

Mechanical Measurements and Metrology

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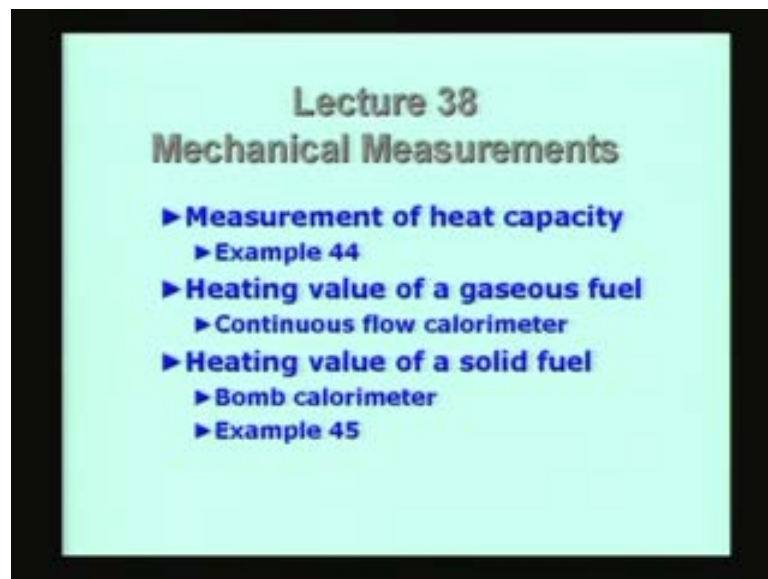
Module - 4

Lecture - 38

Measurement of Heat Capacity and Heating Value of Fuels

This will be lecture number 38 on Mechanical Measurements. Towards the end of the last lecture we looked at the measurement of specific heat capacity or the specific heat of a solid material. We described the calorimeter and we looked at the principle behind calorimeter measurement. In fact in this lecture I am going to continue with that and I will take example 44 and then we will move on to another important measurement namely the measurement of heat, heat of combustion of either a gaseous liquid or a solid fuel.

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So we will describe two calorimeters. One is a continuous flow type calorimeter, and the second one is called a bomb calorimeter. We were looking at the mixing process. During the first phase we are going to drop the hot mass in to the calorimeter vessel and then we are going to study the temperature variation of the calorimeter. The temperature actually increases steadily and after sometime it has to come to a steady state, and if there is no losses the steady state temperature should be a constant value higher than the initial value of the temperature. Of course

because of the losses inherent in the system, this is not going to take place. Actually the temperature will start coming down after increasing to a maximum value, and the cooling process subsequent to the heating process or the heat release process is of important to us to find out what the loss is going to be.

In fact, I have derived the expression, the specific heat of the material the glass beads is equal to $C (T_2 \text{ minus } T_1)$ where C , is the heat capacity of the calorimeter itself with its contents and then L is the loss the second term on the numerator is the loss term which needs to be estimated by the cooling process and the denominator consists of the mass of the glass beads multiplied by the temperature difference, a change from the higher temperature to the lower temperature. In fact the question now is how you are going to estimate the loss. And we will make a simple assumption. Because the temperature difference between the calorimeter and the outer vessel difference is very small, we can assume that the loss must be proportional to the temperature difference between the T and the jacket. The jacket temperature also happens to be the initial temperature of the entire system.

So we will assume that L , the loss from the calorimeter is proportional to some constant K times $(T \text{ minus } T_1)$. So now let us see the consequence of this. The consequence is that, during the mixing process, we can write the following equation $dQ \text{ by } dt$, the rate at which heat is changing with respect to time, is actually the heat given up by the solid must be equal to the rate at which the calorimeter gains heat which is given by $C dT \text{ by } dt$ plus the loss $K \text{ into } (T \text{ minus } T_1)$. The assumption is that this quantity K , I am introducing here as proportionality constant is the same whether it is getting heated or subsequently it is going to cool, so the same constant I am going to use because the temperature difference $T \text{ minus } T_1$ is a very small temperature difference at the most, a few degree s. What I can do now is, to integrate this equation, and if I do that from the start of the mixing process to the end of the mixing process.

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During the mixing process:

$$\frac{dQ}{dt} = C \frac{dT}{dt} + K [T - T_1]$$

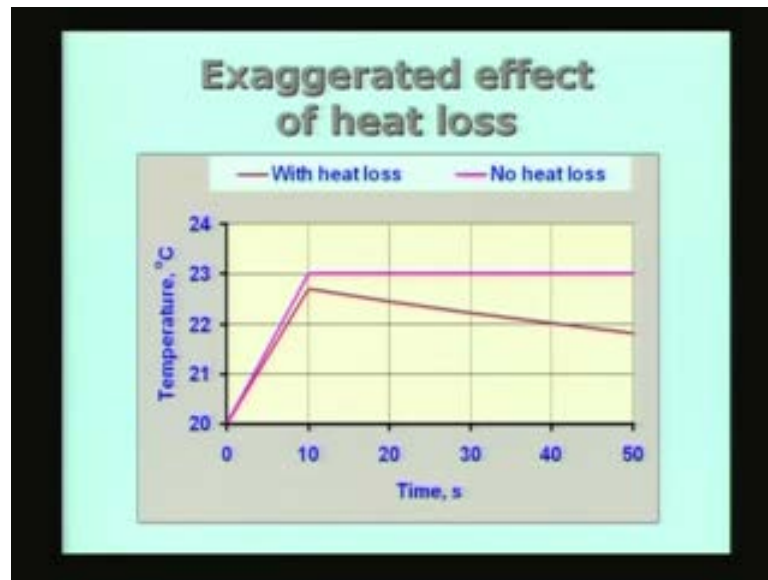
Heat given up by the solid Rate at which calorimeter gains heat Very small temperature difference.

Integrate from $t = 0$ to $t = t_e$

$$\int_0^{t_e} \frac{dQ}{dt} dt = Q = C(T_2 - T_1) + K \int_0^{t_e} (T - T_1) dt$$

So, integrate from t is equal to 0, that is the starting of the mixing process to t is equal to t_e , this is the end of the mixing process. That means, if I integrate, from t equal to 0 to t equal to t_e this should simply give Q , the amount of heat given up by the solid material as it cools from its own temperature which is higher to the final terminal temperature. Similarly, if you integrate this simply this should become C into T_2 minus the temperature change because integral dt by dt integrate between t is equal to 0 and t_e will be nothing but T_2 minus T_1 plus this will give you K into integral 0 to t_e T minus T_1 . During the mixing process, I have got an equation which says that, heat given up by the solid is equal to Q is shared between the two quantities. One is the heat gained by the calorimeter in going from temperature T_1 to temperature T_2 , plus the K times the (integral) which is actually nothing but the loss, this is nothing but the loss. Now let us look at what is going to happen after the mixing process is over, then subsequently I am going to end up having a cooling process.

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So let us look at the data obtained. The data obtained is the lower curve with heat loss, the temperature during the mixing process starts at t is equal to 0 by the end of the mixing process, t is equal to 10 seconds, it reaches the maximum value which is not the value it should have achieved if there was no heat loss. So the temperature is this value, and what it should have been is this. So, if we can find out what this difference is then the job is actually done. And subsequently let us see what happens. The temperature instead of remaining constant as in the no heat loss case in this case it is coming down. And if you allow this to come down for a long time it eventually comes to this value, it will cool down to the jacket temperature.

Now if you look at the cooling process this is again governed by the same cooling relationship K into $(T \text{ minus } T_1)$ gives the temperature variation derivative with respect to time. So using this part of the process, I can in fact find out K . K is nothing but the first order time constant of the system which is getting cooled down. And if I can get the value of K from the cooling curve, I would have obtained the value of K and that can be used in the earlier expression. If you remember there was integral K times (integral) 0 to t_e $(T \text{ minus } T_1) dt$ and that can be obtained as the area under the curve during the mixing process. This is the curve; actually it is almost a straight line so half of the base times the altitude gives the area under this curve and that is going to give me the integral part. The K part is going to come from the cooling curve. During the mixing process we had the equation which is given here. During the subsequent cooling process the left hand side is 0.

So we can say that, during the cooling process subsequent to the mixing process which is complete and after that there is a cooling process. We can say that, 0 is equal to $C \frac{dT}{dt} + K(T - T_1)$. So I can rewrite in the form of K is equal to $C \frac{dT}{dt} / (T - T_1)$. During the cooling process, I will determine the slope of that line. So, if you remember this is the cooling process, this is what has happened and this is the cooling part.

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During the cooling process:

$$0 = C \frac{dT}{dt} + K(T - T_1)$$

$$K = \frac{C \left\{ \frac{dT}{dt} \right\}}{(T - T_1)}$$

estimate K

Therefore if I choose any point here on this, this is the value of T, if I draw a line tangential this is the slope C which is known, this is the calorimeter heat capacity, T value if this is the value, this is the value then we can estimate K from this. So I have estimated the K by using the slope of the cooling part at a point where the temperature is T, I use this expression and substitute the slope of cooling curve. Therefore I get C into dT by dt by (T minus T_1) is equal to K and this K is going to be used in the earlier expression. That means here I am going to put that value of K so use estimated K.

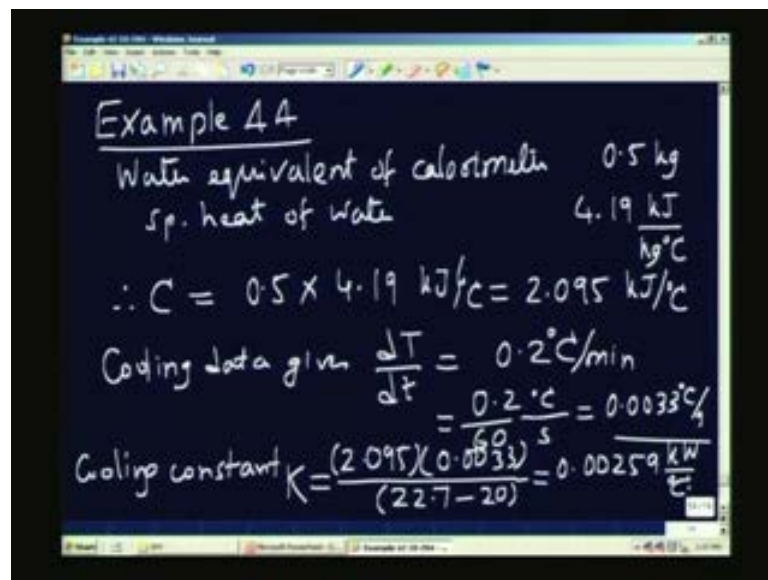
That means, I am going to use the estimated value of K here. I have already indicated how to obtain this integral. From the initial mixing process the temperature, time and data is there, find out the area under that curve in this case because this is almost a linear increase in temperature, and it is nothing but half the base times the altitude so I can obtain this integral easily, the left hand side is Q, and now this integral into (K) is nothing but the loss, and if I go back to the earlier expression, I substitute for L here, and that K into integral (T minus T_1), I put it

here and I get the value of the specific heat of the glass beads in this particular problem.

In this problem we have identified a little bit of cooling. However, well the experiment is performed and however careful we are in doing it still there is some loss and the effect of the loss is taken care of by looking at the cooling process, finding out the cooling constant and using this cooling constant to estimate the loss during the mixing process so that the value which we get is much better than it would be otherwise.

Let us look at example 44. The water equivalent of the calorimeter is given as 0.5 kg, it is like half a liter of water being heated. The specific heat of water is well known, 4.19 kilo joule by kg degree Celsius. Therefore, C is nothing but the product of these two 0.5 into 4.19 kilo joules by degree Celsius which is nothing but 2.095 kilo joule by degree Celsius. The cooling data is already given in the problem, dT by dt the rate at which temperature is coming down is actually negative 0.2 degree Celsius by min, so I will convert it to, 0.2 by 60 degree Celsius by s which comes to 0.0033 degree Celsius by s. Therefore I can obtain the cooling constant. This is your K, this will be $C \frac{dT}{dt}$, that is about 2.095 into 0.0033 by $(T \text{ minus } T_1)$ this data says that T was 22.7 when the slope was calculated as minus 20, this will be your K this comes to 0.00259 kW by degree Celsius. Now all I have to do is to use the expression given earlier.

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Example 44

Water equivalent of calorimeter 0.5 kg
sp. heat of water 4.19 $\frac{\text{kJ}}{\text{kg}^\circ\text{C}}$

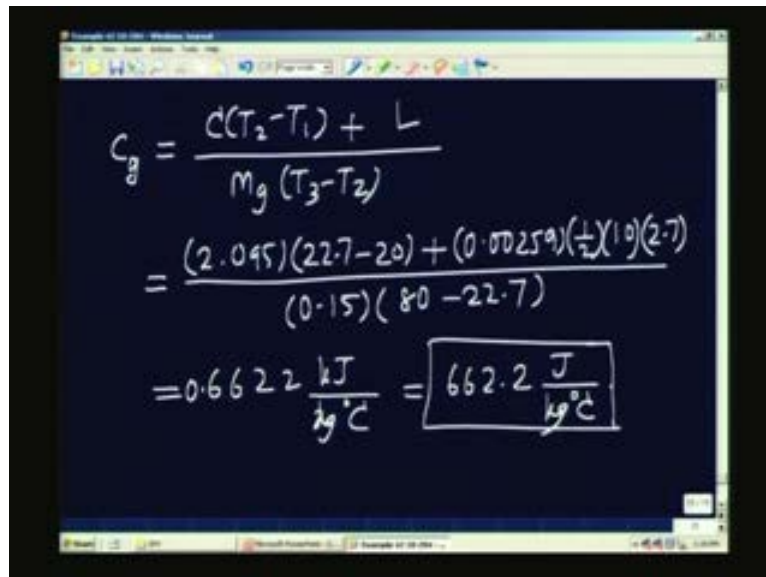
$\therefore C = 0.5 \times 4.19 \text{ kJ/}^\circ\text{C} = 2.095 \text{ kJ/}^\circ\text{C}$

Cooling data given $\frac{dT}{dt} = 0.2^\circ\text{C/min}$
 $= \frac{0.2^\circ\text{C}}{60} = 0.0033^\circ\text{C/s}$

Cooling constant $K = \frac{(2.095)(0.0033)}{(22.7 - 20)} = 0.00259 \frac{\text{kJ}}{^\circ\text{C}}$

So the C of glass beads must be equal C into (T₂ minus T₁), this is the expression which was written down earlier plus loss divided by the mass of the glass beads multiplied by T₃ minus T₂. So C is 2.095, T₂ is 22.7 minus 20 plus loss is nothing K into (integral) and K itself is given by 0.00259 and the integral is nothing but half the base into altitude that is 2.7 divided by mass of the glass beads multiplied by the temperature change for that and that will be 150 gms or 0.15 kg multiplied by 80 minus 22.7 and this gives a value of 0.06622 kilo joules by kg degree Celsius or 662.2 joules by kg degree Celsius, this is the value. So the glass bead which is solid taken in this particular case has got about 662.2 joules by kg degree Celsius at the specific heat.

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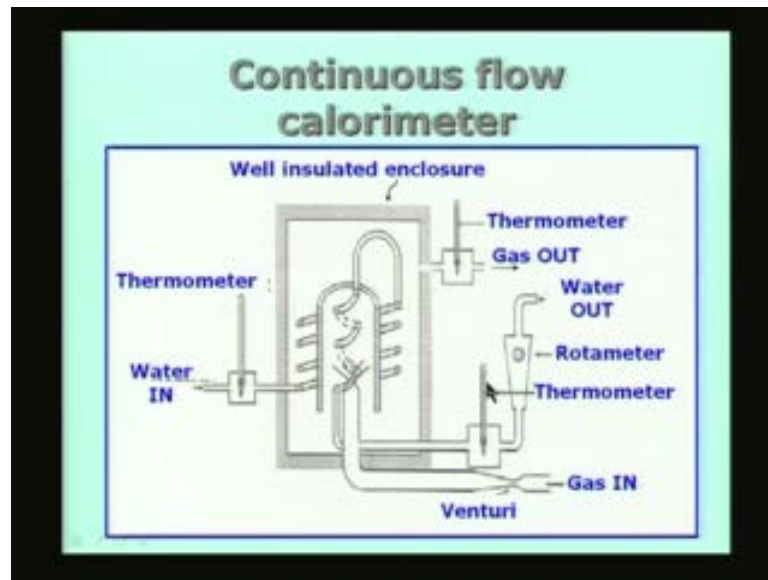
$$C_g = \frac{C(T_2 - T_1) + L}{m_g (T_3 - T_2)}$$

$$= \frac{(2.095)(22.7 - 20) + (0.00259)(\frac{1}{2})(10)(2.7)}{(0.15)(80 - 22.7)}$$

$$= 0.6622 \frac{\text{kJ}}{\text{kg}^\circ\text{C}} = \boxed{662.2 \frac{\text{J}}{\text{kg}^\circ\text{C}}}$$

So to summarize this approach, the calorimeter is used to perform the mixing process, and also the subsequent cooling is used to determine the cooling constant, and this is used to correct for the heat losses for which the calorimeter is subjected. Now let us look at the measurement of the heating value by two different methods. The first case is the measurement of heating value of a gas and the second one will be that of a solid. The principle of the calorimeter used in these two cases is no different from what we did in the case of specific heat. The only thing is the heat liberation process is different. In the case of the specific heat determination, we preheat the sample, and then dump it into the calorimeter to find out the temperature change and then from that we get the specific heat.

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In the calorimeter the heat release is taking place within the calorimeter itself as a continuous process or as a one time heat release process. Of course, again it will be subjected to subsequent cooling just as in the previous case. Let us look at the two cases. The first one is the continuous flow calorimeter. In this case, I want to determine the heating value of gaseous fuel. So what is being done here is, there are two components, one is the gas which is coming in whose flow rate is measured by venturi, the gas consists of a pre mixture of gas and the oxidant, it may be in the form of oxygen or it may be in the form of air and the gas mixture.

So the gas into the calorimeter is actually the mixture of the gas whose calorific value or the heating value I am going to determine and the oxidizer in the form of oxygen or air. And its flow rate is measured, as it enters the calorimeter and it is burnt here in a burner, and subsequently, after complete combustion the burnt gases are going to be cooled by water which is flowing in the opposite direction. So the burnt gases are going to go up like this and come down and then probably go out at the exit here.

The water which is used to cool the gases, is going to enter and its temperature is measured, its flow rate is measured and it passes through all these tubes which are going to be removing the heat from the burnt gases, or the product of combustion and the water is going to move out through the exit here, whose temperature is again measured, it goes through the Rotameter so that the measurement of flow can

be done and the water is taken out. The entire process takes place in a well insulated enclosure.

The enclosure of course in this case is going to be having two roles. One is to prevent any damage to person outside, because there is a chemical reaction taking place, and we would not like people to be in contact with the gases which are going to be generated. And secondly, it also provides insulation so that the entire process is adiabatic. So, in this case what happens is the gas and the oxygen mixture comes in gets completely burned and it is cooled to as close to the temperature to the room temperature as possible, and that is why we have an elaborate cooling arrangement, so that any water which is formed during the combustion process condenses, and is in the form of liquid rather than a vapor.

Therefore, the heating value which we are going to measure is called the higher heater value because the water vapor or the moisture which is formed during the combustion process is in the form of a liquid. Secondly, if the temperature of the gas coming in and the temperature of the gas going out are very close to each other then there is not much of a temperature change from here to here. All the heat generated by the combustion process is actually removed by water.

Of course, there may be a small temperature difference which can be used to correct this. So the continuous flow calorimeter has a continuous flow of certain mass flow rate of gas and oxygen mixture coming in here, and it has got a continuous flow of certain amount of water coming in at a temperature in at a lower temperature and it moves out at a higher temperature.

Similarly, the gas comes in and combustion takes place and the entire amount of heat is released, and it goes out as a slightly higher temperature out of the system. So all we have to do is energy balance where the heat given up by the gas must be equal to the heat taken by water and by this balance we can find out the heat released by the combustion process. In fact we can work out very simple formula for that. Let us assume that the mass flow rate of the gas is the mass flow rate measured by the venturi and the mass flow rate of water is measured by the Rota meter in this particular experiment.

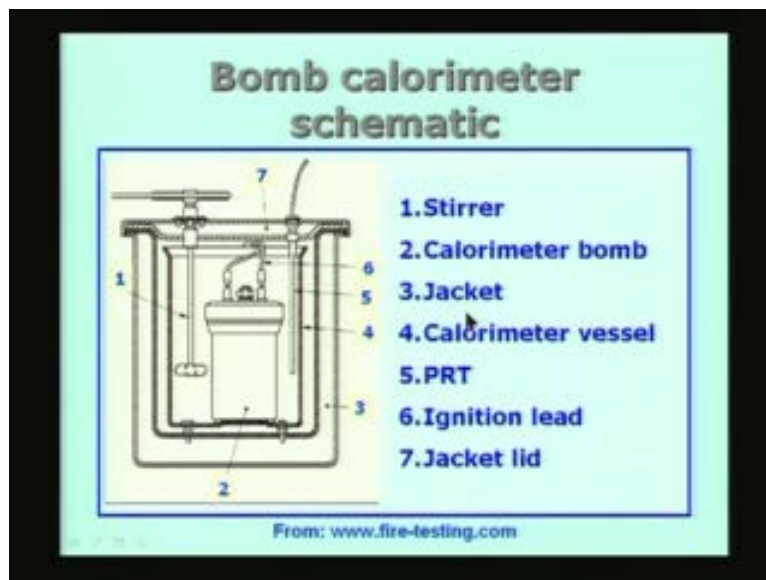
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m_g - Mass flow rate (venturi)
 m_w - Rotameter
 Energy balance:
 $\cancel{m_g} (HV) = m_w C_{pw} (T_{w,exit} - T_{w,entry})$
 $m_g \rightarrow \frac{m(fuel) + m(air)}{J/g \approx kJ/kg}$
 $\frac{m_g C_{pg} T_{g,exit} - m_g C_{pg} T_{g,entry}}{m_g (fuel)}$

So the energy balance is very simple. I am measuring all the temperatures with their entry and exit for both the streams. So we will say, the mass of the gas is being burnt so it is gas multiplied by the heating value must be equal to the mass of the water multiplied by the C_p for water into $(T_w \text{ exit minus } T_w)$ at entry this is for water, plus the gas which is coming in at it's own temperature and goes out slightly at higher temperatures, so what I can do is, I will have to consider the product of combustion so mass of the product of combustion which will be again measured by the flow rate same as m_g multiplied by C_p for the product of combustion multiplied by $T_{gas} \text{ exit minus } m_g C_p \text{ before combustion multiplied by } T_g \text{ at end}$. This may be different.

So all I want is the heating value and that will be the entire thing on the right hand side. If I put a bracket like this and divide it by m_g I get the heating value for this. Of course, the mass of the gas consists of mass of fuel plus mass of air. This heating value is going to be in the units of so many joules per gram or kilo joules per kg. The second case is somewhat difficult. The principle is the same but here there is no continuous flow, it is one of a process. What I have here is a bomb calorimeter, the schematic is shown.

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Let us look at the schematic, and understand the need for each one of the parts and then look at the analysis of the bomb calorimeter. It actually consists of what is called the bomb, this is the bomb. Of course, this is not a bomb which is going to explode; this is called a bomb, because it is going to contain the reaction which takes place when the solid fuel is going to burn. The products of combustion are going to be confined within that region, it is a vessel made up of either steel or a sufficient wall thickness so that it can withstand that inside pressure which is usually of the order of 25 bars and essentially a reaction takes place at that pressure.

So, the calorimeter bomb has an arrangement by which I can put a small pallet of the solid fuel inside the bomb on a sample carrier, and I have an arrangement by which, I can have a small fuse wire which is going to be in contact with it, through which I am going to pass a current to initiate the combustion reaction. Usually an iron wire is used, and the wire itself is going to melt because of high current which is going to go through that and during this process, it is going to generate enough temperature to start the reaction. And the bomb is filled with pure oxygen at about 25 bars. The reason why we want to fill the bomb with high pressure oxygen is to see that the combustion reaction is going to take place completely.

That means, the entire mass of the palette which is taken inside is going to completely burn and the combustion products are going to be formed. The bomb itself is immersed in this vessel here with water, about 2 liters of water is taken in this vessel, and in this vessel there is a stirrer to make the temperature uniform in

this vessel it is well circulated and there is a high precision thermometer which is immersed in that vessel. The thermometer which is immersed in this water must be able to measure temperatures with the resolution of 0.01 or better. That means 0.01 degree or better resolution is required for the thermometer.

In this case, I have shown in a PRT. Instead of PRT one could also use a thermistor or one could use a precision thermometer with mercury in glass. The range of the thermometer will be something like from 15 degree to 30 degree that is from almost room temperature to about 30 degree and it should be possible to measure a temperature change of 0.01 degree Celsius during the heating process. During the combustion process, heat is released the temperature is going to go up, and I must be able to measure the temperature due to 0.01 at least so the ignition is done by the leads shown here and there will be a wire inside and this wire is in intimate contact with the fuel pellet whose calorimeter value or heating value I want to determine. And a suitable power supply is used to start the combustion process.

You will also see that outside the calorimeter vessel, there is another vessel which we call as the jacket which is filled with water which may be circulated so that the temperature remains constant throughout the experiment, before and after the combustion process is initiated. That means that the temperature of the jacket is almost like constant equal to the temperature before the experiment stops. The reason why we have a jacket here, whose temperature is maintained the constant is to prevent heat loss, and therefore I can consider the inside vessel plus the bomb plus whatever is kept inside the bomb which undergoes an adiabatic process.

That means there is no heat transfer between the inner calorimeter and the outer jacket. So, in this experiment what I am going to do is, there are two parts in this experiment. In the first part I am going to use a standard material. Usually the standard material used is the benzoic acid whose calorimeter value or heating value has been accurately determined by various laboratories and the value is available to us. So we will burn certain small amount of benzoic acid usually much less than 1 gm typically may be 0.01 or 0.02 gms of benzoic acid in the form of a small pellet like a tablet and it is burnt completely in the first experiment after filling the bomb to about 25 bars of oxygen pressure inside and inside the bomb we also put a small amount of water usually 1 cc of water is enough, this water will saturate the oxygen and therefore during the combustion process whatever water is formed as a part of combustion process is going to condense. Therefore, the water which is formed in the process of combustion is going to be condensed, and therefore it is not in the form of vapor. That is the idea with which it is determined.

Therefore we will get what is the so called higher heating by using the bomb calorimeter. The experiment is very simple. You take the pallet inside, in this case, the benzoic acid pallet and then put it inside the thing and then charge it to 25 bars, see that there are no leaks and so on and have the temperature recorded and start the recording of this temperature of the PRT or the thermistor or whatever the instrument you are going to use, and then slowly after few minutes you initiate the combustion. Combustion is initiated by passing the current through the wire for about two to three seconds, and then it will melt, and in fact when the wire inside melts the circuit will automatically break.

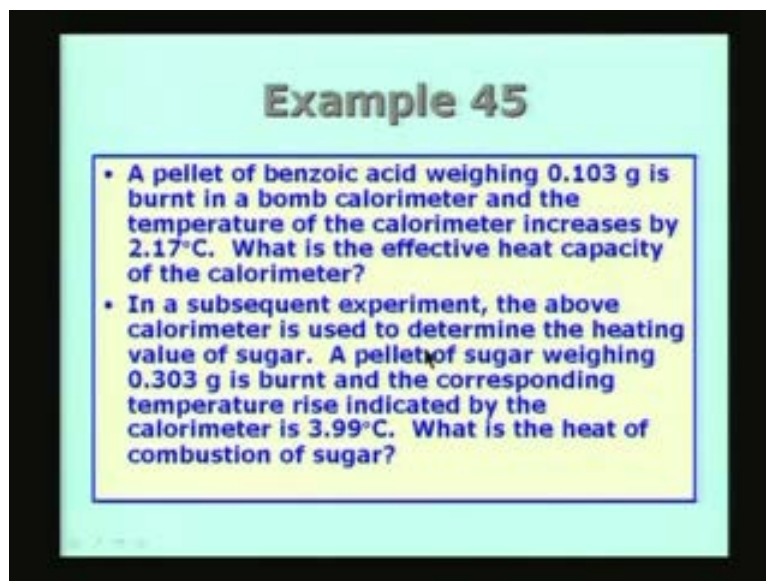
And usually in the circuit a light bulb is also there in series which is going to stop, when the connection is lost the illumination is stopped, and therefore you know that the melting has taken place. And after a few minutes you will see that, the temperature starts raising, and then it stops again, and then becomes more or less constant just as in the case of the specific heat calorimeter we had. In this case, during process of combustion, certain amount of internal energy has been released and because of the temperature of the calorimeter goes up and if we know the calorific value or the heating value of the fuel in this case benzoic acid I can use this as a calibration experiment to find out C for the calorimeter.

You remember the calorimeter we used earlier had C which is the mass specific heat product for the calorimeter. So the first experiment using benzoic acid as a standard material should determine the constant C for the calorimeter. in the subsequent experiment I am going to use whatever fuel I want to get the heating value of the fuel I can use that fuel in the form of pallet and repeat the experiment and whatever C value I have determined in the first experiment I am going to use the C value for the second experiment. Therefore I will obtain the unknown heating value in the second experiment, this is the basic idea.

Let us look at the kind of temperature data which we are going to obtain. This is the bomb calorimeter data, the calorimeter data is shown here, this is the temperature axis; this is the time in minutes. So the record has been started at 0 minute and up to about 6 minutes also there is no combustion it is just the temperature remaining constant, and at this point the combustion process has been initiated and the combustion is over very soon and the temperature increases, and then it goes to a maximum value here, and then it starts coming down again because of the small amount of loss which may be in the system just like what we had in the case of the calorimeter.

Here it extrapolates like this. That is, you draw it backwards like this and you draw this forward like this and draw a vertical line such that the area under this curve here, and the area under this curve is, roughly equal. This is supposed to take care of the losses which may be there in the system. So what you do is you see that this area, and this area are roughly equal. So draw this line such that these two are equal. This is the temperature difference I am going to take for the calculation. So ΔT for the calculation is this temperature value what I am going to take into account. Here is example 45 divided into two parts. the first part is a pellet of benzoic acid which weighs 0.103 g, you realize that the weighing must be done very accurately with a balance which is capable of giving milligram accuracy 0.103 g is burnt in a bomb calorimeter and the temperature of the calorimeter increases by 22.17 degree Celsius, this is the first experiment.

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Example 45

- A pellet of benzoic acid weighing 0.103 g is burnt in a bomb calorimeter and the temperature of the calorimeter increases by 2.17°C. What is the effective heat capacity of the calorimeter?
- In a subsequent experiment, the above calorimeter is used to determine the heating value of sugar. A pellet of sugar weighing 0.303 g is burnt and the corresponding temperature rise indicated by the calorimeter is 3.99°C. What is the heat of combustion of sugar?

So what is the effective heat capacity of the calorimeter? It is determined from this part. In a subsequent experiment the above calorimeter is used to determine the heating value of sugar. A pellet of sugar weighing 0.303 g is burnt and the corresponding temperature raise indicated by the calorimeter is 3.99 degree Celsius, what is the heat of the combustion of sugar? These are the two parts of the problem. Now let us look at some of the useful data or useful information.

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Useful information

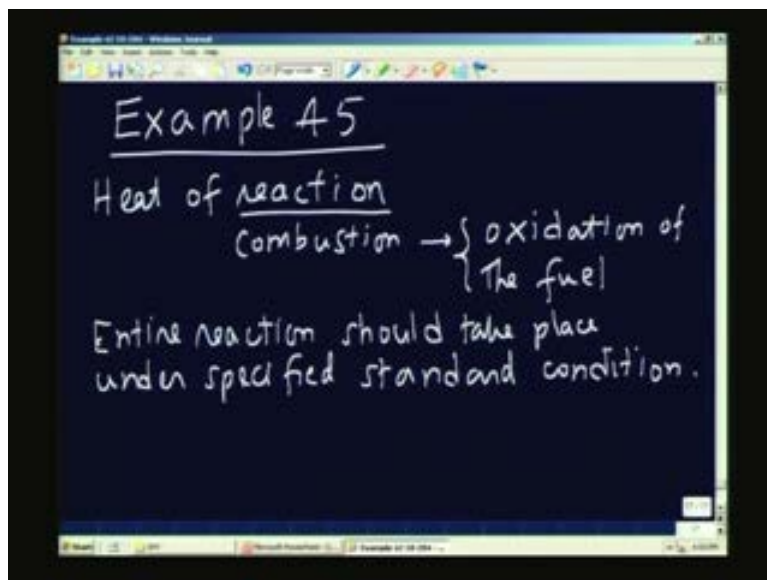
- Benzoic acid has the molecular formula $C_7H_6O_2$ and a molecular mass of 122.12 g/mol. It has a heat of combustion of 3227 kJ/mol.
- Sugar has the molecular formula $C_{12}H_{22}O_{11}$ and a molecular mass of 342.3 g/mol.

Problem 45 is solved on the board.

Benzoic acid has a molecular formula given by $C_7 H_6 O_2$ and molecular mass of 122.12 g by mol and it has a heat of combustion of 3227 kilo joules by mol, this is known from literature. This is supposed to be accurately known. The case of sugar that I am going to burn with the second experiment has a molecular formula $C_{12} H_{22} O_{11}$ and a molecular mass of 342.3 g by mol, this will be useful for solving the problem.

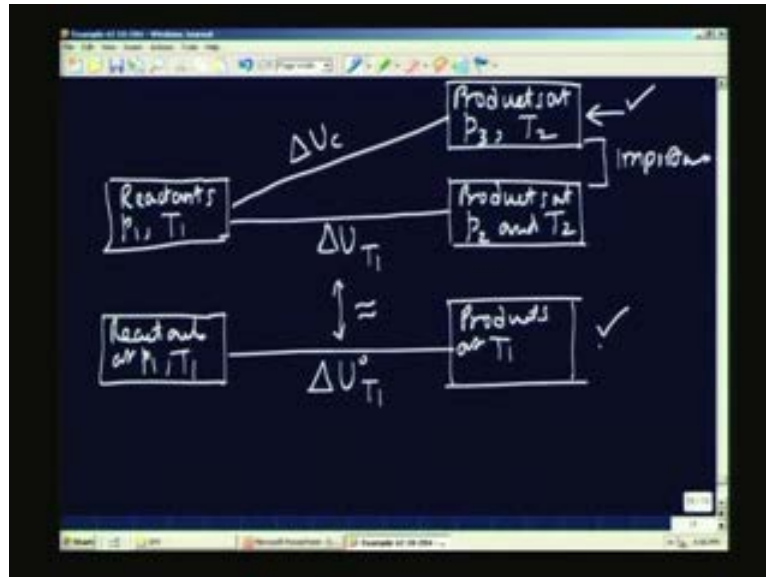
Here is the solution. This is example 45. The problem requires some background. We have to understand what we are trying to measure. The background will be provided as we go along solving the problem subsequently. Usually the heat of combustion, or heat of reaction, in general, combustion is a specific reaction where oxygen is going to combine with fuel to provide the product of combustion. Combustion means, it is nothing but oxidation of the fuel. The definition is that the entire reaction or burning should take place, under some specified standard condition. So the idea is to obtain the value of the heat of reaction as close to this definition as possible, that is our goal. If you do not do that, of course, there will be some small differences between what you obtain in your calorimeter experiment and the heat for reaction for that particular reaction. These differences have to be calculated so that we get the heat of reaction.

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In the bomb, we have reactants, what are the reactants? The pallet of the fuel and the oxygen which is 20 bars or 25 bars so p_1 and T_1 this is the condition. And this is the heat released in the calorimeter called ΔU calorimeter. So we have products at some p_3 and some T_2 , that is temperature at the end of the heating process. In the heat release process the temperature goes up and that is the temperature. However, what I should have had is the product at some p_2 and T_2 . So there is some pressure change which may have taken place during the calorimeter experiment. The product would have to be p_2 and T_2 but there is some change. This is what the experiment is going to give us.

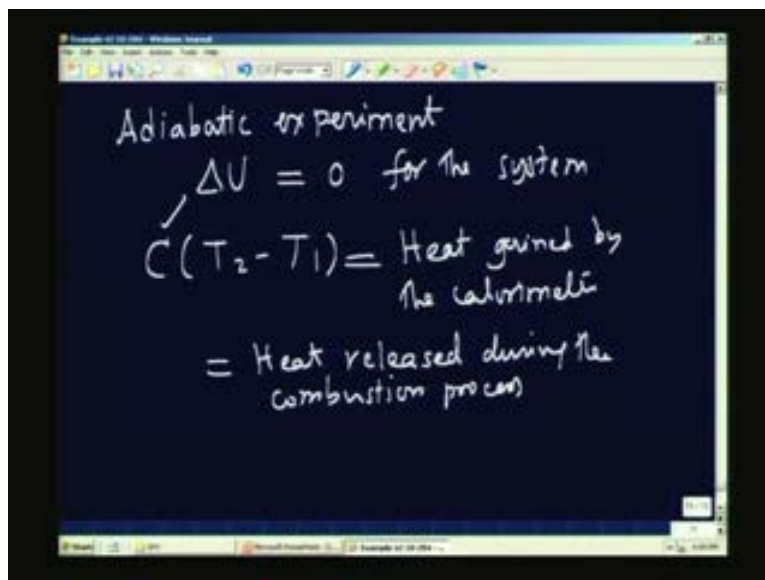
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According to definition, the reactants at p_1 and T_1 have to be converted to products at T_1 itself. This is what we require, and this is what we are going to get. So how do we find out the difference between these two is the whole point of this discussion which I am giving. So let us call this ΔU at T_1 , this is under standard conditions and this is what happening in our case. In normal practice, these two are almost equal, the effect of these quantities are not very severe. However, this difference is important. The experiment is conducted totally adiabatically, it is an adiabatic experiment.

According to Thermodynamics, the internal energy of the system must be constant. The change in the internal energy of the system is equal to 0 ΔU is equal to 0 for the system. The system is made up of two things; one is the material which is burnt, and has become products and the other part is actually the water which is surrounding that and the vessel in which the experiment is performed. There is also some amount of heat released by the wire, when it initiates the combustion reaction and for accurate determination we have to take even this into account.

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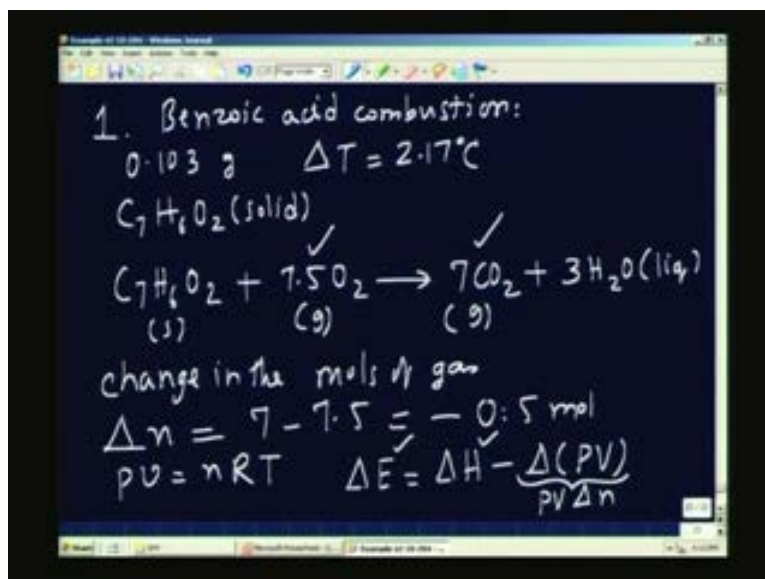
Adiabatic experiment
 $\Delta U = 0$ for the system
 $C(T_2 - T_1) = \text{Heat gained by the calorimeter}$
 $= \text{Heat released during the combustion process}$

There are two things here, the reacting fuel which has undergone a change because of the reaction and the rest of the vessel. So I can say that, $C(T_2 - T_1)$ is the heat gained by the calorimeter. This must be same as the heat released by the fuel, because it is an internal arrangement, and there is no change in the internal energy of the entire system. It is just that the amount of heat released by the fuel during the process of combustion is simply shared by the calorimeter. Of course, I know how much of the material I am burning. Therefore I can write this expression as the mass of the fuel burnt, multiplied by the heat of combustion for the material. We know the mass from the experiment with benzoic acid. This T_2 and T_1 are measured by the experiment. Therefore I will be able to determine the heating value of the fuel. Here is the first part of the problem.

Part one will be benzoic acid combustion. We have the mass of the acid as 0.103 g which is burnt, and the temperature change is 2.17 degree Celsius. We already know that the benzoic acid is given by, $C_7H_6O_2$ this is in the solid form, and the reaction can be written as $C_7H_6O_2$ this is in solid plus I am going to have oxygen in the bomb, and there is enough oxygen so that the combustion is going to completely take place. So the amount of oxygen required for the stoichiometry or the complete burning is given by $7.5 O_2$ this is in the gaseous form, after the combustion is over you get seven CO_2 plus $3H_2O$, this is in the liquid form and this is in the gas form.

This is the liquid form because, we have already saturated the oxygen to start with so that it cannot hold any more water in the form of vapor, therefore it will condense. During this reaction, we had 7.5 moles of oxygen and the number of moles of carbon dioxide formed is 7, therefore there is a change in the moles of gas. And because of this, some amount of energy is required, or heat is required and we will have to take that into account. Therefore Δn , the change in the number of moles is 7 minus 7.5 minus 0.5 moles.

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If you remember, PV is equal to nRT , that is the equation of state. Therefore we also know that ΔE is equal to ΔH minus $\Delta(PV)$, and everything else remains constant, R is constant, temperature T remains constant but the only thing that is changing is, n . Therefore minus $\Delta(PV)$ is nothing but $PV(\Delta n)$ and PV is nothing but RT . Therefore this will be $\Delta n(RT)$. So you can see that ΔH minus $\Delta n(RT)$ and that gives you the relationship between the internal energy and the enthalpy. So we can say that ΔE is ΔH change in the enthalpy minus Δn which is minus 0.5 or the universal gas constant is 8.3143 into 298 that is the standard temperature at which we are interested in calculating and the ΔH because we are burning benzoic acid, and we know that the heating value is already given to us as 3227 kilo joules for mol, this will be a negative value, because heat is released, this will come plus and this whole thing is going to be 0.5 into 8.3143 into 298 so this comes to minus 3225.8 kilo joules by mole. This is actually in joules, this is in kilo joules.

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$$\begin{aligned}\Delta E &= \Delta H - (-0.5)(8.3143)(298) \leftarrow J \\ &= -(3227) \frac{kJ}{mol} + 0.5 \times 8.3143 \times 298 \\ &= -3225.8 \text{ kJ/mol} \\ Q &= \frac{(0.103)}{(122.12)} (3225.8) \text{ kJ} = 2.721 \text{ kJ} \\ &= C \Delta T \\ \therefore C &= \frac{2.721}{2.17} = \boxed{1.254 \frac{kJ}{^{\circ}C}}\end{aligned}$$

So, the heat released during the combustion of benzoic acid will be 0.103 g is burnt, so I have to calculate the number of moles that will be divided by the molecular weight 122.2 which was already given in the slide multiplied by 3225.8, this will still be in kilo joules and this comes to 2.721 kilo joules. This is the heat released in the first experiment, and this is equal to C into (delta T). Therefore C is equal to 2.721 by 2.17 which is delta T therefore this comes to 1.254 kilo joules by degree centigrade. This is the value obtained from the first experiment for the calorimeter constant C.

Here is experiment 2. I am going to have sugar whose formula is given by $C_{12}H_{22}O_{11}$ (Refer Slide Time: 58:48) and 342.3 is the molecular mass and the data gives the amount of temperature change where temperature change is 3.984 degree Celsius, and the same calorimeter is used. Therefore C is the one which is found in the previous experiment. You will also notice that in the case of sugar, there is no change in the moles, the number of moles of the gas is equal to oxygen and on the right hand side I am going to get CO_2 the same number, and there is no delta n and delta n is 0.

Therefore, whatever heating value I obtain automatically there is no difference in the quantities of the heating enthalpy and the internal energy. So we will say that delta n is equal to 0, you can work it out by writing the stoichiometry for this particular case, finding that the number of moles of the gas in the beginning and the end are exactly the same. One mole will be 342.3 g and the amount of burnt is

3.303 by 342.3 this is the number of moles of the sugar which will be nothing but 0.000885 mole burnt and delta T is given, and C is equal to 1.254 kilo joules by degree Celsius.

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Handwritten calculations on a digital screen:

$$\begin{aligned}
 & 2) \quad C_{12}H_{22}O_{11} \quad (342.3) \\
 & \Delta T = 3.984^\circ C \quad \Delta n = 0 \\
 & C = 1.254 \text{ kJ/}^\circ C \\
 & \frac{0.303}{342.3} = 0.000885 \text{ mol of sugar} \\
 & \text{Heat gained by the calorimeter} \\
 & Q = C \Delta T = (1.254)(3.984) \\
 & \quad = 4.995 \text{ kJ} \\
 & \text{Heat of reaction} = \frac{4.995}{0.000885} = 5646 \frac{\text{kJ}}{\text{mol}}
 \end{aligned}$$

Therefore with this value, I can find out the heat gained by the calorimeter Q is equal to C into delta T 1.254 from the previous value multiplied by 3.984 this will give you 4.995 kilo joules. So this must be equal to the moles of the fuel burnt multiplied by the heat of reaction. Therefore heat of reaction equal to this divided by the number of moles which is given by 0.000885 this gives you a value of 5646 kilo joule by mole. This is in fact the heating value of sugar. This is an interesting example; sugar in the form of a pallet is taken burnt in the calorimeter and we can determine the calorific value. In engineering practice we will call it the calorific value. In chemistry or in physics they would refer to it as the heat of reaction. Mechanical engineers use the term calorific value more often. Therefore you can say that the calorific value of sugar is about 5.65 kilo joules by mole of sugar, so this is the example. Thank you.