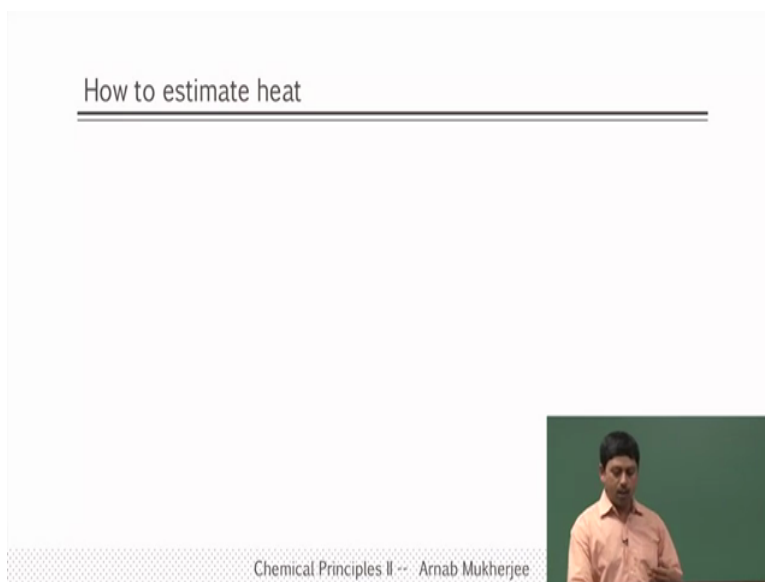


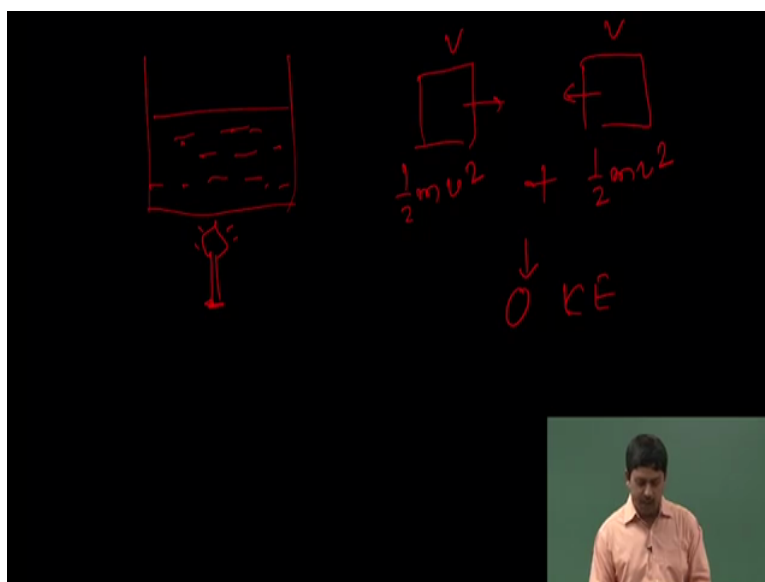
**Chemical Principles 2**  
**Professor Dr. Arnab Mukherjee**  
**Department of Chemistry**  
**Indian Institute of Science Education and Research, Pune**  
**Work and Heat Part 02**

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So we have talked about work and now we are going to talk about heat. Now what is heat?

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Now people, so you know we can think of heat as that you have a container let us say full of water and you are using a burner. I am trying to draw a burner and suddenly you will see that in all sense of hot and cold the water has become hotter, right you can touch it, it is lukewarm, that is what we do. Now right now we understand probably what is happening but

people you know long back thought and we have shown you also the history of thermodynamics that (1:03) thought that there is some kind of a caloric fluid that is going inside from outside which is there it is hot, the burner is hot and that is going inside the water and it is heating it.

So that is understandable that something is going on, but what happens when let us say 2 objects or let us say 2 cars, I cannot draw the cars so I am just drawing this squares are coming with a velocity  $V$ , so it has a kinetic energy of let us say half  $mv^2$ , it has a kinetic energy of  $mv^2$ , so the total kinetic energy is basically  $mv^2$  and they come they collide with each other and it has 0 velocity, 0 kinetic energy.

So from  $mv^2$  it goes to 0, so where does that energy go? People already knew that energy is you know is conserved because that means whatever energy is there it will be conserved it will be there, so does it mean that conservation of energy does not hold? Because initially they had velocities, now they do not have velocity, what is happening where did that velocity go?

So people realized that when they touch that object it was hot. Similarly I told you about that cannon boring experiment also that with that cannon ball when they try to make a hole and all then it became so hot that it could boil the water that was also a kind of mechanical work, right that converted to heat. So there is some relation between these motions, velocities with the heat that people knew.

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$\Delta Q \propto \Delta T$   
 $\Delta Q \propto m_w$   
 $\Delta Q = m_w \Delta T$  water  
 $1 \text{ cal} = 1 \text{ gm } 1^\circ\text{C}$  definition.  
 For a metal rod,  
 $\Delta L \propto L$   
 $\Delta V \propto V$   
 $\alpha = \frac{\Delta L}{L}$   
 $\alpha = \frac{\Delta V}{V}$

We will see that we can actually even before going there we can qualitatively estimate a certain things, one things is that let us say talk about water, we know that if we put some amount of heat that means if we heat the water for 5 minutes, the water will be, the temperature will you know increase to some amount. Now let us say we heat the system for 10 minutes, will the temperature be same? No, it will be more, if you heat for much longer time.

So these are qualitative observations that people had and they saw that the heat is proportional to temperature. Now you instead of let us say take one small beaker water and then take a bigger beaker water and again heat them for 5 minutes individually, will the water be you know temperature remain same, it will not be the same, right. So because it depends on the amount of water, that is why when you take a big when people cook, right they need lot more time to cook for you know 10 people than to cook for 2 people because it will be quicker, or you know this we always see when we make tea for example tea for 1 people is very quick, but you know if you make it for 10 people you need to put lot of heat lot of time in order to boil the water.

So which means that the heat is also proportional to mass, right mass of water let us say, now turns out that these are the two quantities that the heat will depend on mass of water and the temperature for water. So given these two things one can actually see that okay by knowing how much water is taken into consideration and how much temperature increase has happened one can estimate the amount of heat and that we can call that.

So we can now define a new unit for heat as calorie, so 1 calorie will be when 1 gram of water is increased by 1 degree centigrade the temperature is increased by 1 degree centigrade. So this is by definition we are taking that, so there is no constant in this, in this particular water so whatever the constant so what kind of constant do you think will have?

[Processor-Student conversation starts]

Student: For water it will be empirical.

Professor: Yes, it can be but you know it is your definition so you want to put the definition of calorie, see because you are starting with the definition how do you otherwise estimate the amount of heat so you take 1 Kg of water or 1 gram of water and you see that the temperature increases from 22 degree to 23 degree, what is the value you are going to ascribed to that heat that you have put in you say that that is 1 calorie, so you are defining 1 calorie by the fact that

when 1 gram of water increases its temperature by 1 degree, you see it is your definition, right.

So this is how calorie is defined, I would write here the definition. Now you write that it looks that okay so once we define that it will not be the same for everything, right for example we take a rod and in order to extend that rod or sorry in order to increase the temperature of that rod by 1 degree do you think only 1 calorie heat will be required? So what does, how much you know let us say to increase by 1 degree for a rod particular rod let us say iron rod what do you think it will depend on the amount of heat for a metal rod, metal rod what on which kind of quantity the temperature increase will depend on?

That means in order to increase the temperature by 1 degree, what is the property what is the thing it will depend on? What is the property of that metal? Let us say we are taking iron rod, so let us say if I take iron rod and I want to increase by 1 degree, so will the heat be same all the time or it will depend on something?

Student: (())(7:19).

Professor: Nature of?

Student: Rod.

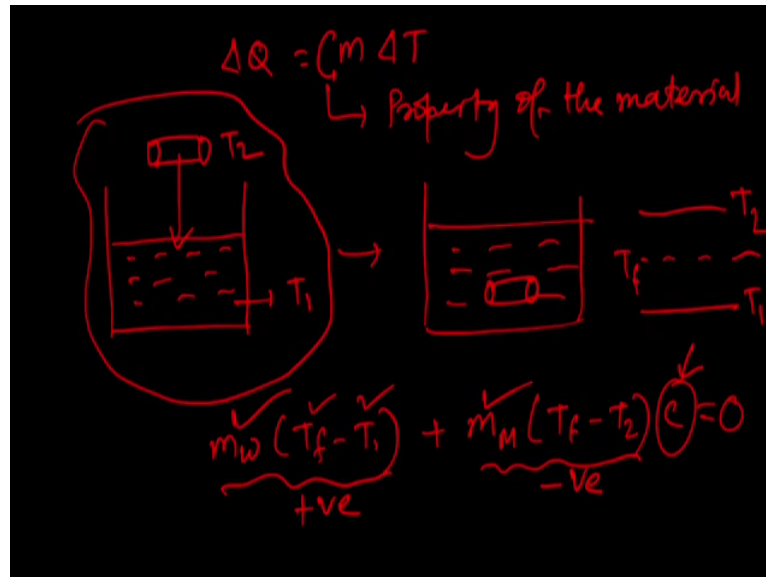
Professor: No, I have told you that it is actually iron rod, anything else that you can think of? It is an iron rod let us say. Now mass will come into the picture, now in the case of iron rod so let us say if I give you a rod or let us say cylindrical rod then in that case mass will be evenly distributed, right and therefore you can say the length of the rod consider for example you take 1 metre rod the amount of heat is required to increase the temperature by 1 degree will not be the same if you take 2 metre rod because you can think of that as take 2 metre rod cut into two pieces, you get two 1 metre rods, you give heat and increase 1 degree, you give another some heat and increase 1 degree, when you join them you would have given the same additional heat, right which means that it will depend on the length of the rod.

[Processor-Student conversation ends]

So in that case of let us say when you change a certain length or let us say increase of length because we have also seen that temperature, increase of temperature will be proportional to increase of length for a metal thing. So this will be proportional to length of the rod. Similarly increase of volume for a gas molecule will be proportional to the volume, so this turns out

that there is some coefficients of thermal expansion which is alpha that depends on that for a particular metal which is a metal (prop) for a particular material which is a material property that it says that how much expansion is there for a given value of the quantity, right.

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So in case of other systems not metal, not water, your heat then will depend on mass of the system temperature and something called specific heat that is the property of the material. Because if you take iron rod, then increase in temperature will not be the same if you take copper rod, or aluminium rod, right. So that means the tendency for increasing the temperature rod absorbing the heat because and to you know increase the temperature every material will react differently.

So once you know the specific heat of the system then by measuring the temperature, see heat measurement it is not a direct thing, you have to associate that with temperature measurement and we have already discussed how temperature can be measured because these are the quantities that we defined, temperature can be again measured by the thermometers that we have gas thermometers and many other things.

So essentially we are actually talking about one material property to another material property finally, we have taken the gas thermometer to understand how to define the temperature and then we are using that temperature to understand how to define the heat qualitatively and also quantitatively but we do not yet understand the microscopic picture of that.

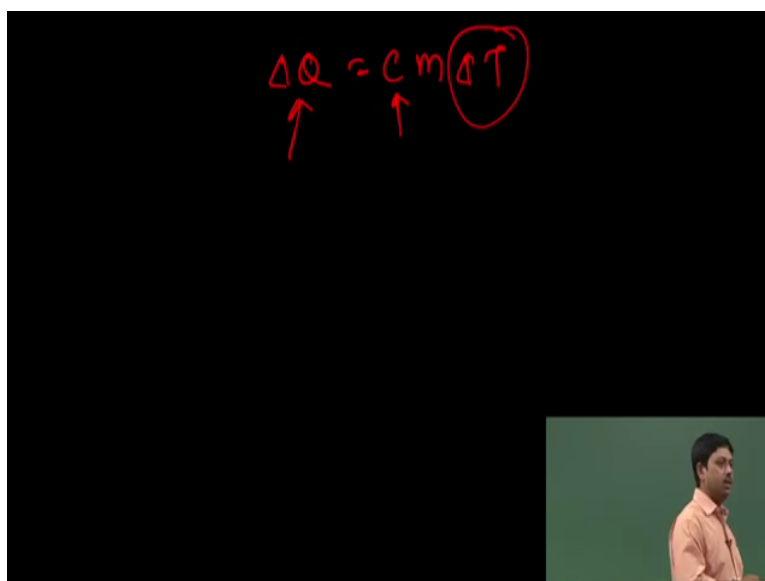
Now how do you get the specific heat of the system? So let us take that, let us say that we have taken water system water in a beaker and let us say its temperature is  $T_1$  and I have a metal rod which temperature is  $T_2$ , now I have to I do not know the specific heat of the material, okay let us say  $(C)$ (11:06). Now when I dip into that then the system will have water in which the metal rod will be there. Final temperature will be somewhere in between let us say this  $T_2$  was larger than  $T_1$ , so final temperature will be somewhat in between again thermal equilibrium will come into the picture, right when two objects are in contact with each other there will be thermal equilibrium and temperature will be the same.

So when they are in equilibrium then the temperature of the metal rod and temperature of the water will be the same. Now if we assume that the whole process is done in an isolated manner that means no heat is coming in and out of this particular combined system then we can say that and since  $T_1$  was higher so what will happen is that the water will get heated up and the metal rod will get cool down because metal rod had higher temperature by assumption.

So the change in heat for the water will be mass of the water and final temperature minus initial temperature because specific heat of the water why you do not have  $C$  there because it is taken to be 1 and that is why we can define that category as 1 calorie plus mass of the metal rod I am taking capital  $M$ , then  $T_F$  minus  $T_2$  and specific heat and overall it will be 0.

Now since  $T_2$  was larger than  $T_F$ , this is the negative quantity and this is the positive quantity, right so we can balance them and you will be able to find the specific heat of the system because you know this one, you know this one, you know this one, you know this one, and only thing that you do not know is the  $C$ . So without knowing the specific heat of the system just because you have defined heat in terms of water we can now calculate the heat of the specific heat of the other system as well and then once we calculate the specific heat of the other system then we will know how much heat goes into the system.

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So once we know the  $C$ , so let us say we will write again  $C m \Delta T$ , once we calculate for a particular system the  $C$  then later on by measuring the temperature we will be able to calculate the heat that goes into that particular system, right. So we are using one standard and therefore we are measuring all other things, okay that is the idea.

(Refer Slide Time: 13:42)

How to estimate heat

- What is heat? Is it caloric fluid?
- For Water,  $\Delta Q(\text{cal}) = m_w(\text{gm}) \cdot \Delta T(\text{degree})$
- 1 calorie is to increase the temperature of 1 gm of water by 1 °C
  
- For any other materials
- $\Delta Q(\text{cal}) \propto m_w(\text{gm})$  at fixed  $\Delta T$
- $\Delta Q \propto \Delta T(\text{degree})$  at fixed  $m_w$
- $\Delta Q(\text{cal}) \propto m_w(\text{gm}) \cdot \Delta T(\text{degree})$
- $\Delta Q(\text{cal}) = C m_w(\text{gm}) \cdot \Delta T(\text{degree})$ ,  $C$  is the specific heat and it depends on material
  
- $\Delta L = \alpha L$
- $\Delta V = \alpha V$

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In the bottom right corner, there is a small inset video of a man in an orange shirt speaking.

Now let us see that we have discussed all that, we have discussed all of these things that are here.

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### Heat change during phase change (Latent Heat)

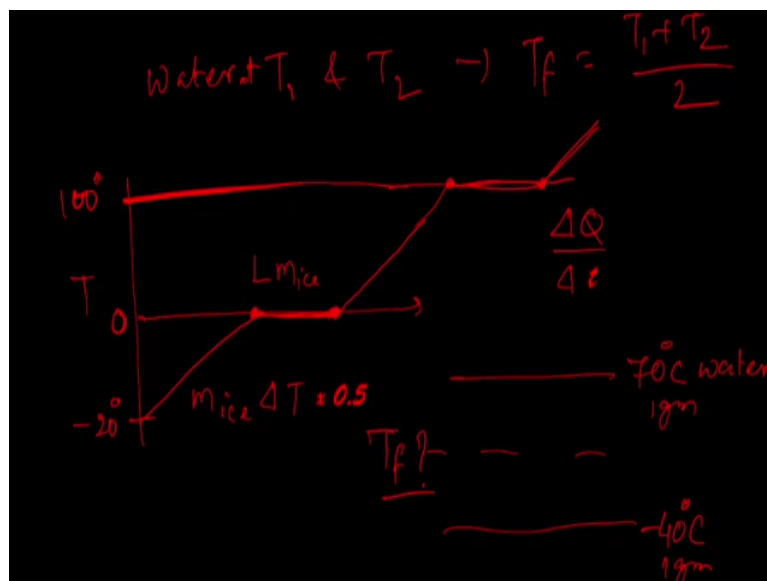
- During the phase change, temperature does not increase because heat is used to change the phase. Amount of heat is proportional to the amount of material undergoing phase change,  $\Delta Q(\text{cal}) \propto m_w(\text{gm})$
- The proportionality constant is called Latent heat,  $\Delta Q(\text{cal}) = L_w(\text{cal}) m_w(\text{gm})$
- Latent heat is the property of the material. As we will see, it is related to the internal energy of the substance.



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Now the question is that what will be happening in during the you know phase change of a system.

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So when the two systems are in the same phase that means if I take a system of water at  $T_1$  and  $T_2$ , then we know that  $T_f$  will be simply  $T_1$  plus  $T_2$  by 2 that is not a problem, but let us say if I have ice and we give heat to the system, what is going to happen? So let us say that this is the temperature of the system and we start with ice, now what is the temperature of the ice? What do you think the temperature? 4 degree? What is the temperature of the ice?

Student is answering: 0 degree and below.



He is right, 0 degree and below because ice can also stay below 0 degree, right. For example our fridge has minus 20 degree defreeze the ice is there at that, so it can go below 0, so that means below 0 it remains as ice. For example water, water remains within the range of above 0 to 100, is it or not? So similarly it can go below 0, so let us say let us start with minus 20 degree centigrade of ice and we give heat to the system, so what is going to happen?

Because you are giving heat to ice and ice is there in the same phase means ice phase is remaining till 0 degree, so the temperature is going to increase linearly because there also it will be mass into the  $\Delta T$  will be the amount of heat that is going there, but once it hits 0 degree, what is going to happen? Temperature is going to increase anymore? Temperature is going to remain constant.

However, you are still giving heat, you are giving heat let us say at continuous rate  $\frac{dQ}{dt}$ , you are giving every 5 minutes some calories of heat, every 1 minute some calories of heat, right. So more time is now more heat equivalent to, so you are constantly heating the system at a given rate, the heat is flowing into the system at a given rate and what you observe that when it hits 0 degree the temperature is no longer changing, temperature remains same but you see that ice is melting.

So what is happening is that the heat is now working against the against what? Ice now heat is now working against the internal energy of the system, is it or not? So earlier we will talk about that earlier it was what it was doing is that it was changing its kinetic energy, now it is trying to change its potential energy, okay however, kinetic energy plus potential energy is there in internal energy so it is always changing the internal energy anyway, but earlier it was only changing the kinetic energy, potential energy also but not that much because it is still remaining ice, not significantly.

But when it starts melting from ice to water then the potential energy of the system which comes from the interaction between the particles that now is going to change and therefore, ice is now going to melt to water. Now when all the ice melts, now this one is latent heat, right. So again it will be so here it will be mass of ice into  $\Delta T$  of ice, here the temperature is not going to change however, heat you are supplying so that is the latent heat of the system multiplied by the mass of ice, right that much heat is going.

What is the latent heat of ice? 80 calorie, so it is let us say if it is 1 gram so it will be 80, 80 calorie will go into melting 1 gram of ice at 0 degree centigrade to water that means that

much energy is now used to break the hydrogen bonds in the eyes and not all of them, right partially because water also has hydrogen bond.

When all of them melts then it is again trying to you know it is going to increase and then will reach 100 degree centigrade then again latent heat of vaporization will come into the picture and it will spend more calorie again and then more than that it will be the superheated steam more than 100 degree because after vapour it is not going to remain as vapour, right more heat you put is going to go into the kinetic energy of the system because it is already you know loss you know all the potential energy that it had now it is just going to go into the kinetic energy of the system.

Now the fact that I am telling you little bit beforehand will come clear later that why we are saying that when it goes into the gas system then only the kinetic energy that is going to change that will become clear later. So now so the kind of problems you know you can try is that let us say you have a system that water is at 70 degree centigrade and ice at minus 40 degree centigrade same 1 gram let us say 1 gram of water and 1 gram of ice if you mixing them together what will be the temperature?

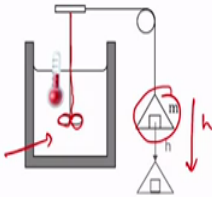
You can try that, it is slightly complicated because this latent is coming into the picture, right. If you have let us say 1 gram of ice but if you have let us say huge amount of water at 70 degree then you are sure that final one it will be water only and then you can calculate all the heat that is required to melt the ice and then increase that and everything, right. But if you do not know what will be the final result so there are 3 things possible, one is that combined system will become ice, combined system will become water or it will be an water ice mixture.

So you have to see all possible combinations to ultimately see that what is the final result that you are going to get, okay. So this is the most complicated problem that can be possible in this calorimetric problems.

(Refer Slide Time: 20:20)

What is Heat?

Joule's Paddle Wheel Experiment



*Mechanical equivalence of heat.*

- $KE = PE = mgh$
- But, Joule found,  $KE < mgh$
- $mgh = KE + \text{equivalent increase in temp}$
- Loss in KE = gain in heat (4.2 J/cal)

*$(KE - mgh) \propto \Delta T$*

*Heat = ~~kinetic energy~~*

KE = mgh

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Now we have to understand what is heat? So we understood what is heat, how? That heat is something that increases the temperature that way we understood what is heat, but microscopically what is heat? Or how do we understand when the cars collide, the kinetic energy whatever was there before  $mv^2$  of the two cars suddenly goes to 0 and things getting hotter.

Now where does that go into? So both the Cannon Boring experiment and Joule's Paddle Wheel experiment showed that heat is nothing but energy or heat is nothing but kinetic energy of the system. How he did that? So he took let us say a system of you know water in which there is this kind of paddle is there like a fin kind of thing which can rotate like the you remember when we know when you cook dal and the dal, you know dal right dal does not get boil properly then you do that, right. So that kind of arrangement if it is there along with a pulley such that when you pull that pulley that will rotate, so what will happen it will churn the water, right.

So that kind of system is attached here, along with a pulley and a mass is addressed at a particular position let us say. So now he release the mass and the mass drops by an amount of  $h$ . Now what would happen in that case? If that is the case then when the mass goes below by  $h$  the kinetic energy should be  $mgh$ , right potential energy gets converted to kinetic energy, now that was what expected that a mass falls by height  $h$ , my potential energy of  $mgh$  will convert to kinetic energy of  $mgh$  because energy is conserved.

What you observed is that the kinetic energy was not  $mgh$ , was less than that, okay. Where did the kinetic energy go? He showed that that whatever the kinetic energy was less than that, right so whatever the loss in kinetic energy that he had which means  $KE$  minus  $mgh$  has been converted to proportional to the  $\Delta T$  of the water. So the loss in kinetic energy has been converted to increase in temperature of the water meaning increasing heat of the water because temperature is proportional to heat.

So therefore, it could be established that heat is nothing but kinetic energy or energy of the system I would say, right because you cannot really distinguish the kinetic energy and all that it was having potential energy, right gravitational potential energy is dropped down to kinetic energy and then got there, right. You will see later on that we can understand that more by the kinetic energy of the system the heat.

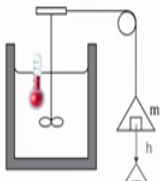
But here we can say that the internal energy of the system which was there as  $mgh$  has some of that has converted to heating the water and that is why he wanted to do this Niagara Falls experiment that the top of the Niagara Fall and water falls by 50 meters and the bottom should have different temperature because the mass that is falling will produce that energy because and indeed like he did not find much of a difference but when people other people actually measured in a cloudy day they got some difference in the temperature between the top and the bottom of the Niagara Falls and we all the time we will see that this.

So this established the mechanical equivalent of heat, so that means mechanical energy whether it is motion of a car or dropping of something is equivalent to heat, it is like what we perceived as heat and what we perceived as internal energy that depends on our own measurement, when this paper is there just like this, this paper right now does not have any heat, right but it has the potential energy, if we burn it burn it means if we just give one small spark that is just to initiate, right after that we are not doing anything is giving us heat, where does it give us? From whatever stored here, so it is just the way we actually want to ascribe certain things to materials or properties.

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### What is Heat?

Joule's Paddle Wheel Experiment



- $KE = PE = mgh$
- But, Joule found,  $KE < mgh$
- $mgh = KE + \text{equivalent increase in temp}$
- Loss in KE = gain in heat (4.2 J/cal)

So,  $\Delta U = q$  (when no work is being done)

$\Delta U = w$

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So now it is heated in this thing (I will just clear the page marking), you see now that now when we do not do any work, so let us say work is not there, then our internal energy is equal to heat because what happens is that the potential energy got converted to heat there was no work at that point, right. So we saw before that  $\Delta U$  was equal to  $w$ , now we see that  $\Delta U$  equal to  $q$ .

(Refer Slide Time: 26:20)

### First Law of Thermodynamics

$\Delta U = q + w$

For an infinitesimal change in state,

$dU = dq + dw$  (First Law of Thermodynamics)

The first law is a **postulate** that states that there is a property  $U$  that is a function of state variables and can be changed in either of the two ways. Also, it is not dependent on the path. The amount of  $dU$  would be same whether similar amount of heat is transferred or work is done.

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So when you combine them together, what we get is called first law of thermodynamics,  $\Delta U$  equal to  $q$  plus  $w$ . So if  $w$  is 0, then  $\Delta U$  will be equal to  $q$ , if  $q$  is 0 then  $\Delta U$  is equal to  $w$ . So first law of thermodynamics is nothing but conservation of energy, only thing is that it specifies into heat and work that and also you know people talk about chemical work and

all that but that is already hidden in internal energy itself, we can take that as internal energy itself the chemical work.

So now for an infinitesimal change we can write so this delta whenever we write delta U it indicates that one point to another point, change from one point to another point, q and w are just amount of work and amount of heat but when you talk about an infinitesimal change that means a very small amount then typically we use this notation d small d so dU indicates an infinitesimal change in the internal energy, dq is an infinitesimal change in the heat and dw is the infinitesimal change in the work.

So we write dU is equal to dq plus dw and you see now that when work done on the system is positive then your internal energy is increasing that is how, so by convention we have to when we write the first law this way we have to take the convention that work done on the system is positive, if we did not some of the books write in a different way, in that case you have to put a minus sign, in that case we can take work done by the system, okay but use one convention.

So the first law is postulate that states that there is a property U that is a function of state variables and can be changed in either two ways either heat or work. Also, it is not dependent on path, so it is a postulate that will say that when you talk about two states it will only depend on the states whichever way I can come from one to two does not matter. So you saw that in our two calculations that you use two routes or two paths, right we got two different work, but if you calculate the internal energy you will find that that is 0, okay.

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The image shows a blackboard with handwritten equations in red ink. At the top, the equation  $U = \frac{3}{2} N k_B T = \frac{3}{2} R T = \frac{3}{2} P V$  is written. Below it, a process is described:  $P_0, 2V_0 \rightarrow 2P_0, V_0$ . Underneath this, the initial and final internal energies are calculated:  $\frac{3}{2} \times 2P_0 V_0$  and  $\frac{3}{2} \times 2P_0 V_0$ . The first law is then written as  $dU = dq + dw$ . For this process, it is shown that  $0 = dq + dw$ , leading to the conclusion  $dq = -dw$ . A small inset video shows a person in an orange shirt standing next to the blackboard.

So what is the internal energy of the system for an ideal gas can you tell me? Internal energy of an ideal gas is  $\frac{3}{2} k_B T$  and we know that or for one mole or let us say  $\frac{3}{2} RT$ ,  $\frac{3}{2} N_A k_B T$  or  $\frac{3}{2} RT$ , so  $\frac{3}{2} RT$  is  $\frac{3}{2} PV$ , right. So we started from  $P_0, 2V_0$  to  $2P_0$  and  $V_0$ , right, correct. So what was the energy here?  $\frac{3}{2} 2P_0 V_0$ , so  $3P_0 V_0$ , right what is the energy here?  $3P_0 V_0$ , so internal energy in this process did not change but we got some work.

So when you write this  $dU$  equal to  $dq$  plus  $dw$  and this was turning out to be 0 which means that our  $dq$  is minus of  $dw$ . So whatever we calculated for  $dw$  minus of that actually is produced as heat in that two paths, so one path we got more work therefore it will be less heat that will be generated, another path we got less work will be more heat that will be generated more or less I am saying because of the sign, okay.

So you will see that has an implications because we want to minimize the heat producing to the environment to get the maximum work done by the system, okay.

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### First Law of Thermodynamics

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$\Delta U = q + w$

For an infinitesimal change in state,

$dU = dq + dw$  (First Law of Thermodynamics)

The first law is a **postulate** that states that there is a property  $U$  that is a function of state variables and can be changed in either of the two ways. Also, it is not dependent on the path. The amount of  $dU$  would be same whether similar amount of heat is transferred or work is done.

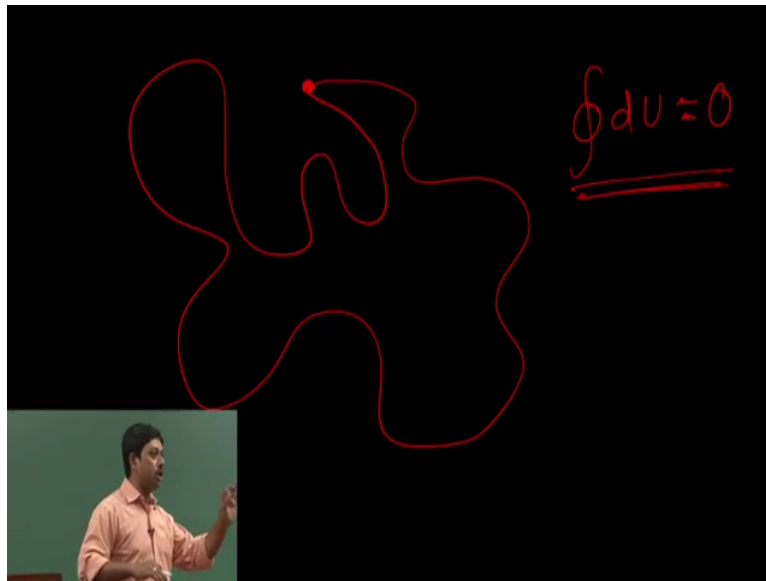
The first law is also called as the "law of conservation of energy"

For a cyclic process, the change in the internal energy is zero. This is represented mathematically as,  $\oint dU = 0$ .

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So first law I already told that.

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And for a cyclic process it does not depend on path anymore, so if you start from here and you do whatever you want to do, you do, it does not depend on path, right if it reaches finally to the last point then we denote that as a cyclic integral it will be always 0 cyclic integral always indicates that we start from somewhere whichever whatever we do we come back to the same point. So it is always 0 by postulate by definition we do not take U because we do not take U to be dependent on path, both dq and dw have to be path dependent then only they can balance that because if only one of them is path dependent, other two cannot be path independent, one is path independent but other two are path dependent, dq and dw and they balance this thing.