in heat is all that we need to look at so, this is the point here.

So, for example, in this Styrofoam system, we could add salt slowly, we could add salt as a spoonful of salt I mean say the same amount of salt, I could have add particle by particle by particle into it, I could add it all in one go it does not really matter at the end of the day, it will still be the same amount of salt in the same amount of water and therefore, the enthalpy change will be the same so, that is the idea here. Now, many times in thermodynamic systems, we are interested in the properties of the system at high temperatures.

So, not at room temperature, but at high temperature is the point that we are interested in looking at the system and therefore, there are some variations on this calorimeter that are used. So, one is called a drop calorimeter so, again principle wise it is the same, but operationally there are some differences, you simply have a furnace at the temperature T2 and a sample sitting at temperature T1 and then you drop the sample from T1 at T1 into this furnace at T2 and then you look at what is the heat involved in the process of this temperature this sample reaching this temperature T2.

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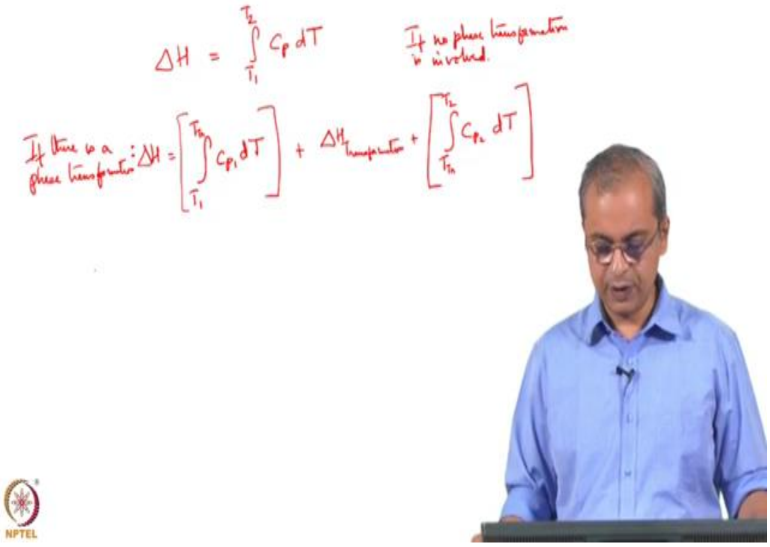

$$\Delta H = \int_{T_1}^{T_2} C_p \, dT$$ If no phase transformation is involved.

If there is a phase transformation: $\Delta H = \left[\int_{T_1}^{T_{tr}} C_{p_1} dT\right] + \Delta H_{transformation} + \left[\int_{T_{tr}}^{T_2} C_{p_2} dT\right]$

So, if you look at it, the ΔH assuming that there is no phase transformation, assuming there is no phase transformation when it goes from T1 to T2 then,

$$\Delta H=\int_{T1}^{T2} CpdT$$

Here, we will also assume that we are working with one mole of the system and so, you know. So, if it is molar specific heat then we are we do not have to make any other adjustments to it, we get

$$\Delta H=Cp \times dT.$$

So, this is the way we would do it if there is no phase transformation. Now, on the other hand, you could also have the possibility that as you go from T1 to T2, there is some temperature in the middle some transformation temperature Tr at which there are some phase transformation that is occurring. So, then what we will have some variation on this, but essentially still in the same mode. So, you will have ΔH equals so, we will now go from T1 to T transformation Cp we will say that it is first phase 1.

So, Cp_1dT then you will have. So, this is one term then you will have ΔH transformation and then you will have one more term which is from T transformation to T_2Cp_2dT. So, this is how you will go from one phase to another and if there is a phase transformation. So, this is in the case that there is a phase transformation, if there is a phase transformation then you have this equation.

So, you can see that you can put something into a calorimeter and then you can get this information and you can work independently between T1 and Tr, you can work independently between Tr and T2 and you can do the whole thing, you can get ΔH transformation. So, a lot of different pieces of information you can get out of this system.

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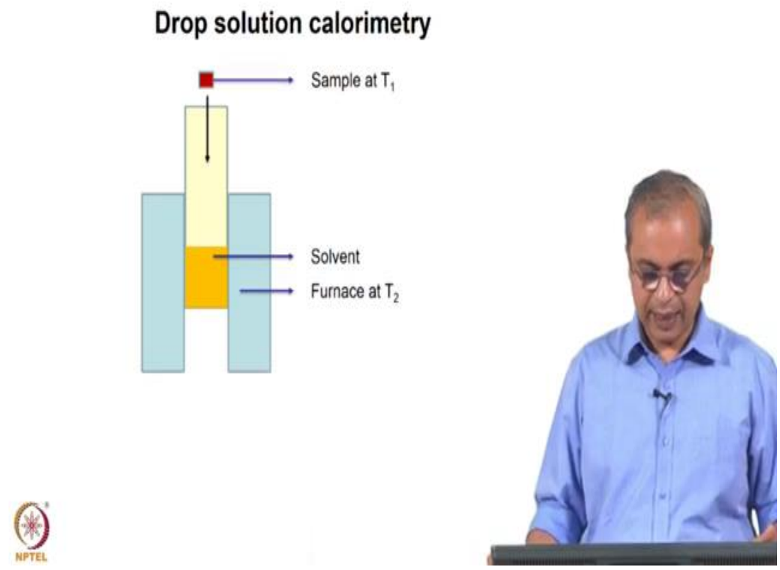

Drop solution calorimetry

There is another version of this which is called a drop solution calorimeter where we have some high-temperature solvent into which you put a tiny quantity of some other material which now not only reaches the temperature T2, it also goes into solution at the temperature T2. So, I will also point out that this is I have written this kind of in an elaborate way here and if the Cp is not very different in the two phases, you may simply have integral Cp dT from T1 to T2, but you cannot assume those things.

So, if it is the same then it will be the same otherwise you will have more detailed information of this sort. So, for example, if you do this drop solution calorimeter metric then we can write a similar equation.

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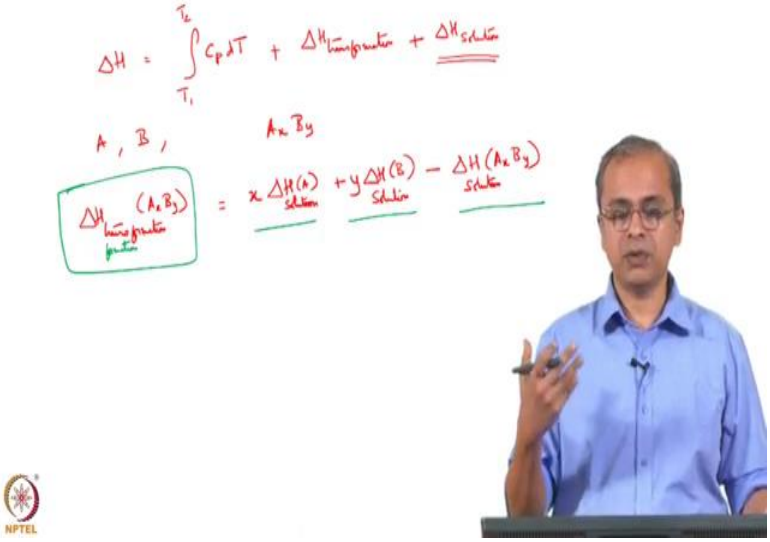

$$\Delta H = \int_{T_1}^{T_2} C_p\,dT + \Delta H_{transformation} + \underline{\underline{\Delta H_{solution}}}$$

A, B, $\quad A_x B_y$

$$\boxed{\Delta H^{(A_x B_y)}_{\substack{transformation \\ formation}}} = \underline{x\,\Delta H^{(A)}_{solution}} + \underline{y\,\Delta H^{(B)}_{solution}} - \underline{\Delta H^{(A_x B_y)}_{solution}}$$

So, you can have ΔH is equal to integral T1 to T2 Cp dT assuming that there is no change in the specific heat between T1 and T2 if there is a phase transformation, you will have ΔH transformation and if the since you are now put it into solution, some solid solute went into solution, you have ΔH solution.

So, you have these terms ΔH that you measure will be all these terms and of course, as I said, here it is only it is between T1 and T2 if you have a transformation in which if there is a transformation and the Cp changes then you will have T1 to Tr with the first Cp and then Tr to T2 and the second Cp. So, the nice thing about doing this is that if you have this ΔH solution and you have this separately for a phase A and for a phase B then you can find out for a transformation.

Let us say you can you form a phase A_x B_y then we write,

$$\Delta H_{Ax\rightarrow By} = x\Delta H^{A}_{sol} + y\Delta H^{B}_{sol} - \Delta H^{Ax\rightarrow By}_{sol}$$

So, you can do the drop, it is called the drop solution calorimetry, you can do drop solution calorimetry for the A_x B_y system so, you can do that here so, you can for each of these you can do separately.

So, for A_x B_y, you can do drop solution calorimetry, for B alone you can draw drop solution calorimetry, for A alone you can do drop solution calorimetry. So, once you get these three pieces of data of the drop solution calorimetry for A, for drop solution calorimetry for B and for the alloy A_x B_y then you can put this information together and you get this transformation of A_x B_y.

So, so, you see you can play around with these different pieces of information that you can get from the calorimeter and then you can do some calculation and you can arrive at the transformation for different phases that may form for the formation of transformation of formation in this case, for the A_x, B_y system. So, one of the things you would also be careful about is that especially when you do this calorimetry in the nanoscale when you do in the nanoscale, many materials because they have high surface area can also be quite reactive and often for example, they may be hygroscopic so, they may have pulled in some water.

So, you have to account for the water also because when you go from temperature T say T0 to T1, if you are also you are not just heating the sample, you are also heating things like the water associated with this sample and then, therefore, you have to account for it when you. So, when you write this equation you cannot simply write only for A_x and B_y and so on, you would also remember how many moles of water were present and then account for it and those are all things the finer details that you need to look at when you do calorimetry so that your equation gives you the value that you are looking for.

Now, I showed you at least a few different versions of calorimetry. So, for example, and this is all at constant pressure so you get Cp values there is also a different version of it called a bomb calorimeter where there is a container inside another container. So, the container where the reaction is going on is tightly controlled in volume and therefore, you get and can withstand significant pressures and that is constant volume measurement and so, you get a Cv value out of it.

So, like this you have a lot of different variations and I said as I said this is kind of fundamental from the perspective of thermodynamics because it gets you this Cp value Cv value and so on from which you can get the enthalpy values or you can get enthalpy from that you can get the Cp values and much of the thermodynamic data that you get in terms of free energy changes and so on are all related to this enthalpy changes and therefore, this is very important.

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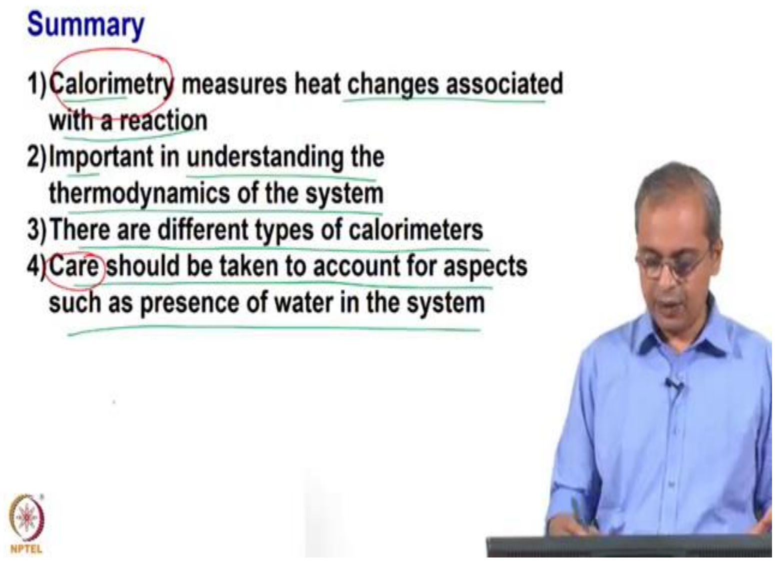

Summary

1) Calorimetry measures heat changes associated with a reaction
2) Important in understanding the thermodynamics of the system
3) There are different types of calorimeters
4) Care should be taken to account for aspects such as presence of water in the system

So, to summarize what we discussed with respect to the calorimetry, calorimetry measures heat changes associated with the reaction. So, that is the first thing that we want to keep in mind, that it measures heat changes associated with the reaction. It is very important from the perspective of understanding, the thermodynamics of the system because many of thermodynamic parameters can be calculated directly out of the enthalpy data that we get and because from there we will get the Cp and Cv values and from there we get all the other information.

So, therefore, from foremost thermodynamics people working with thermodynamics, calorimetry is very fundamental equipment they do a lot of theoretical work if you ask them for experimental work thermodynamics people who are doing experiments with respect to thermodynamics will often require a very high precision calorimeter. We also saw in this class that you can make a wide range of different calorimeters starting with something like a small glass a cup, ceramic cup or a glass cup or Styrofoam cup at your home.

The primary requirement being that it has to be well insulated and then you have a thermometer in it and a stirrer in it and then you can measure some changes in temperature due to some reaction that is happening there. More sophisticated calorimeters primarily are much more sensitive to changes in temperature and are much better insulated and therefore, they isolate the system in a much more well-defined manner and they are, therefore, naturally quite a bit more expensive.

You can run the same experiment I mean to the extent that it is safe to do those experiments, you can run the same experiment in these different types of calorimeters. And, you will get answers at least the trend will be the same you will see the similar kind of trend if it is an exothermic reaction you are going to measure increase in temperature if it is an endothermic reaction you are going to see a drop in temperature and so on. And so, that measurement is going to be there. So, the difference primarily lies in exactly how much of a temperature drop you measure or how much of a temperature increase you measure.

So, you may be off a little bit and therefore, that will change the value of ΔH that you are thinking that you have arrived at with respect to what has actually happened in the system and that is why your experiment may differ from what is there in the literature and that is the point that you have to remember. I also indicated that there are different types of calorimeters not simply in terms of the quality of the build or the precision or the level of insulation and so on.

We also have some variations based on whether you want to measure Cp or you want to measure Cv or you are trying to do a measurement which is closer to room temperature relatively speaking or you are looking at measurements which are at much higher temperatures. So, for example, the drop calorimeter and the drop solution calorimeter that I discussed would be the kinds of calorimeters you would work with if your research area is in the area of ceramic materials.

So, there you are already is talking of systems that require much higher temperatures where we will see phase changes. So, if you are trying to compare different phases of the system and they say the relative stability of those phases then you need to have a calorimeter which can operate at those higher temperatures for you to see the relative stability of those two and phases and to make some judgment on it base make some measurements first of all about those related phases and on the basis of those measurements make some judgment.

So, that is why you need those calorimeters such as the drop calorimeter and drop solution calorimeter. Care should be taken to account for aspects such as the presence of water in the system this is very important particularly when you go to the nanoscale, you have to be careful and alert to things that may adhere to the system materials that you are working with. So, you may be thinking that you are working with say zirconia and you are primarily working with zirconia.

But it may not be only zirconia, you may have some water associated with its hygroscopic materials, the hygroscopic tendency of the material may be more pronounced at some scale and it may also vary from face to face. So, one phase of a particular material may be more hygroscopic, one another phase may be less hygroscopic and so on. So, you should be aware of what is the water involved and there are ways in which you can subtract off the water from the system and therefore, talk only of the system at hand.

So, that is the kind of care that you need to take. So, in summary, the calorimetry process is very useful for thermodynamics, you simply have to take additional care of how you go about it and you have different possibilities or how you can utilize it. So, that is our summary for this particular discussion, we will look at a little bit more on how it impacts some calculations going forward and then try to see what impact it has in the nanoscale.

Thank you.