Chemical and Biological Thermodynamics: Principles to Applications
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Lecture - 04
First Law of Thermodynamics

In this lecture, we are going to discuss the first law of thermodynamics. Thermodynamics may appear to be a mathematical science because there are so many equations that we have to deal with, but actually the laws of thermodynamics are based on several experimental observations and one such experimental observation is that heat and work are equivalent ways of changing the internal energy of a system. Change in internal energy of a system, we are writing as delta U.

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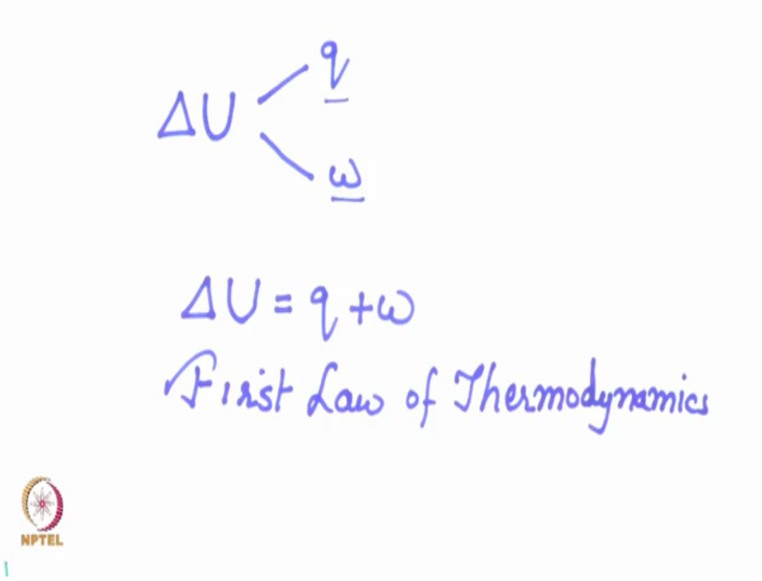
ΔU — $\underline{q}$, $\underline{w}$

$\Delta U = q + w$

First Law of Thermodynamics

So, what I am saying is that heat and work are equivalent ways of changing the internal energy, whether we heat the system or we do work on it, the internal energy of the system is changing or increasing and the system is blind to it. That is how the energy is being given to it. It is like taking an example of let us say if we consider q and w as let us say 500 rupees currency note or 1000 rupees currency note and we go to a bank and deposit.

The statement that we get is that the total amount deposited it in the bank irrespective of recognizing whether you have deposited 500 rupees note or 1000 rupees notes or 2000 rupees notes. So, in the same way the system is blind to what is coming, whether the energy is flowing in the form of heat or work, but it is leading to change in internal energy of the system. So, if I write in a formal way delta U is equal to q plus w, this is the formal statement of the first law of thermodynamics. This is a mathematical statement of first law of thermodynamics and as we will see that this is a very useful mathematical equation.

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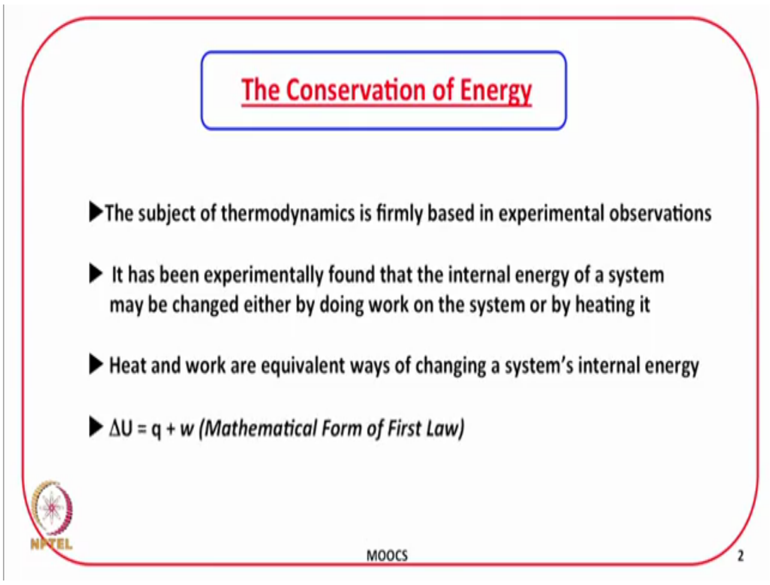

The Conservation of Energy

- The subject of thermodynamics is firmly based in experimental observations
- It has been experimentally found that the internal energy of a system may be changed either by doing work on the system or by heating it
- Heat and work are equivalent ways of changing a system's internal energy
- $\Delta U = q + w$ *(Mathematical Form of First Law)*

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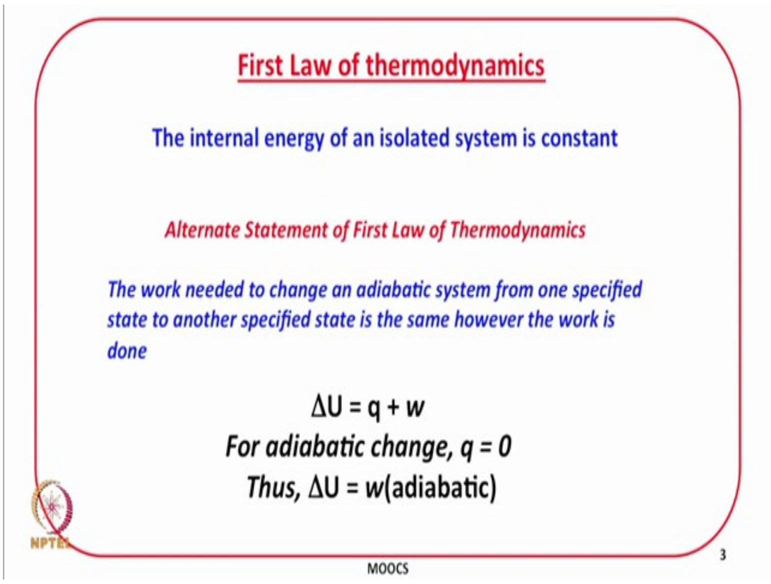

First Law of thermodynamics

The internal energy of an isolated system is constant

Alternate Statement of First Law of Thermodynamics

The work needed to change an adiabatic system from one specified state to another specified state is the same however the work is done

$$\Delta U = q + w$$

For adiabatic change, $q = 0$

Thus, $\Delta U = w(\text{adiabatic})$

MOOCS

Then, as we discussed in the previous lecture that we can express the internal energy changes as well as the heat in the form of work and that is what I mentioned that work is the most fundamental quantity in thermodynamics, and today I will demonstrate that we can express the change in internal energy exclusively in terms of work and the heat also in terms of work.

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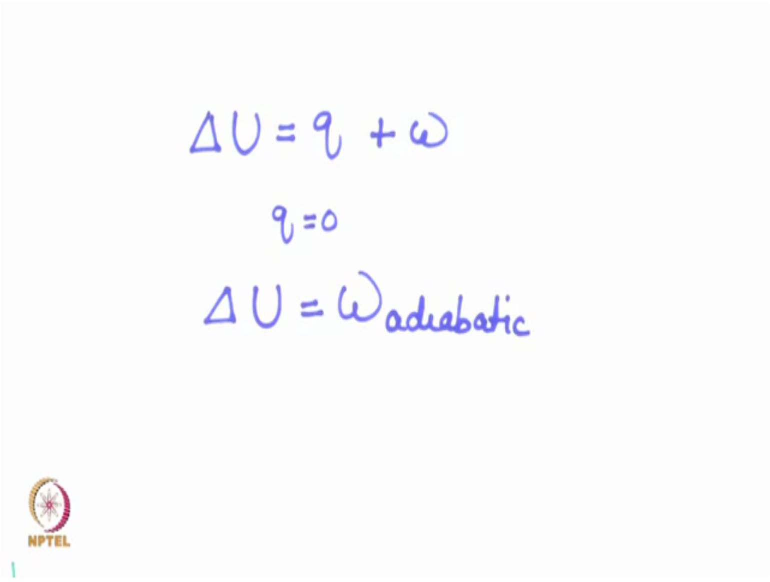

$$\Delta U = q + w$$

$$q = 0$$

$$\Delta U = w_{adiabatic}$$

So, the equation that we just derived is delta U is equal to q plus w and let me consider a process which is W adiabatic. W adiabatic process means q is equal to 0. So, I will write now delta U is equal to w adiabatic.

Remember that we have discussed that work is a path function, but see what we are doing here is, we are connecting a path function with a property which is a state function. A path function is becoming equal to difference in the properties of which is a state function. That means according to this equation, the work done in changing a system from one specified state to another specified state under adiabatic conditions is going to be same irrespective of how the work is done. Let us take an example.

Let us say I take 5 kg of water and we need to change the temperature of water by some amount and if we keep adiabatic conditions, then the work required to change this temperature will be same. Whether this work is done in a mechanical form that is by stirring it with the paddles or by passing an electric current, the same amount of work will be required and this forms an alternate statement of the first law of thermodynamics, that is the work needed to change an adiabatic system from one specified state to another specified state is the same. However, the work is done and internal energy being a state property, the change in internal energy.

Now we have connected with work and hence, demonstrating that the internal energy or the change in internal energy can be exclusively written in the form of work. Work is something which we can actually see with our eyes being happening. You remember that earlier I discussed that work is said to be done in a process. If that process can lead to change in height or a weight somewhere in the surroundings, so that we can actually see with our eyes.

Now, after having demonstrated this connection between delta U and w, now I will demonstrate that we can also express heat exclusively in terms of work here. We have taken an example of an insulated system, that is which does not allow the transfer of heat as forming the adiabatic process. Now, let us assume that we just remove the insulation and once we remove the insulation; that means, now if the work is done on the system, then some of that work energy can leave the system in the form of some form of energy and we usually we call that energy as heat.

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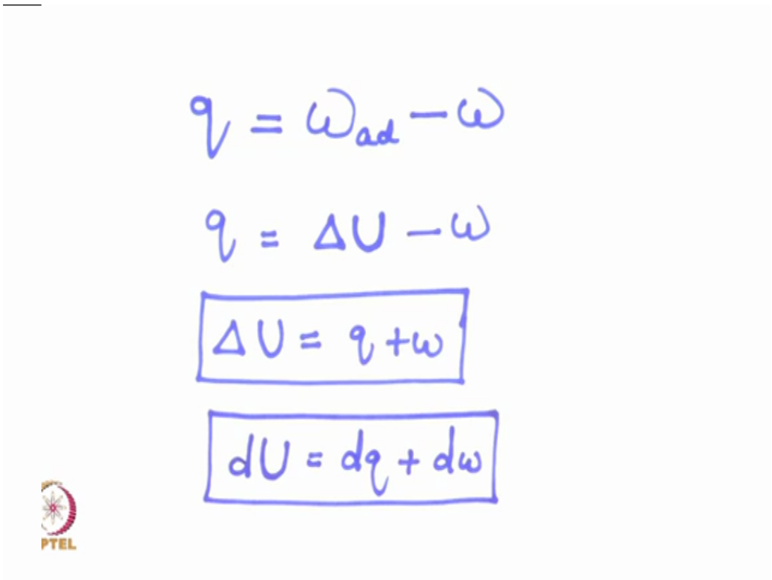

$$q = w_{ad} - w$$

$$q = \Delta U - w$$

$$\boxed{\Delta U = q + w}$$

$$\boxed{dU = dq + dw}$$

So, therefore, earlier we had work under adiabatic conditions and now, if we remove the insulation let us say the new work is w to get the same change, then this difference in the work is equal to energy that has left the system and that energy is heat.

Because now the system is not adiabatic insulation is not there, therefore some amount of the work done on the system can actually leave the system in the form of, some form of energy which is called heat. So, if the initial and final states are same, then this difference in the work done is equal to heat and from the previous discussion, we just discussed that it is equal to delta U and if I rearrange this, I get the first law of thermodynamics back from an alternate discussion.

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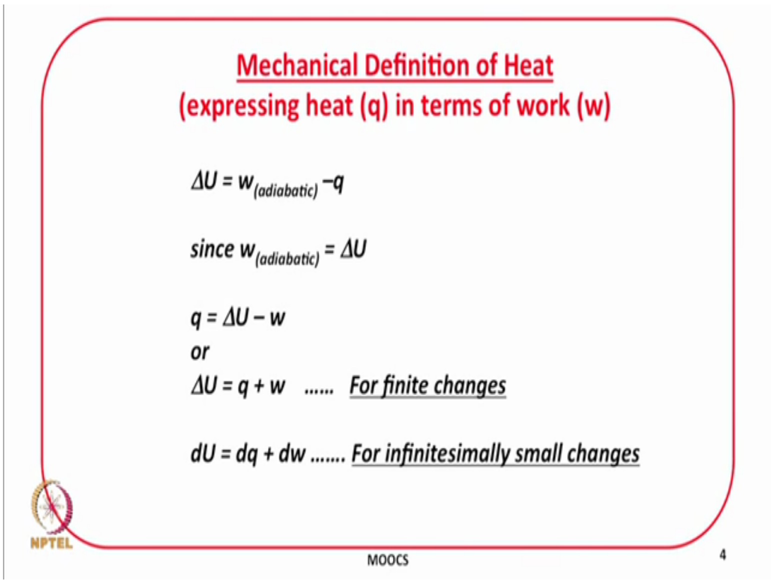

Mechanical Definition of Heat
(expressing heat (q) in terms of work (w))

$\Delta U = w_{(adiabatic)} - q$

since $w_{(adiabatic)} = \Delta U$

$q = \Delta U - w$

or

$\Delta U = q + w$ …… For finite changes

$dU = dq + dw$ ……. For infinitesimally small changes

Now, let us take a look at the slide. The delta U will be w adiabatic minus q and since w adiabatic is equal to delta U, therefore q is equal to delta U minus w or delta U is equal to q plus w. This is what I just described and this is for a finite change. delta U is equal to q plus w is for finite change and for infinitesimally small changes, I can simply write d U is equal to d q plus d w and this is another equation which will be very useful when we deal with the infinitesimally small changes and then derive several other equations, but the point to recognize here is this equation that we have demonstrated that we can express heat exclusively in terms of work. So, therefore, once again I reemphasize that work is the most fundamental quantity; both the internal energy changes in internal energy and heat can be expressed in terms of work.

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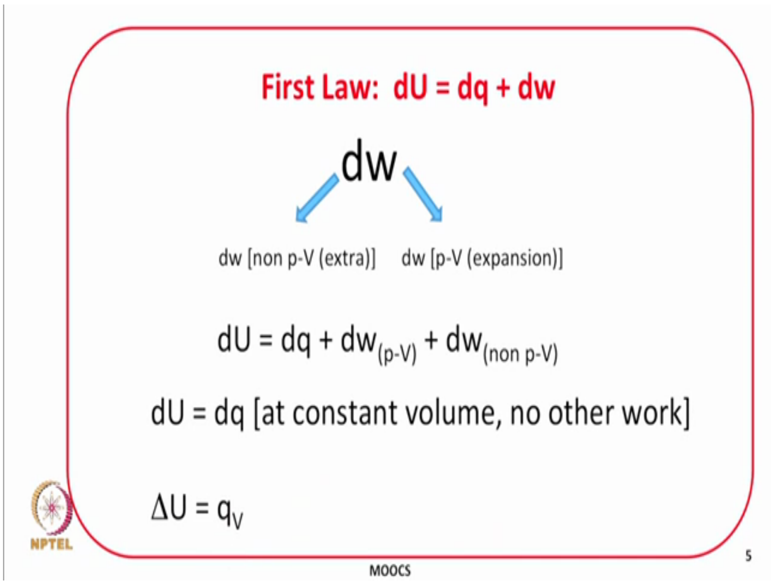

First Law: $dU = dq + dw$

$dU = dq + dw_{(p\text{-}V)} + dw_{(non\ p\text{-}V)}$

$dU = dq$ [at constant volume, no other work]

$\Delta U = q_V$

Let us recall now the first law d U is equal to d q plus d w, where d w represents the work done. The work done can be of two types. First one is the known pressure volume work which in some books you will see that they write as extra work and the second type of work is the work of expansion which is also called the pressure volume work, ok.

Now, suppose if we do not allow the system to do any extra work. If no known pressure volume work is done and if the volume is held constant that means there will be no pressure volume work also done. What I am trying to say is that we have d U is equal to d q plus d w.

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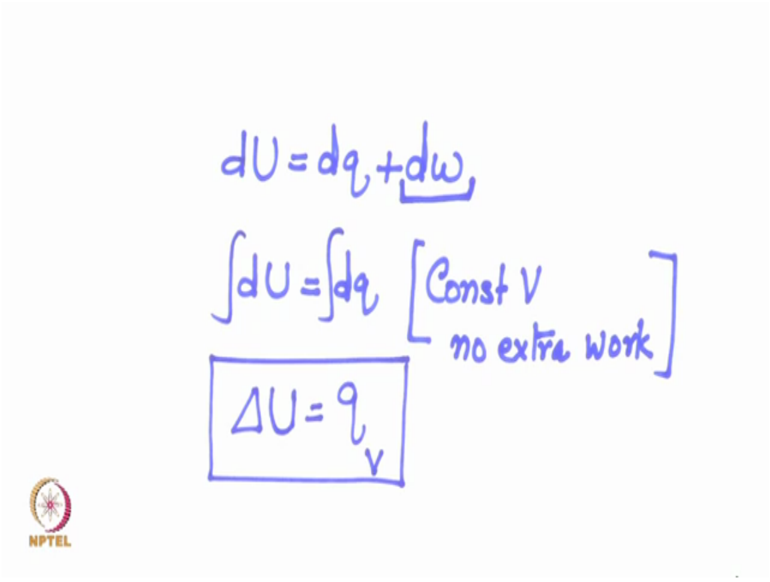

$$dU = dq + \underbrace{dw}_{}$$

$$\int dU = \int dq \quad \left[\begin{array}{l}\text{Const } V \\ \quad \text{no extra work}\end{array}\right]$$

$$\boxed{\Delta U = q_V}$$

If we do not draw any work from the system, that is the system is not allowed to do any non-pressure volume work or pressure volume work, pressure volume work will be zero when the volume is held constant and if there is also no extra work, then d U will become equal to d q. What are the constraints? The constraints are constant volume and the other is no extra work.

So, let us now take a look at the slides that d U is equal to d q plus d w as I mentioned above. It is pressure volume work or non-pressure volume work and in case there is no work done whether it is of pressure volume work or non-pressure volume type, then d U is equal to d q and for a finite change what you need to do is just integrate and what you have delta U is equal to q v. The heat supplied to a system at constant volume is equal to change in its internal energy. So, experimentally if we want to determine the change in internal energy, one way of finding it out is by measuring the heat supplied to system provided the volume is kept constant.

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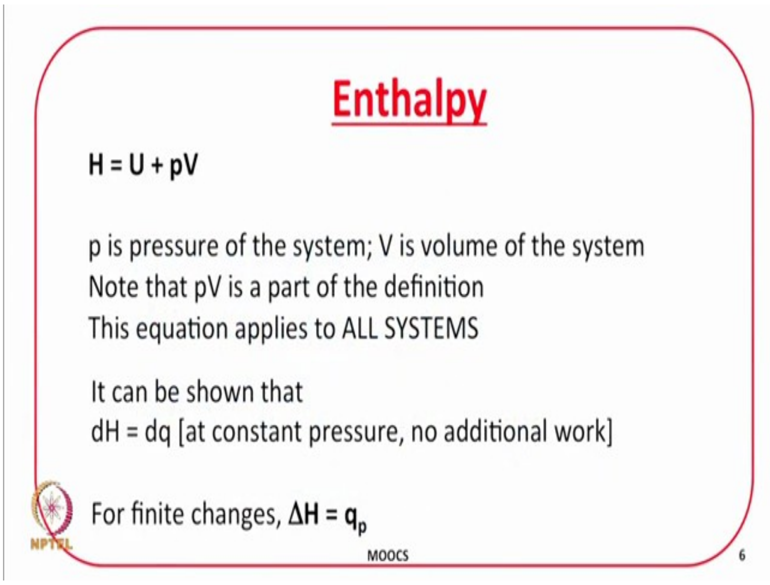

Enthalpy

$H = U + pV$

p is pressure of the system; V is volume of the system
Note that pV is a part of the definition
This equation applies to ALL SYSTEMS

It can be shown that
$dH = dq$ [at constant pressure, no additional work]

For finite changes, $\Delta H = q_p$

Now, let us discuss enthalpy. Suppose if the volume is not held constant, you allow the system to expand or compress, let us say expansion. We can consider pressure constant at the volume change. Now, the amount of heat supplied is no more equal to change in its internal energy. It is a different quantity now because some of the heat supplied can be used to drive back the surroundings and we will see here that if the pressure is held constant, then the amount of heat supplied turns out to be equal to change in enthalpy. Let us see how it comes.

How do we define enthalpy? Now, it is a very common question asked in several interviews and sometimes there is a confusion in the definition of enthalpy. Let us get rid of that confusion. Enthalpy, how do you define an enthalpy?

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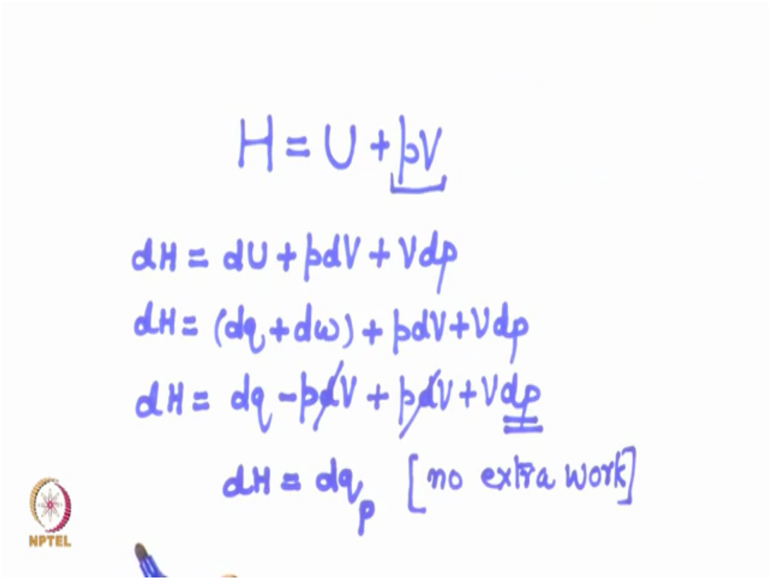

$$H = U + \underbrace{pV}$$

$$dH = dU + pdV + Vdp$$

$$dH = (dq + dw) + pdV + Vdp$$

$$dH = dq - \cancel{pdV} + \cancel{pdV} + V\underline{dp}$$

$$dH = dq_p \quad [\text{no extra work}]$$

The definition of enthalpy is H is equal to U plus p V, where U is internal energy of the system, p is pressure of the system and V is the volume of the system. The confusion sometimes can come because of this p V term because p V is equal to n. R T is generally used for ideal gases, but remember here that this p V is a part of the definition. This definition applies to all the systems irrespective of what is the state of the system, so not to be confused with the ideal gases. The definition of enthalpy is H is equal to U plus p v, all right.

Now, let us say there is some advancement of the process. The change d H is going to be equal to d U plus p d V plus V d p. So, d H is equal to d U by first law is equal to d q plus d w. This comes from d u, then plus p d V plus V d p. Now, let us consider mechanical equilibrium between system and surrounding. So, then this equation becomes d q. If there is a mechanical equilibrium between system and surrounding, I can write d w as minus p d V as I discussed, as we discussed in the previous lecture that d w is equal to minus p d V in case there is a mechanical equilibrium between the system and surrounding and also, there is no other work done that is known pressure volume work also is equal to zero.

So, in that case this equation becomes of this form and this cancel and if pressure is held fixed, then d H becomes equal to d q at constant pressure and also, the condition is that there is no extra work or other work or whatever way you want to call it and that is what is seen in the slide. The d H is equal to d q at constant pressure no additional work and for a final change when you integrate it, delta H is equal to q p.

So, the things to remember are that if we are interested in measuring delta U, this will be equal to q V and delta h. This will be equal to q p here. The volume is held constant here.

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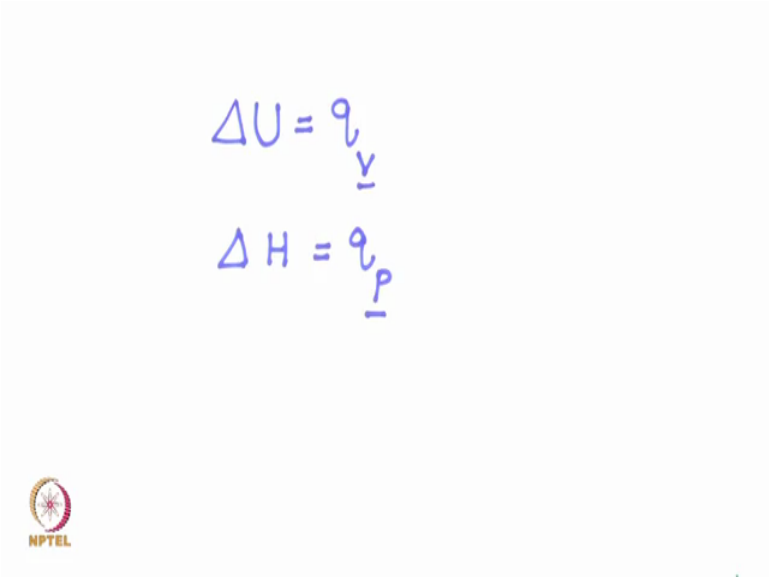

$$\Delta U = q_{\underline{V}}$$

$$\Delta H = q_{\underline{P}}$$

The pressure is held constant and in both the cases, there is no additional work done and later on we will discuss that how to experimentally determine what kind of calorimeters are required to measure the values of delta U and the values of delta h.

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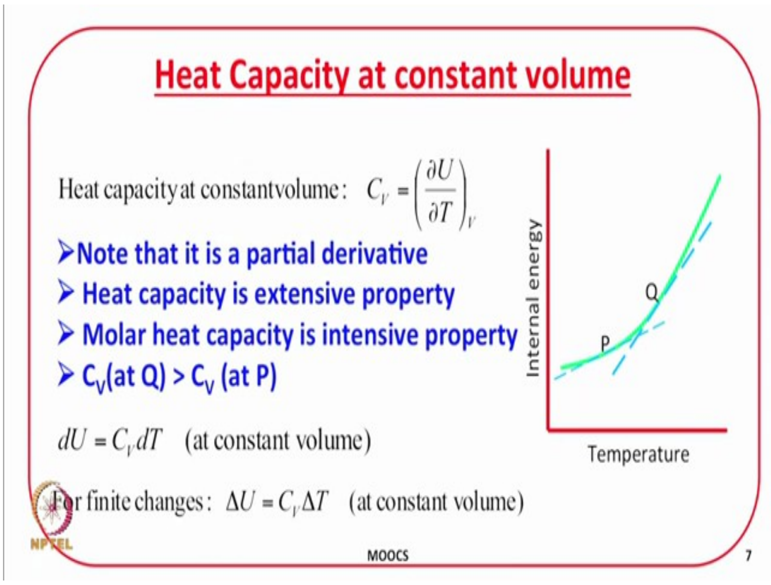

Heat Capacity at constant volume

Heat capacity at constant volume: $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

- Note that it is a partial derivative
- Heat capacity is extensive property
- Molar heat capacity is intensive property
- C_V(at Q) > C_V (at P)

$dU = C_V dT$ (at constant volume)

For finite changes: $\Delta U = C_V \Delta T$ (at constant volume)

Now, we will discuss another very important thermodynamic quantity and it is called the heat capacity.

What is heat capacity? The definition of heat capacity is the amount of heat required to change the temperature of a system by 1 Kelvin and obviously, if the temperature of the system is to be changed, it will definitely depend upon the conditions that is whether the pressure is held constant or the volume is held constant. So, therefore, we will discuss two types of heat capacities; one is the heat capacity at constant pressure and the heat capacity at constant volume.

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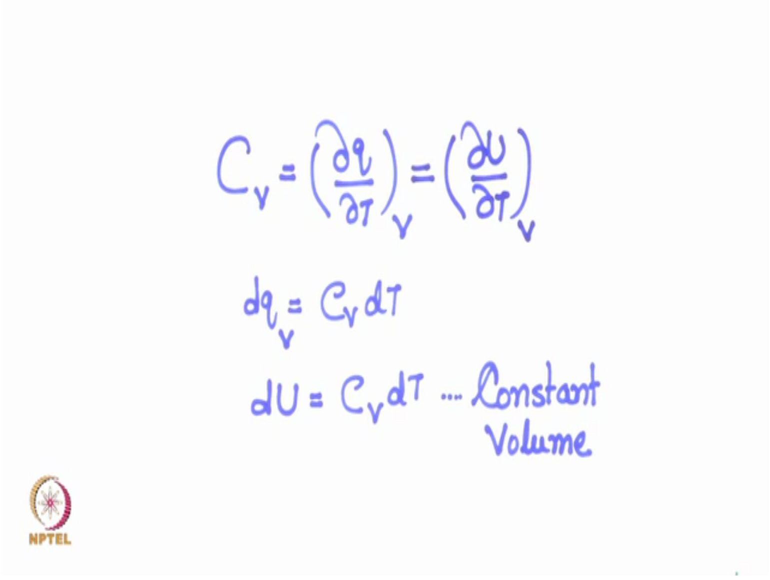

$$C_V = \left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$dq_V = C_V dT$$

$$dU = C_V dT \text{ .... Constant Volume}$$

C V is defined as the partial derivative dou q by dou T at constant volume. The amount of heat required to change the temperature of a system by unit at constant volume and from this equation, I can write that d q is equal to C V d T at constant volume and we have just shown that d q at constant volume is equal to d U is equal to C V d T. What is the constant? You have constant volume if the volume is held constant and the temperature is changed, we can straightaway use this equation d U is equal to C V d t. However, as we will show later on that for a perfect gas, for an ideal gas this equation always applies irrespective of whether the volume is held constant or not, that we will discuss later.

Let us take a look at the slide. The heat capacity at constant volume is defined as C V is equal to dou U by dou T at constant volume because d q at constant volume is equal to d

U. Therefore, dou q by dou T at constant volume becomes d U by d T or dou U by dou T at constant volume. Take a look at the figure. The internal energy is temperature dependent and usually the internal energy is varying with temperature in a non-linear fashion and we can see that the slopes of the curve at point p and at point q are different and the slope of the curve is equal to dou U by dou T at constant volume. This represents the heat capacity at constant volume. That means, the heat capacity at constant volume for this system at point p, where the temperature is of certain value is different than the heat capacity at another temperature.

Note that heat capacities by definition, it is a partial derivative. It is a partial derivative because one of the variable you are keeping constant that is volume is held constant. Heat capacity is an extensive property because the amount of heat required to change the temperature by unit degree will depend upon the size, however if you calculate per mol, the molar heat capacity will become intensive property because you will be defining it as per mol. As I just discussed that the C V is temperature dependent. Generally the C V at point q is greater than C V at point p, unless the temperature range is very very small, then it may be considered constant. We just discussed that d U is equal to C V d T always if the temperature if the volume is held constant and for finite change and if we take the able integrated form of this, you can calculate delta U and delta U will be equal to C V times delta T. This is at constant volume.

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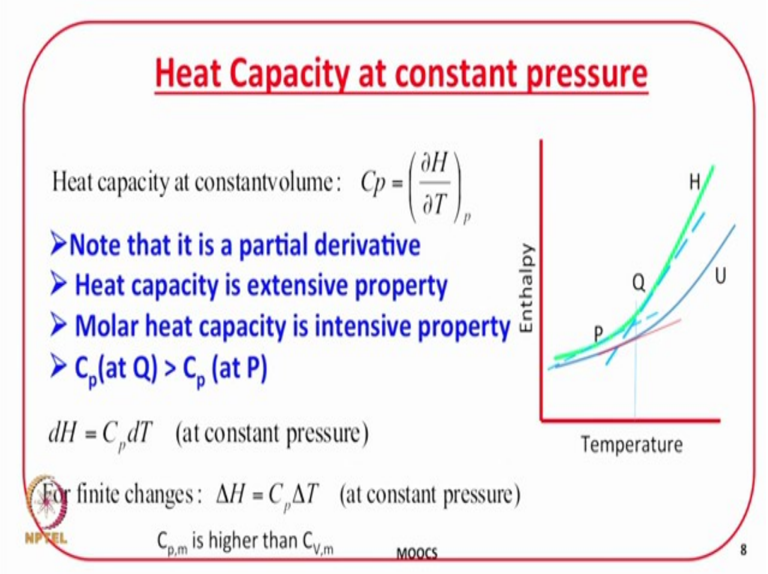

Heat Capacity at constant pressure

Heat capacity at constantvolume: $Cp = \left(\frac{\partial H}{\partial T}\right)_p$

- Note that it is a partial derivative
- Heat capacity is extensive property
- Molar heat capacity is intensive property
- C_p(at Q) > C_p (at P)

$dH = C_p dT$ (at constant pressure)

For finite changes: $\Delta H = C_p \Delta T$ (at constant pressure)

$C_{p,m}$ is higher than $C_{V,m}$

Now, let us discuss the heat capacity at constant pressure.

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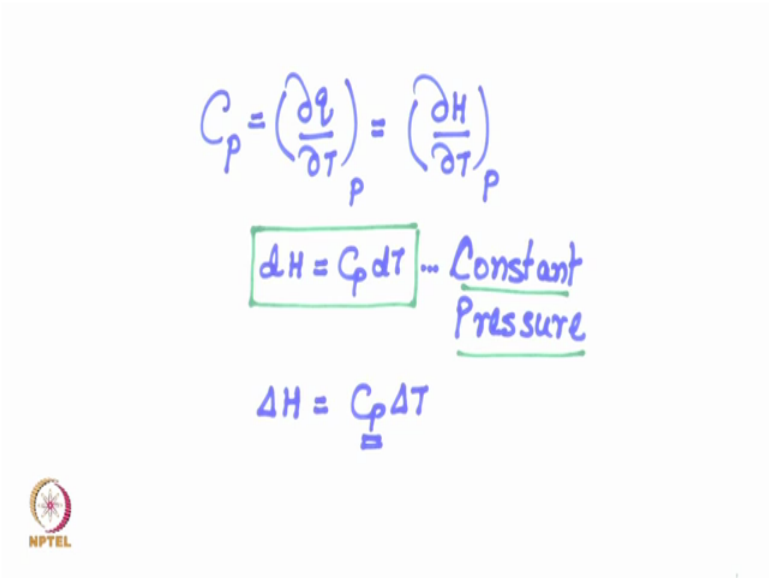

$$C_p = \left(\frac{\partial q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$\boxed{dH = C_p dT} \cdots \underline{\text{Constant}}\ \underline{\text{Pressure}}$$

$$\Delta H = \underline{C_p} \Delta T$$

Now, if the pressure is held constant, then definitely now the amount of heat required to change the temperature by one degree will be different and how we define C p. This is heat capacity at constant pressure. This is equal to dou q by dou T at constant pressure and since we just discussed that the heat at constant pressure is equivalent the change in enthalpy, so I will write this as dou H by dou T at constant pressure.

Writing this in another form d H is equal to C p d T, again I will write as constant pressure and for a finite change delta H is equal to C p times delta t. If C p is not depending upon temperature, otherwise the temperature dependence has to be accounted for. We will discuss later. So, here again this equation d H is equal to C p d T at constant pressure is always applicable as long as you hold the pressure constant, however again we will demonstrate later on that if you are applying this to perfect gas, then this always can hold true. For perfect gas you do not have to hold the pressure constant then this equation can be straight away used for perfect gas.

Let us take a look at this slide where we define the heat capacity C p H dou H by dou T at constant pressure and if you look at the figure, enthalpy is also temperature dependent, but generally the enthalpy varies more sharply compared to internal energy and this is because now you are holding the pressure constant and earlier we were holding the volume constant. When we were discussing the C V that heat capacity at constant volume and if you hold the pressure constant, then some of the energy can be used as to do work and therefore, one may require more heat to change the temperature by a unit degree. So, therefore, the slope of H versus T is going to be higher than the slope of U versus T and that is the value of C p in general is greater than the value of C v. Here again please note that it is a partial derivative. Heat capacity is an extensive property, molar heat capacity is an internal intensive property and the final point to note that C p is greater than C V because you can see here at the points p or point q in the figure, the slopes are different and the slope corresponding to the plot of H versus T is higher than the slope corresponding to U versus t. Therefore, C p m is greater than C V m.

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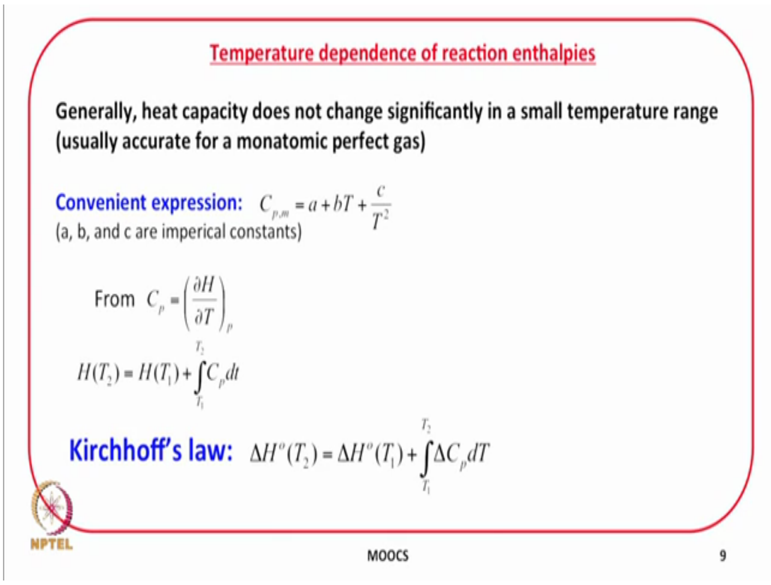

Temperature dependence of reaction enthalpies

Generally, heat capacity does not change significantly in a small temperature range (usually accurate for a monatomic perfect gas)

Convenient expression: $C_{p,m} = a + bT + \frac{c}{T^2}$

(a, b, and c are imperical constants)

From $C_p = \left(\frac{\partial H}{\partial T}\right)_p$

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dt$$

Kirchhoff's law: $\Delta H^o(T_2) = \Delta H^o(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$

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What are the advantages of C p and C v? There are many applications of C p and C v. Let me first discuss the temperature dependence of reaction enthalpies. It is a very useful thermodynamic quantity which will allow connecting one thermodynamic property to another at different temperature without doing experiment, additional experiment.

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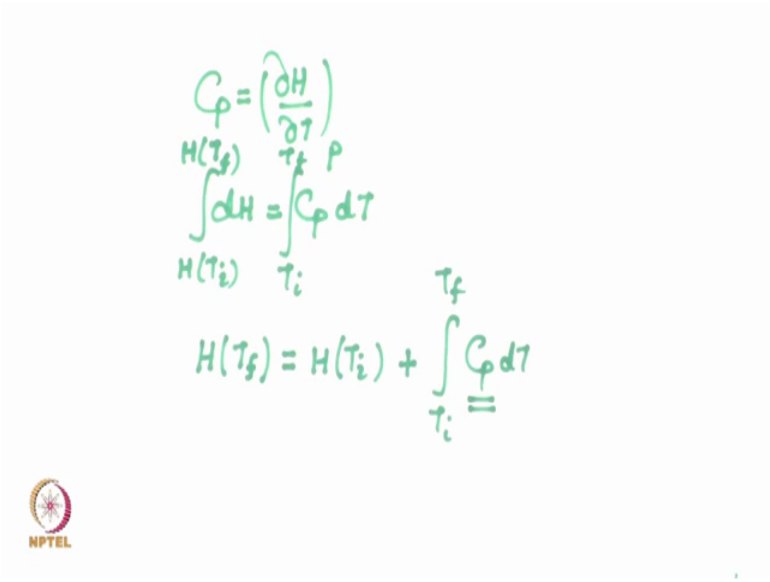

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\int_{H(T_i)}^{H(T_f)} dH = \int_{T_i}^{T_f} C_p \, dT$$

$$H(T_f) = H(T_i) + \int_{T_i}^{T_f} \underline{\underline{C_p}} \, dT$$

So, look at this definition. C p is equal to dou H by dou T at constant pressure. So, d H is equal to C p d t. I am assuming that the pressure is constant, right. So, this is H at T i and let us say the final limit H s T f and we have T i to T f, fine. So, H at T f is equal to H at T i plus integration T i to T f C p d t.

Now, depending upon whether the heat capacity at constant pressure is temperature dependent or not, it can be either taken out of integral or the appropriate expression can be used, usually the heat capacity C p for a very narrow range of temperature can be considered as temperature independent and very safely or very accurately, it can be taken for an ideal gas for a small range of temperature C p. It usually does not depend upon temperature. In that case, it can be taken out of integral, but in any case if the temperature range is small, then to a fairly good level of accuracy, heat capacities can be considered independent of temperature, otherwise an appropriate equation should be used.

Let us take a look at the slide. In case the heat capacity is not independent of temperature, then a convenient expression, it is again an experimental observation that molar heat capacity C p m usually varies with temperature. According to a plus b T plus C by T square, where a b and C are empirical constants from the definition of C p as I just discussed with you, the temperature dependent of, dependence of enthalpy can be different and if I apply this to the changes under standard state conditions, I can introduce deltas and this forms the Kirchoffs law, very important. It connects the reaction enthalpy at one temperature with the reaction enthalpy at another temperature.

What you need is the information on the values of heat capacities delta C p, delta C p which is the change in heat capacity when the reaction proceeds either one can experimentally determine it or one can calculate it. If you know the heat capacities of the products and reactants, then by using the suitable psychometric numbers, the difference in heat capacities of product and reactants will give you the value of delta C p.

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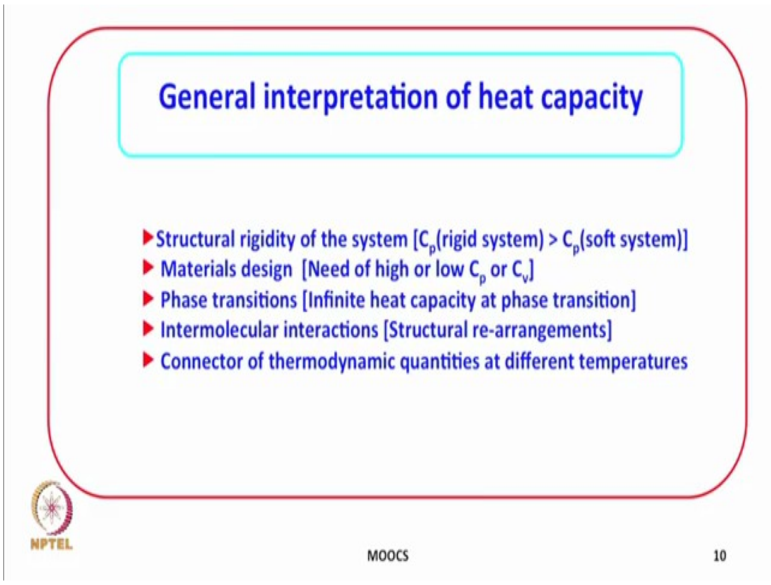

General interpretation of heat capacity

- Structural rigidity of the system [C_p(rigid system) > C_p(soft system)]
- Materials design [Need of high or low C_p or C_v]
- Phase transitions [Infinite heat capacity at phase transition]
- Intermolecular interactions [Structural re-arrangements]
- Connector of thermodynamic quantities at different temperatures

So, finally, as I said that C p and C V are very important thermodynamic quantities, how do we generally interpret heat capacity? The general definition that is the amount of heat required to change the temperature by 1 Kelvin and if we think a little bit deeper, then the amount of heat required to change the temperature of a system will definitely depend upon the type of system. It will depend upon the structural rigidity of the system because if the system is very rigid, if there is a very strong bonding in a particular substance, then to raise the temperature by 1 Kelvin, a lot of heat will be required. So, I can write in general that C p of a rigid system will be higher than the C p of a soft system.

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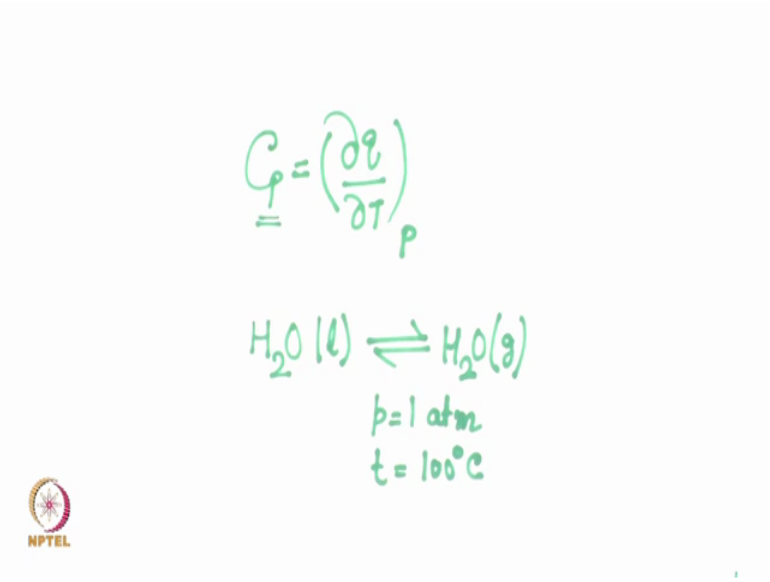

$$C_p = \left(\frac{\partial q}{\partial T}\right)_p$$

$$H_2O\,(l) \rightleftharpoons H_2O\,(g)$$

$p = 1$ atm

$t = 100°C$

In the design of materials for example, C p which is defined as or C p or C V which is defined as dou q by dou that constant pressure, if upon supplying the heat, the change in temperature is very little and then, the heat capacity is very high. If that is what we want, we want some material which should not respond to heat supply to it in terms of last changes in temperature and then, you want to hike heat capacity material that is in that case the heat supplied will not lead to a reasonable changes in temperature. However, if heat capacity for heat capacity to be very low, the amount of heat supplied will lead to larger changes in temperature.

So, if we want a system which should immediately respond to the heat, we should. A small application of heat should lead to large changes in the temperatures or large you know of the large change in the temperature of the system to which the heat is supplied, then the heat capacity is going to be very low phase transitions. Again if we look at this definition, a phase transition can be let us say if I just took water liquid to water vapor at 100 degree Celsius and one atmosphere, where as a p is equal to one atmosphere and temperature is equal to 100 degree Celsius, this is a phase transition.

At phase transition, the heat capacity becomes infinite because whatever is the heat supplied to the system at phase condition that is used to drive the endothermic phase transition, it does not change the temperature. That is why the phase transitions are accompanied with infinite heat capacity values and another important information that comes out of these values of heat capacities is on intermolecular interactions. A detailed discussion will require a long time, but to explain very briefly that any structural rearrangements as a result of intermolecular interactions should be reflected in the values of C p and C V because after all C p and C V depends upon the rigidity of the system, the nature of bonding and if the intermolecular interactions are leading to alterations in the nature of interactions nature of bonding, then C p and C V should respond to it.

So, therefore, C p and C V are very important thermodynamic quantities which can be used to get a lot of information and which has lot of applications and as I just discussed as one example using Kirchoffs equation that it is a connector of thermodynamic quantities at different temperatures.

So, I hope that the first law of thermodynamics which describes the changes in internal energy in terms of heat and work is very clear, and the various equations which we developed have lot of applications which we will discuss in the tutorial session.

Thank you very much.