**Characterization of Construction Materials**
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**Lecture 7**
# Calorimetry: Introduction and types of Calorimeters – Part1

Hi everyone, today we will discuss one of the important technique which is used to understand construction material that is Calorimetry. So just to begin with, what does Second law of Thermodynamics say, change is inevitable. Basically, everything naturally tends to its most stable state. So, some materials benefit from the change becoming more useful. But for most materials what happens change presents reduction in useful properties and loss in quality.

So, for many materials around us changes can be obvious like discoloring of paint for an example or rusting of metal, you have seen etc. Other changes can be subtle not as obvious you cannot see it such as polymorphic changes in crystal, fatigue in metal, surface absorption of vapour. In majority of cases changes can have a considerable influence on the useful properties of a material.

So, calorimetry has found its value for recognizing these subtle differences which you cannot capture using any other technique. So basically calorimetry can quantify change in terms of rate, how much and the probability of a change to occur.

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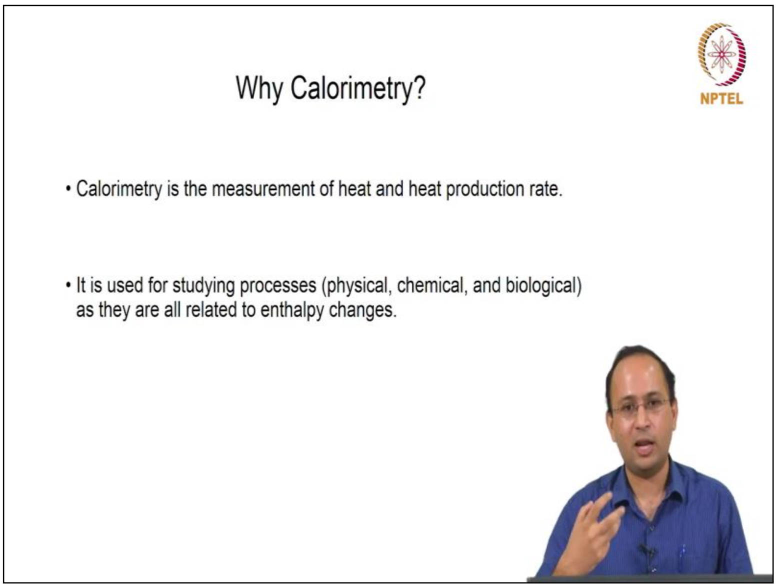


So, we are talking about change and the kind of change so, the first question we address is why we need calorimetry. Calorimetry is nothing but the measurement of heat and heat production rate. It is used to study processes ranging from physical, chemical and biological as they are all related to enthalpy changes. As long as there is enthalpy change there will be heat signal coming out of a system and as long as we can measure that heat we can use this technique.

So, basically calorimetry is made of calore is a latin word which means heat, metric is made from Greek word which means to measure hence it is measurement of heat.

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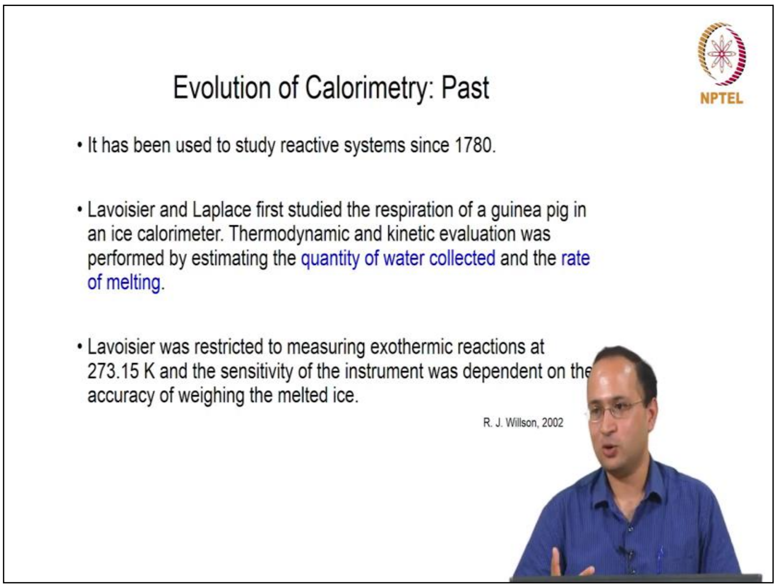


In this lecture we will see how it was developed. It is very important to know the history, where we are and how we come to where we are, how the technique was developed and what is it about; and what are the applications because that is also important to know where it can be used. We will look into the variety of applications then we will focus on its application to understand construction materials like cement for an example or mortar or concrete.

If you check the history Calorimetry has been used to study the reactive systems for a long time more than 200 years since 1780. Reactive system, please pay attention to the word reactive as long as there is some reaction because we are talking about change. So it has been used to study reactive systems, so what was the first instance if you look at the history. You find that it is very interesting study by Lavoisier and Laplace, they were the first ones to develop this ice calorimeter.

They studied the respiration of a guinea pig in an ice calorimeter. Basically, they were looking into thermodynamic and kinetic evaluation by estimating the quantity of water collected. So it is about guinea pig respiration when as long as there is a respiration, it will melt the ice and they were quantifying the water which was being melted.

The two important things to be understood in this context are the amount of water which is formed through melting and rate of melting. So these people for the same purpose used the ice calorimeter. Basically they were just measuring water. Obviously, you need a good balance. So Lavoisier, their study was restricted to measuring exothermic reaction. We are talking about the exothermic reaction means the heat is released and the same is used to melt the ice. The sensitivity of that instrument was dependent on the accuracy of the weighing of melted ice.

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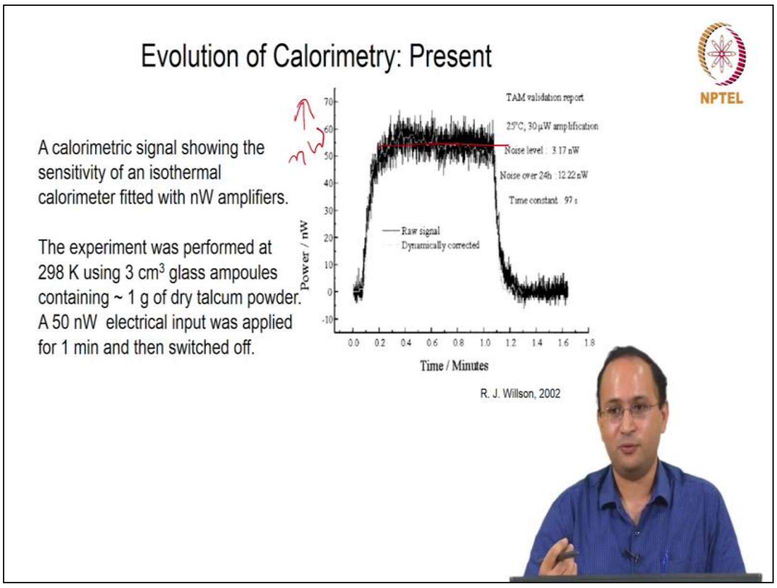


But now things are different and with the advancement of technology, we can measure signals in the order of nano-watts. So here, what you see is a Calorimetric signal showing the sensitivity of an isothermal calorimeter fitted with nano-watt Amplifiers. This experiment was performed at 298 Kelvin using 3 cubic centimeter glass ampoules, containing 1 gram of dry talcum powder. They put 50 nW electrical input in the system and you can measure the signal in few seconds. The idea of showing you this is that we can measure the signals in the order of nano-Watts with the use of current technology.

We can also measure very slow reactions where we have a signal in micro watt order, that is very small.

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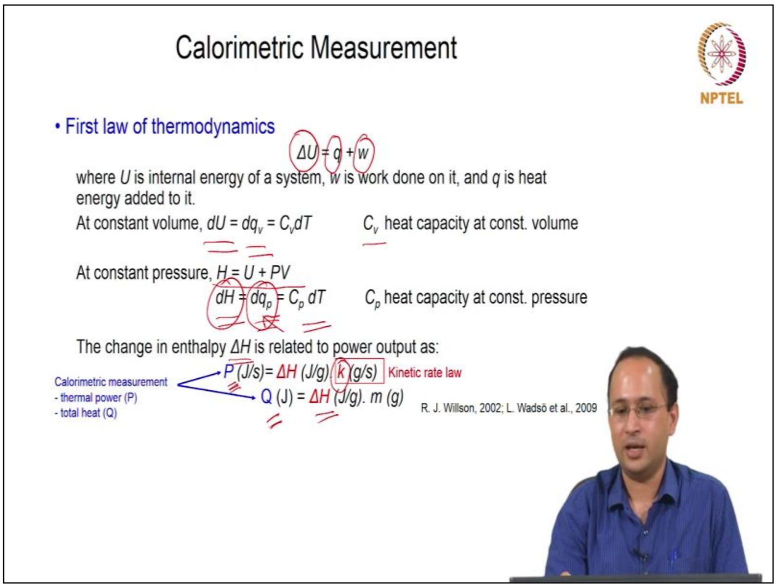


As long as you can measure the heat you can use calorimetry but what we get from calorimetry and how we can use it is discussed here. As we know about the first law of thermodynamics that says the change in the internal energy of the system is equal to heat energy which you put in plus work done as shown in equation below:

$$\Delta U = q + w$$

Where, u= internal energy of the system

q= heat energy added to system

w= work done

Now, for constant volume, the work done will be zero, so, du- the change in energy can be related to the change in heat at constant volume which equals to Cv dT as shown in equation below.

$$du = Cv\ dT$$

where, Cv is the heat capacity at constant volume.

Similarly, if you look at the constant pressure so, enthalpy H is equals to u plus PV, now the change in enthalpy dH can be related to change in heat at constant pressure, which equals to Cp dT as shown in equation below.

$$dH = Cp\ dT$$

Where Cp is the heat capacity at constant pressure.

For measuring the enthalpy coming from different processes all we need to measure is the ‘Q’ or the heat. So basically, the change in enthalpy which is ΔH can be related to the power output because it is among the two signals which are obtained from calorimeter namely P and Q. P is nothing but thermal power. Power is in the units of watts or joule per second. So we see that the power in Joule per second can be equated to ΔH which is the enthalpy in Joule per gram times the rate K which is expressed in gram per second. This gives information about the kinetics of the reaction

$$P(J/s) = \Delta\mathrm{H}(\mathrm{J/g}).\,\mathrm{k}(\mathrm{g/s})$$

So, thermal power is P and you can also get Q which is the total heat by integrating power over the time period. This 'Q' is the total heat which is released during a process. Obviously it will be equal to ΔH times mass.

$$Q(J) = \Delta\mathrm{H}(\mathrm{J/g}).\,\mathrm{m}(\mathrm{g})$$

So, from calorimetric measurement you get these two quantities P and Q. And by knowing P and Q you can get ΔH, and similarly, you can get K which is kinetic rate law and this tells about how fast processes are taking place and whether it is a decaying process or something else. By these two measurements we get to know lot about the system. So, basically you can see here how powerful it can be right just by measuring having these two measurements. You can tell lot about the system.

Any process if it is taking place, you always want to know how fast it is taking place. For an example, consider rusting of a metal, you want to know how long will it take for whole metal to get rust. Also you want to know what will happen, after five years or ten years, how much material would have been degraded till that, so this all you can only find out when you know the value of K.

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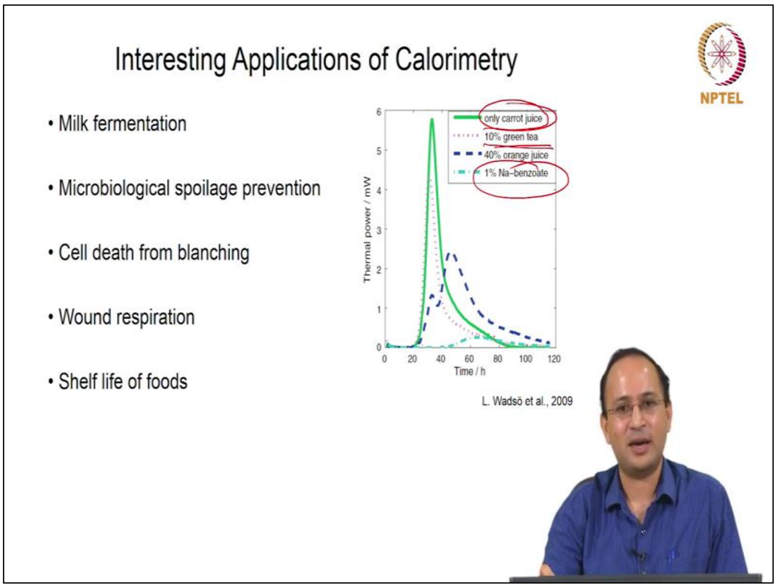

Now, we look into some interesting applications of calorimetry. So now, we know the basics that calorimetry is nothing but the measurement of heat which could be either heat rate or total heat. The milk fermentation is an application of isothermal calorimetry as because the microbiological fermentation produces heat. It is used for mapping the properties of microbial culture used for assessing differences between different cultures, measure their doubling time, how fast they grow and looking at the influence of additives because we are also talking about the fermentation as we are interested in it.

Another example could be microbial spoilage prevention. So, the general goal of preventing microbial spoilage can be reached by many methods like, you can use natural and synthetic chemical preservatives and thermal treatments. So, Isothermal Calorimetry can be used to study the effect of such methods by studying samples treated with different methods or measuring the thermal power before and after the application of method. You want to study the effect of something, so you can carry out this study and see what happens. When you use an additive, what happens to the heat signal can be assessed using this method.

Cell death from blanching is also an application, blanching is what we see when we put spinach in hot water and it loses its colour. So calorimetry can be used to quantify basically the cell damage and when you are doing that you are causing cell damage. So, increasing intensity of heat treatment, for an example, progressively reduces the number of viable cells in the tissue sample and results in a corresponding reduction in the rate of metabolic processes. So, the blanching process can also be optimized by the use of calorimetry.

Similarly, you can use it for wound respiration, looking on to the commonality between these applications like as long as there is heat, does not matter where it is coming from we will be able to monitor the process. So, it is well known that when you cut a vegetable it causes the cell damage and which sets off several different protection and repair process in the non wounded cells. So, Calorimetry can be used to study the effect of wounded area.

One can use this to investigate wound induced processes and how the rates of these can be reduced for prolonging shelf life and decrease of flavour. Calorimetry is a potentially useful tool for shelf life predictions.

Several attempts have been made in this direction for an example; Isothermal Calorimetry has been treated as a method to detect microbial spoilage. You want to know when things spoil for an example, spoilage of meat, eggs, carrots. So, by quantifying this microbial spoilage shelf life can be estimated. These are some interesting applications I just wanted to draw your attention to which will motivate you further to use this technique.

So, this can offer a solution in terms of quality control. What do you see in this plot is related to the shelf life of carrot juice.

So you have this corresponding signal, you are trying to enhance this shelf-life of carrot juice by adding different things. What we see is that when we add 10% green tea, it does something to carrot juice but the effect is not much significant. We also see that when we add sodium benzoate, it significantly slows down the process. So, for the high doses of sodium benzoate significant delay in the onset of growth is seen.

But it does not completely prevent all micro-organism from growing. You can see still some heat signals. But at least you are delaying the process. So what type of microorganism that is present in the juice cannot be inferred. We only can see that in microorganisms, the process is getting delayed.

Calorimetry is in is in many case an ideal method to start a study which gives a general overview about how fast process takes place and what factors control the process rates. It is all about rates and how fast the changes are occurring. So, you can at least say now that when you have sodium benzoate, you are delaying the microbial spoilage.

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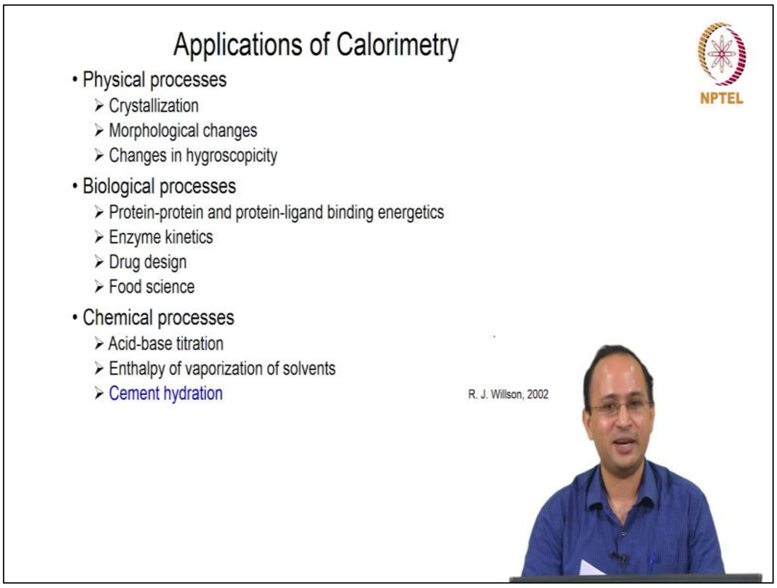


So basically any process whether it is physical, chemical, biological can be monitored. For example, crystallization of amorphous materials can be studied using calorimetry. A useful method for analysis is to couple a heat calorimeter where you can get the signal with a vapour perfusion device as you want to induce some changes.

So in this case, what you can do, you can change the partial pressure and that can be used to change the degree of amorphousness or you can induce some crystallinity that can be monitored using calorimetry. Another change can be morphological changes like, we talked about polymorphs. Crystalline materials exhibit different number of polymorphic forms.

Material is dependent on how many different orientations the molecules can be arranged to form a crystal lattice. It is all about the arrangement of molecules in a lattice that can have significant effect on the physico-chemical properties of a material. So, Calorimetry can be used as a method for identification of polymorphic forms by exploiting differences in physical properties.

It is because when you are introducing the changes, you are changing the physical properties. The calorimetric investigation into hygroscopicity typically involves RH perfusion means you change the relative humidity and you see how much sorption is taking place. So, a material is subjected to increasing levels of water vapour and the mass increase is followed by measuring the associated enthalpy change.

These are some physical processes. We have not talked about biological processes for an example, so it can be also used to study the biological processes, as long as there is heat signal.

So, idea is to see the application of calorimetry in different fields. So, it is very commonly used to study Protein-Protein and protein-ligand binding energetics which is very important in Bio-Pharmaceutical industry.

So biological systems evolved and are maintained in accord with the laws of chemistry and physics. Indeed at molecular level, highly complex biological processes can be regarded as variations of non covalent and covalent interactions. Thermodynamics reveals the essential energetic principles of biological phenomena as it provides general formalism for describing as in terms of its energy.

So calorimetry can be again used to quantify the heat effects accompanying association between molecular entities. Similarly enzyme kinetics can be studied using calorimetry. Enzymes are macro molecular biological catalysts that accelerate chemical reactions. Now the molecules upon which enzymes may act are called substrates and the enzyme converts the substrates into different molecules known as products.

So, all the metabolic processes in the cell needs enzyme catalysis, in order to occur at the rates fast enough to sustain life. So, the rate of enzymatic reactions is proportional to the heat flow associated with the formation on breakage of chemical bonds. These all processes what is happening is that you are getting heat signal and you are measuring it.

Calorimetry is also used for drugs design. In case of drug design, when a test compound binds to a target protein for an example, it follows a heat change. Hence allows precise measurement of binding affinity.

So the calorimetry in the presence of other ligands rapidly provides information on the mechanism of action of the test compound identifying the intermolecular complexes that are relevant for structure based design. Only idea is to draw your attention to these different varieties of applications without going in to deep explanation.

Similarly, we can use it to understand chemical processes. Now, the kind of chemical processes this technique is used for are like to study acid base titration and determining enthalpy of vaporization of solvents. It can also be used to understand cement hydration because the reaction between cement and water is also a chemical reaction and an exothermic reaction where you release heat and if you can measure that heat then you can study the cement hydration phenomenon.