Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 04
Second Law Of Thermodynamics

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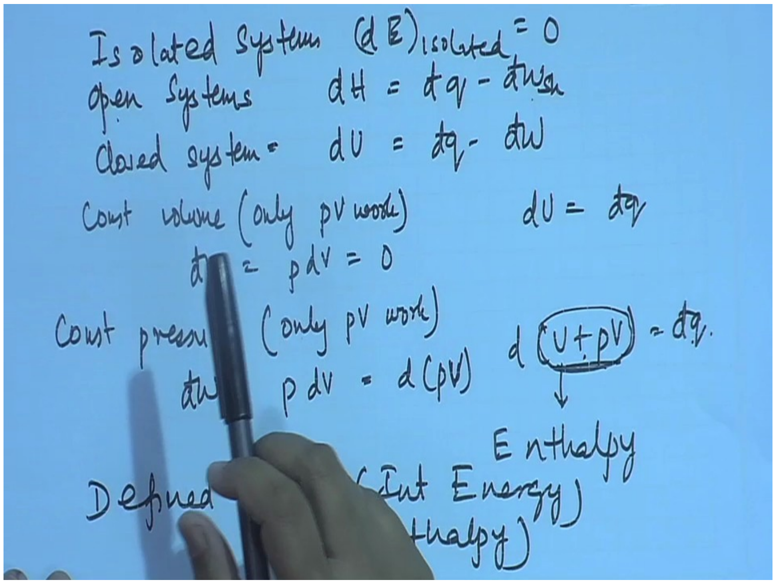

Isolated System $(dE)_{isolated} = 0$

Open Systems $dH = \bar{d}q - \bar{d}w_{sh}$

Closed system $dU = \bar{d}q - \bar{d}w$

Const volume (only pV work) $dU = \bar{d}q$

$\bar{d} \quad = p\,dV = 0$

Const pressu (only pV work) $d\left(\boxed{U+pV}\right) = \bar{d}q.$

$\bar{d}w \quad p\,dV = d(pV)$ $\downarrow$ Enthalpy

Defined (Int Energy)

thalpy)

Well, good day to all of you to continue with our discussions on the first law of thermodynamics what did we do? In the last class we have ended with the law of or the statement of the first law for different systems and we found out that usually we find out that even for close systems since it is very easy to maintain a constant pressure and we always prefer to perform processes under atmospheric pressure. So therefore we encounter constant pressure processes very frequently.

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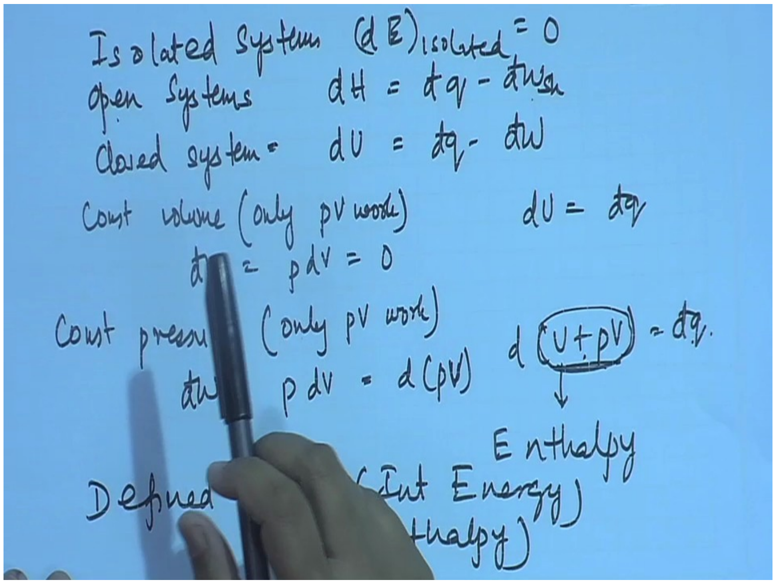

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Closed system = $dU = đq - đW$

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Enthalpy

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So for such processes we find that the term u plus pV usually dominates and the same thing happens for the open systems as well as a result of which we had in or rather we have included the term enthalpy in our energy balance or in the first law system. Now before since enthalpy so very important and we will be dealing with it very frequently, so before I proceed further I would be I would like to spend a very short while discussing the important or the some interesting aspects of the enthalpy of a system.

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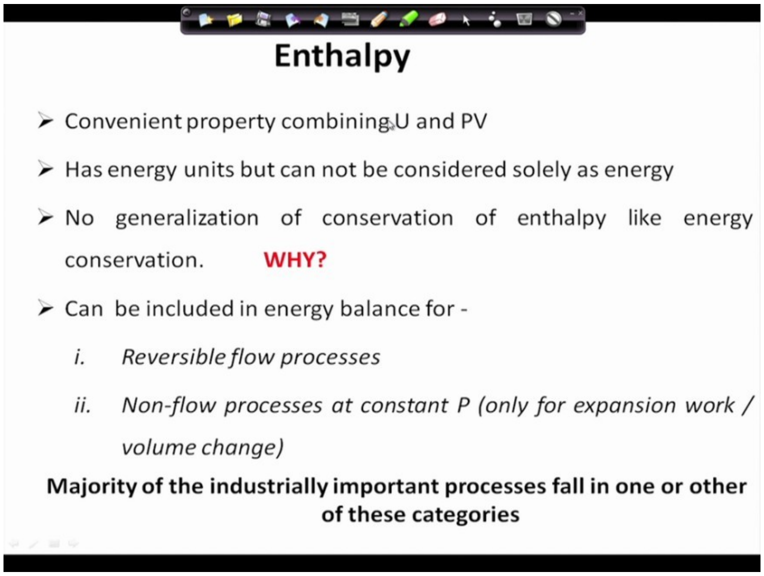

Enthalpy

- Convenient property combining U and PV
- Has energy units but can not be considered solely as energy
- No generalization of conservation of enthalpy like energy conservation. **WHY?**
- Can be included in energy balance for -
  - i. *Reversible flow processes*
  - ii. *Non-flow processes at constant P (only for expansion work / volume change)*

Majority of the industrially important processes fall in one or other of these categories

Now what is enthalpy basically it is a convenient property as you know which combines U and PV or in other words it combines internal energy and the flow work and we have seen that it has energy units but the important question is can we conserve enthalpy just like we have conserved energy, for isolated systems the first law gave us the law of conservation of energy in isolated systems, right? So in the same way do we have something like the conservation of enthalpy?

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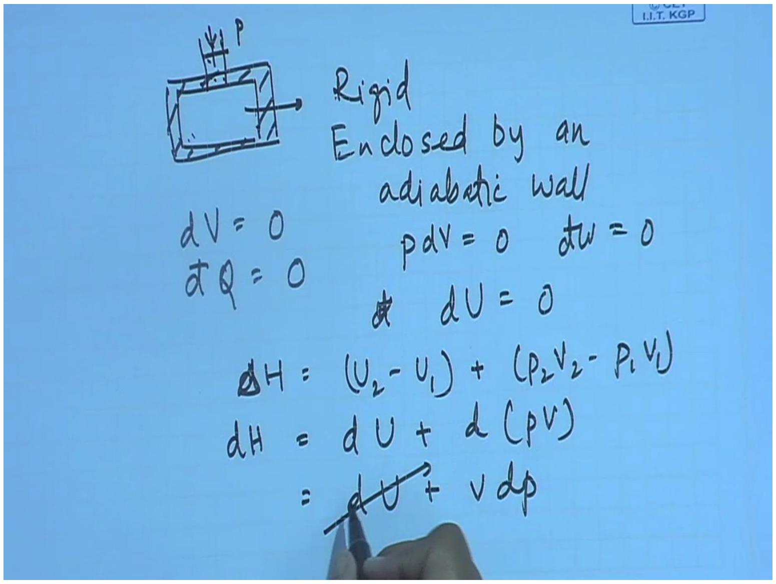

Rigid
Enclosed by an adiabatic wall

$dV = 0$

$đQ = 0$

$pdV = 0 \quad đW = 0$

$dU = 0$

$\Delta H = (U_2 - U_1) + (P_2V_2 - P_1V_1)$

$dH = dU + d(pV)$

$= \cancel{dU} + V dp$

So let us see that, now if you that find suppose we have a rigid vessel where maybe it is rigid it is immovable and maybe an isolated system so therefore there is no amount of internal energy change in it. Say for example we have got some particular system which is enclosed by a adiabatic boundary condition. So therefore this vessel it is rigid and enclosed by an adiabatic wall and just here we have a piston cylinder sort of an arrangement, okay.

It is fully enclosed but we have a piston cylinder kind of arrangement from where we can impose a pressure P on the system since it is rigid it cannot move, so therefore my dV equals to 0, right? And since it is enclosed by an adiabatic wall so therefore I know that my dQ equals to 0, fine. And since there is no other work being performed on it, so therefore naturally my PdV equals to 0 or my dW equals to 0 and since it is a closed system, so naturally for this particular system I know my dU is also equal to 0.

Now I keep on increasing the pressure on the system, right? So therefore when I keep on increasing the pressure on the system but since it the system inside it cannot move and there is no heat transfer, so therefore the dU remains constant in the system since dQ equal to 0 dW equal to 0 holds even when I am applying pressure, so therefore what happens to the enthalpy change of the system? The enthalpy change is in this particular case my d or rather delta H that is equal to U2 minus U1 plus P2V2 minus P1V1. If I write it in differential form this is dH equals to dU plus d of PV my volume remains constant, so therefore this becomes dU plus VdP.

I know my dU equals to 0 but dH is not equal to 0 because dP is not equal to 0, so therefore what do I find? I find that even when dU equals to 0 even when we find that there is no energy change of this particular system the enthalpy of the system can increase since the pressure of the system is increasing.

So therefore in reality we cannot have something like the conservation of enthalpy just like we have conservation of energy or in other words enthalpy is not a true energy like enthalpy energy. And enthalpy can be included in the energy balance equation for 2 instances which we have already shown, the first instance was for the open system which I have shown where we were performing reversible flow processes and the second case is non-flow processes at constant pressure where only expansion work or volume change work is involved.

So therefore we find that enthalpy can be included in energy balance equation for under only 2 circumstances the one for which I have derived the equations and incorporated enthalpy in my first law those 2 processes are reversible flow processes and non-flow isobaric processes provided they are undergoing only PV type of work and fortunately I should tell you that majority of the industrial important processes they fall in one or other of these 2 categories.So therefore we include enthalpy in our energy balance equation and we usually forget that enthalpy is not a true energy in its strictest terms.

Now the other thing which I was thinking of discussing before closing the chapter on first law is that we can apply first law for different close systems, right? I give it to you as an exercise for applying first law and finding out the work interaction for isobaric I have already done isochoric also I have already done but adiabatic, poly-tropic and isothermal processes you can take ideal gas as the working fluid and you can do it even for a generalized system as well.

Now whenever for these particular systems we find that there is some amount of heat interaction or there is some amount of work interaction and that brings about a change in property of the

System, the only property change which occurs due to heat interaction is usually the temperature change, temperature change can occur both by heat interaction as well as work interaction but how much amount of the temperature change will occur due to some amount of heat input on the system that depends upon the heat capacity of the system, with the same amount of heat input different systems will not exhibit the same amount of temperature change.

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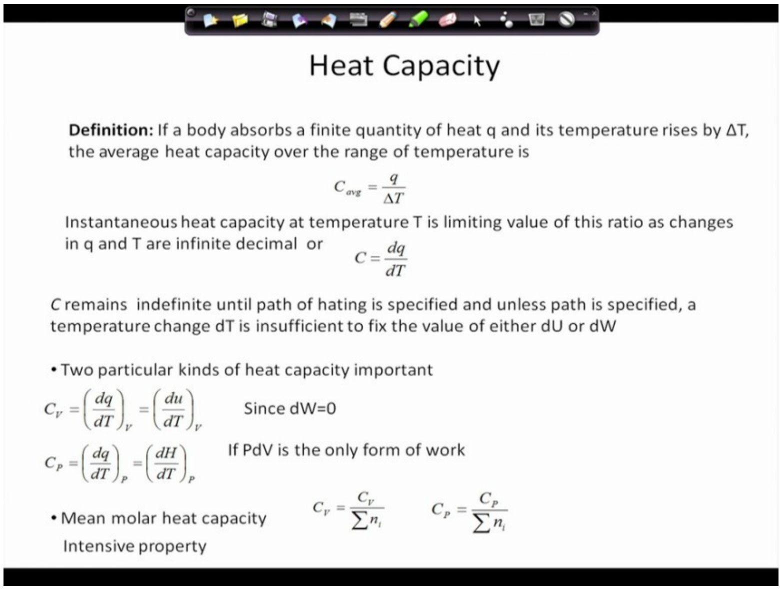

Heat Capacity

Definition: If a body absorbs a finite quantity of heat q and its temperature rises by ΔT, the average heat capacity over the range of temperature is

$$C_{avg} = \frac{q}{\Delta T}$$

Instantaneous heat capacity at temperature T is limiting value of this ratio as changes in q and T are infinite decimal or $C = \frac{dq}{dT}$

C remains indefinite until path of hating is specified and unless path is specified, a temperature change dT is insufficient to fix the value of either dU or dW

- Two particular kinds of heat capacity important

$C_V = \left(\frac{dq}{dT}\right)_V = \left(\frac{du}{dT}\right)_V$ Since dW=0

$C_P = \left(\frac{dq}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P$ If PdV is the only form of work

- Mean molar heat capacity $C_V = \frac{C_V}{\sum n_i}$ $C_P = \frac{C_P}{\sum n_i}$

  Intensive property

You are already aware of the heat capacity but again since it is quite a unique property so I would like to spend some time on the heat capacity of the system. As this is very evident you have been studying it from your school days, so you know that the heat capacity of the system is defined as the amount of heat which it absorbs and the temperature rise which occurs as a result of this heat change for the instantaneous heat capacity it is usually defined by this particular form.

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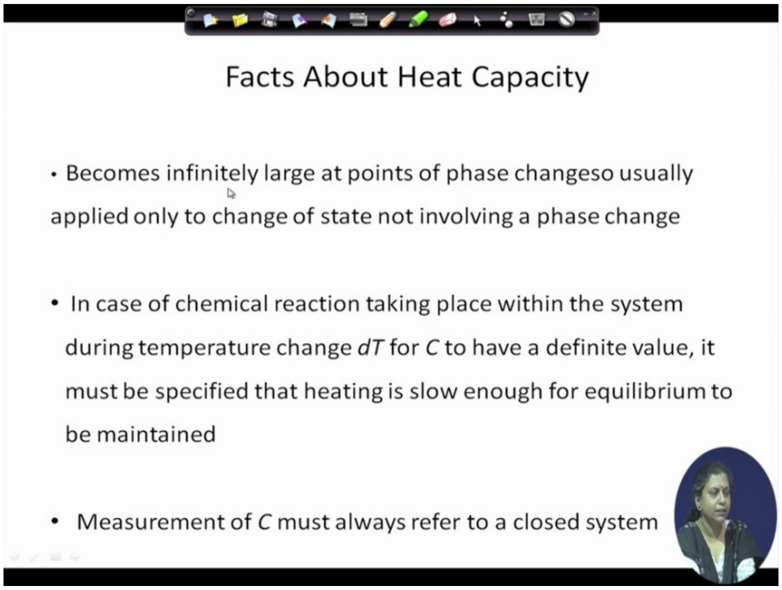

Facts About Heat Capacity

- Becomes infinitely large at points of phase changeso usually applied only to change of state not involving a phase change
- In case of chemical reaction taking place within the system during temperature change *dT* for *C* to have a definite value, it must be specified that heating is slow enough for equilibrium to be maintained
- Measurement of *C* must always refer to a closed system

Now there are some important things which I would like to mention the first important thing is that heat capacity has got a meaning only when the heat input brings about a change in the temperature of the system. So therefore it is meaningless when phase change occurs because under that condition becomes infinitely large since the heat transfer in this case does not bring about any temperature change.

The other important thing a very interesting thing is that supposed due to this heat input when there is a chemical change occurring then we find that may be due to the chemical change there is some amount of heat which is evolved or some amount of heat which is absorbed in, so therefore the heat can be absorbed for the chemical change along with increasing the temperature of the system.

Now under such conditions we will find that if we try to evaluate C and if the reaction is occurring at a very slow rate and internal equilibrium is not established then the C which we are going to measure and the C which we are going to measure when internal equilibrium is established are going to be different. So therefore it is very important to note the condition under which we are measuring C where a chemical reaction is taking place within the system and usually it is specified that the heating here is slow enough for equilibrium to be maintained.

The C which is measured under that condition is the C which we should be taking because if the measurements are taken very fast such that before internal equilibrium is attained we try to measure the temperature rise amount and the amount of heat which is going on then they the value of C which we will be getting will be different from the value of C which we will be getting when internal equilibrium is established and the measurement is rather the heating is very slow and internal equilibrium is established.

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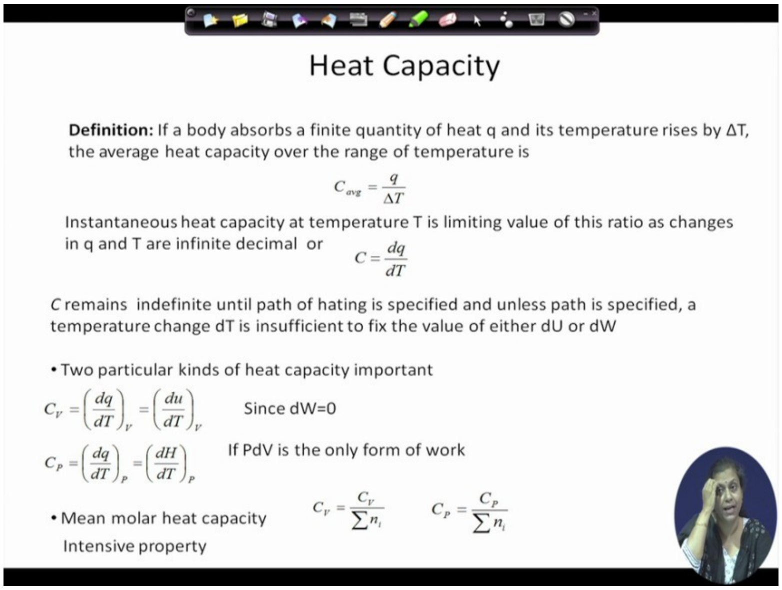

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- Mean molar heat capacity $C_V = \frac{C_V}{\sum n_i}$ $C_P = \frac{C_P}{\sum n_i}$

  Intensive property

For the same arguments C usually refers to a closed system and the most important fact about the heat capacity is although it is a property of the system it is a path dependent and it has got no meaning until the path of the heating is specified. So therefore for each path of heating we can have a different value of C and the 2 most commonly used are particularly important kinds of heat capacity are the heat capacity at constant volume and the heat capacity at constant pressure.

We find that the heat capacity at constant volume is just the rate of increase of the internal energy of the system with temperature and the heat capacity at constant pressure which we use much more frequently is the rate of increase of the enthalpy with temperature it is important to remember that this includes the flow work along with the increase in internal energy of the system provided PdV is the only form of work. So therefore although it is a property of the system it is path dependent, the heat capacities are extensive properties while the molar or the mass heat capacities they are intensive properties.

Well, the next thing which I would like to mention is that so long we have been discussing about the law of conservation of energy. Now we find that whenever a process takes place then for that particular process the total amount of energy interaction with the surrounding is equal to the total amount of energy increase or rather total amount of energy change within the system but even while obeying this particular concept also we find that some processes can be possible some processes can not be possible.

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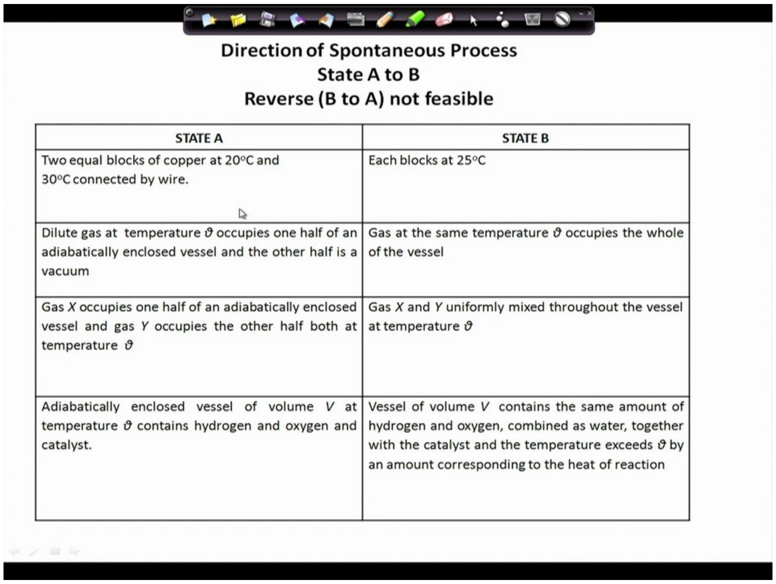

Direction of Spontaneous Process
State A to B
Reverse (B to A) not feasible

STATE A	STATE B
Two equal blocks of copper at 20°C and 30°C connected by wire.	Each blocks at 25°C
Dilute gas at temperature ϑ occupies one half of an adiabatically enclosed vessel and the other half is a vacuum	Gas at the same temperature ϑ occupies the whole of the vessel
Gas X occupies one half of an adiabatically enclosed vessel and gas Y occupies the other half both at temperature ϑ	Gas X and Y uniformly mixed throughout the vessel at temperature ϑ
Adiabatically enclosed vessel of volume V at temperature ϑ contains hydrogen and oxygen and catalyst.	Vessel of volume V contains the same amount of hydrogen and oxygen, combined as water, together with the catalyst and the temperature exceeds ϑ by an amount corresponding to the heat of reaction

For example I take up few processes which are shown here, suppose for each case I would like to go from state A to State B what is it? It is some very simple I have 2 equal blocks of copper at 20 and 30 degrees centigrade I bring the 2 blocks together and then each block is at 25 degrees centigrade I can spontaneously come from state A to State B but the reverse I have 2 blocks at 25 degrees centigrade I bring them together and then I find one block goes to 30 and the other block comes to 20 degrees centigrade that particular process is never possible.

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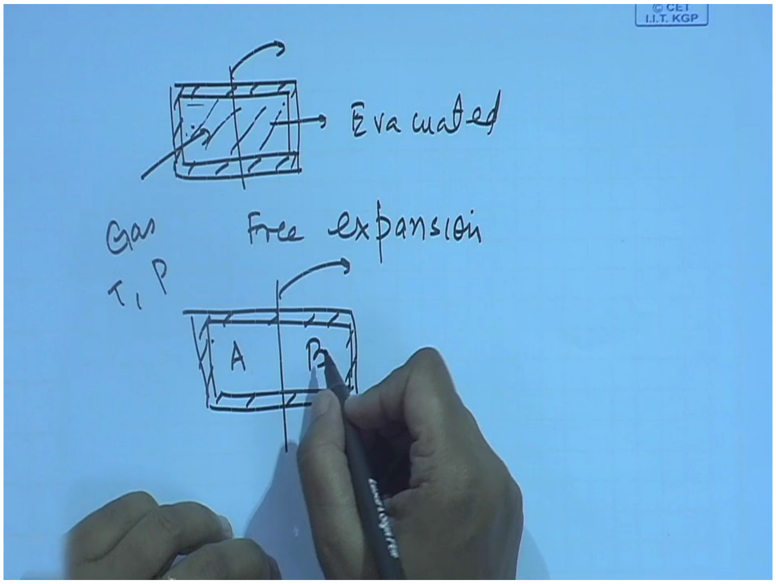

Again in the similar way suppose we have some particular gas at one half of an insulated container the phenomena of free expansion as it is called. We, maybe this is an insulated container in this particular container this portion is evacuated and here we have some particular gas at say some particular temperature T and somebody particular pressure P I remove this particular partition the gas automatically it expands and fills the entire space here but when the gas has filled and I try to push some particular partition the gas will automatically never come back and fill one half of the container.

So while this free expansion, this phenomenon of free expansion as it is called this is a spontaneous process the reverse never occurs. In the same way suppose I have one other container again say I assume an insulated container and I have gas A here and I have gas B here, I remove this I find that gas A and B mix together to form a homogeneous mixture but I have to use tremendous amount of energy if I want to separate this homogenous mixture into gas A and B and I try to confine gas A at one portion of the partition gas B at the other portion of the partition it is never possible in this particular way. I can keep on citing several such examples where we find that while the process in one particular direction is possible the process in the our other direction is never possible even when it does not flout the the law of conservation of energy.

In all the systems you find that 2 blocks at 20 and 30 degrees centigrade and each coming to 25 degrees centigrade the amount of heat transfer which would have occurred with the same amount of heat transfer we can always postulate the 2 blocks at 25 degrees centigrade can be made to contact and one comes at 20 the other goes at close to 30 degrees centigrade the same amount of energy interactions in pen and paper will show you that same the amount of energy interactions can take place when we go from state A to B and when we come from state B to A but all of us know that while state A to B is highly possible state B to A is never possible.

Now why does it happen? Why do some particular processes are feasible while the reverse process is not feasible? Why some processes occur spontaneously and others do not occur spontaneously.

At one point of time it was thought that whenever any process it gives out heat it is spontaneous whenever it has to absorb heat it is not spontaneous but then people found out there are several endothermic reactions as well which are spontaneous. So therefore they felt the same way the Joule's experiment while we could use the way to heat the water we could not use the thermal energy of the water in order to perform work unless we make some other arrangements as I have discussed. So why are all these things happening? Then people found out that well the primary reason is that some processes are feasible and others are not feasible.

For example heat always flows from a higher temperature to a low lower temperature never the reverse thing happens, so why are these things happening? So therefore in order to define these things the second law of thermodynamics has come up and the second law of thermodynamics that postulates that heat can flow from, rather that postulates that while some processes are feasible while the reverse processes are not feasible.

Well, there are 2 statements of the second law of thermodynamics which I will just be displaying tomorrow but what I am going to discuss right at the moment is that while the people found out that some processes are feasible they wanted to develop or they wanted to propose a quantitative measure of why some processes are feasible why some others are not?

Whether it can be quantitatively predicted so that suppose they want to perform any particular process they would find that particular quantity they would be evaluating that particular quantity and based on the results they get they would be able to decide in which direction they should proceed.

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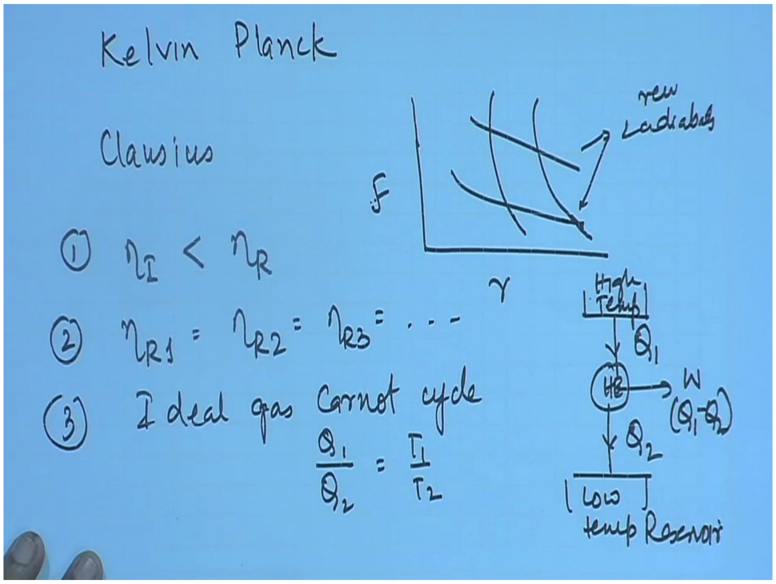

Kelvin Planck

Clausius

① $\eta_I < \eta_R$

② $\eta_{R1} = \eta_{R2} = \eta_{R3} = \ldots$

③ Ideal gas Carnot cycle $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

So the second law was in attempt in this particular direction. The second law has a large number of statements one statement is by Kelvin Planck the other statement is by Clausius. Now let me tell you that all these statements they are with reference to the heat engines and the heat pumps because mostly as I have told you that the oldest and endeavors of man were in terms of heat engines and heat pumps. So Kelvin Planck statement in a nutshell it says does the same thing which Joule had observed that it is impossible to continuously absorb heat from or rather to convert heat into work by working with a single reservoir that would lead to a perpetual motion machine of the second kind and if that were possible then Joule could have performed the experiments in both the directions.

And Clausius said that if heat has to be transferred from a body at lower temperature to a body at higher temperature then work has to be done to make this particular transfer possible, right? So these were just qualitative statements, now based on this further developments were done the first development was a Carnot cycle and the Carnot's theorem which followed from them. What was the Carnot cycle? The Carnot cycle was a reversible cycle or the reversible heat engine cycle where Carnot had devised it in terms of a PV work of a gas contained in a cylinder.

Let me tell you Carnot cycle is just a reversible cycle comprising of 2 adiabats these are the 2 adiabats and the 2 isotherms 2 reversible adiabats and 2 reversible isotherms it can be made to apply on any particular system performing any type of work, so the correct representation is instead of representing it in terms of a PV plot it is better to represent in a plot of F and r where F is the thermodynamic driving force, r is the thermodynamic displacement F and r can be P and V it can be Sigma and A it can be anything depending upon the system.

Now in this particular Carnot cycle there were some very important theorems which he had proposed. Now among this theorems the first thing which we proposed is that any irreversible cycle has a efficiency much lower than a reversible cycle. So therefore the efficiency of a reversible cycle will be the maximum. The next thing is for all reversible cycles operating between the same 2 high-temperature and low-temperature reservoirs no matter whatever path they take the efficiency of all reversible cycles will be the same irrespective of the working medium and irrespective of the processes if they are reversible cycles they will have the same efficiency for each and every cycle and the efficiency will be higher as compared to a irreversible cycle.

Now based on this they proposed that a ideal gas Carnot cycle that means when ideal gas is used as a working substance in a Carnot cycle then for that particular situation he found out that Q1 by Q2 equals to T1 by T2 this has been developed from the concept of efficiency of the cycle. Now we know how to define the efficiency of a heat engine Carnot cycle was devised for a heat engine where in very brief let me tell you a heat engine is a device which takes up heat from a high-temperature reservoir and this heat engine it transfers heat to a low-temperature reservoir and thus work it takes up heat Q1 rejects heat Q2 and thus work with the remaining amount of energy Q1 minus Q2, right?

Now suppose we use ideal gas as the working fluid in this heat engine then Carnot found out that Q1 by Q2 is equals to T1 by T2. Later on Kelvin he thought or rather it was his great intuition he thought that why only ideal gas has the working fluid if suppose we can devise a temperature scale where the heat has the thermometric property then definitely we should be able to propose an absolute temperature scale completely independent of the working substance where the temperatures of the 2 reservoirs will be in proportion to the amount of heats taken up and rejected in them and therefore we should be able to produce or rather we should be able to devise an absolute temperature scale and this gave rise to the concept of the absolute temperature scale.

Since it is outside the domain of phase equilibrium thermodynamics and I have got a limited time I have just 20 hours so therefore I will not be going into the details of this but you can take up any textbook and go through the definition and the development of the absolute temperature scale, right?

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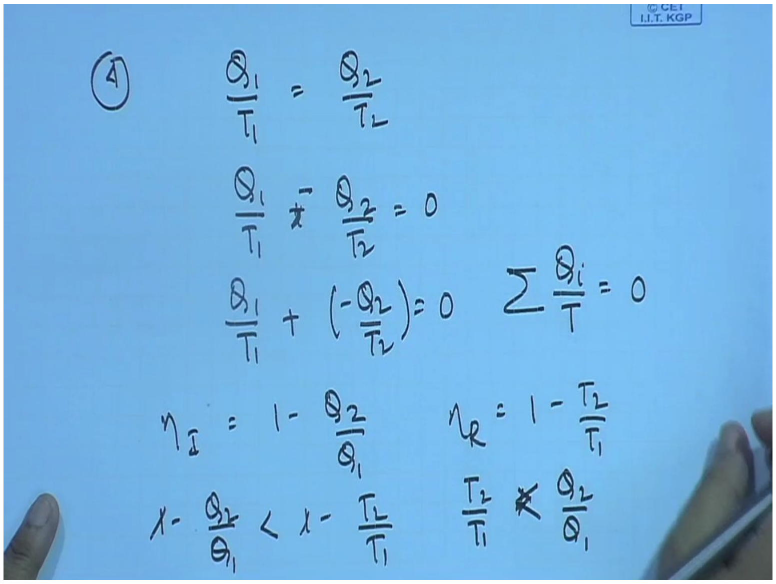

④

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$\frac{Q_1}{T_1} \overset{-}{\cancel{+}} \frac{Q_2}{T_2} = 0$$

$$\frac{Q_1}{T_1} + \left(-\frac{Q_2}{T_2}\right) = 0 \qquad \sum \frac{Q_i}{T} = 0$$

$$\eta_I = 1 - \frac{Q_2}{Q_1} \qquad \eta_R = 1 - \frac{T_2}{T_1}$$

$$\cancel{1} - \frac{Q_2}{Q_1} < \cancel{1} - \frac{T_2}{T_1} \qquad \frac{T_2}{T_1} \cancel{<} \frac{Q_2}{Q_1}$$

But what is of importance to us is, that based on this we find that the very important proposition was suggested it was that for any particular working substance when it is performing a reversible cycle as a Carnot cycle that means the reversible cycle comprises of 2 adiabats and 2 isotherms then in that case we can always write down that Q1 by T1 equals to Q2 by T2 or in other words Q1 by T1 minus Q2 by T2 equals to 0.

And if you remember that Q1 has been taken up or rather heat provided to the system so therefore it is positive Q2 is heat rejected from the system that is why it is negative than taking this sign into account we can always write it down in this particular form which gives us the equation as Sigma Qi by T equals to 0 and if we have an irreversible Carnot cycle then in that case what do we know?

We know that the efficiency of an irreversible Carnot cycle is one minus Q2 by Q1 and the efficiency of a reversible Carnot cycle is one minus T2 by T1. So therefore in this particular case we know this is less than this or in other words we can always write it down as T2 by T1 it is less than Q2 by Q1.

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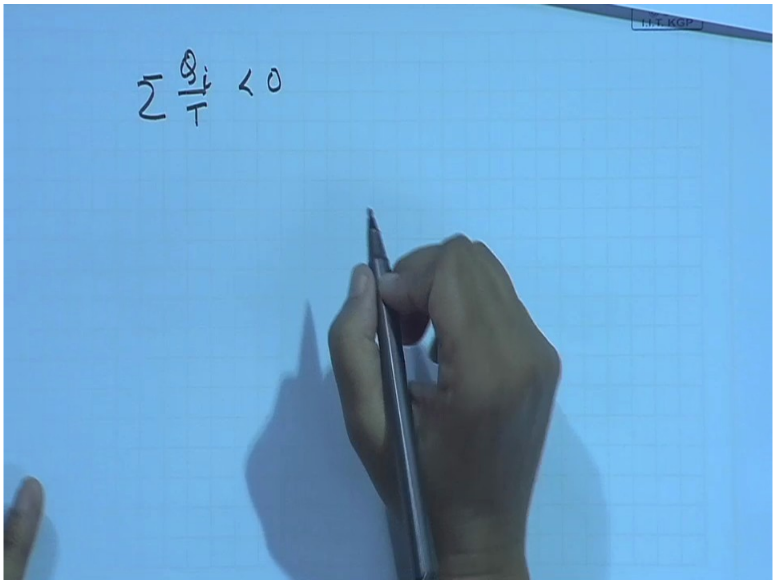

$$\sum \frac{Q_i}{T} < 0$$

Or in other words in the same way we can write it down as Qi by T Sigma this is less than 0, so therefore in any particular working substance operating in a Carnot cycle we find that Sigma Qi by T is less than equal to 0 for a Carnot cycle where the equality sign is applicable for the reversible process and the inequality sign is applicable for a irreversible process. Now next we also know that any particular cyclic process plotted on a F-r plot that can be broken down into a series of Carnot cycle.

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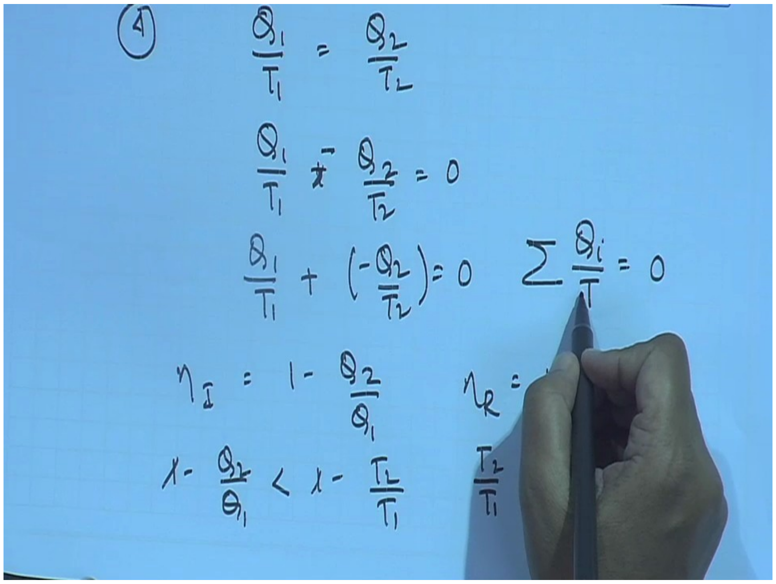

④

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$\frac{Q_1}{T_1} \overset{-}{\cancel{+}} \frac{Q_2}{T_2} = 0$$

$$\frac{Q_1}{T_1} + \left(-\frac{Q_2}{T_2}\right) = 0 \qquad \sum \frac{Q_i}{T} = 0$$

$$\eta_I = 1 - \frac{Q_2}{Q_1} \qquad \eta_R =$$

$$\cancel{1} - \frac{Q_2}{Q_1} < \cancel{1} - \frac{T_2}{T_1} \qquad \frac{T_2}{T_1}$$

I am not going into the details of all this because I assume that you know the basics of thermodynamics or you can find it out in anybody particular textbook of thermodynamics. For any particular process we can break it down into an adiabatic process, an isothermal process, adiabatic process and another isothermal process and we can bring the adiabats as close as possible because they are never going to intersect with one another and therefore any reversible cycle can be broken down into a series of Carnot cycles and for each of the Carnot cycle this particular equation holds if it is a reversible cycle.

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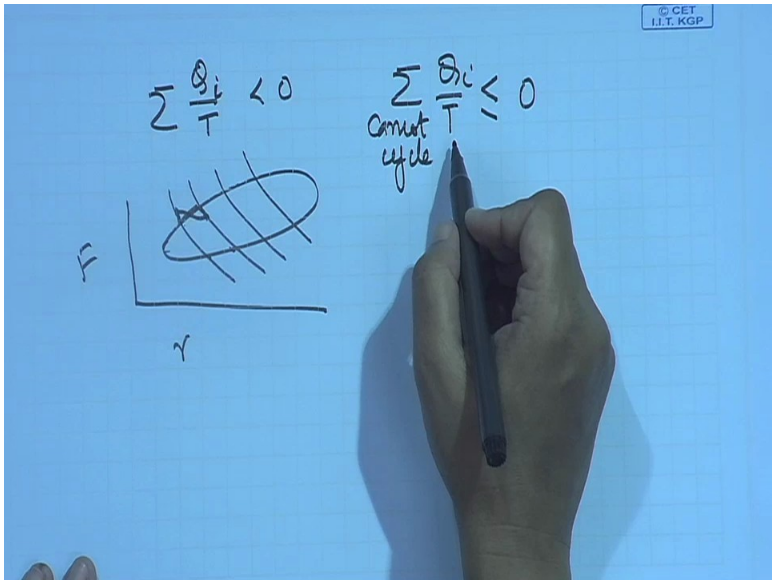

$\sum \frac{Q_i}{T} < 0$

$\sum_{\text{Carnot cycle}} \frac{Q_i}{T} \leq 0$

And this particular equation holds if it is an irreversible cycle.

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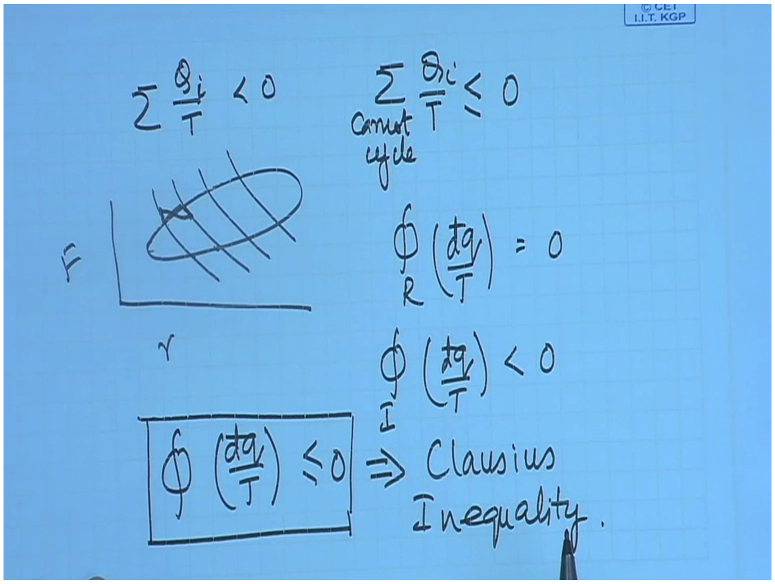

$\sum \frac{Q_i}{T} < 0$

$\sum_{\text{Carnot cycle}} \frac{Q_i}{T} \leq 0$

$\oint_R \left(\frac{dq}{T}\right) = 0$

$\oint_I \left(\frac{dq}{T}\right) < 0$

$\boxed{\oint \left(\frac{dq}{T}\right) \leq 0} \Rightarrow$ Clausius Inequality.

So for any particular reversible cyclic process we can always write down this is equal to 0 and for any particular irreversible process we can always write down this is less than 0. So combining the 2 we can always write down dq by T for any particular cyclic process it is less than equal to 0 which is another consequence of the Carnot's theorem and this was first proposed by Clausius and it is known as the Clausius inequality. And from here stems out the criteria for feasibility of different processes which we will be discussing in the next class where I will be introducing the concept of entropy and we will be discussing the feasibility of the different processes just like I had introduced internal energy and enthalpy from the first law I will be introducing entropy from the second law and once we have introduced this we have understood the energy interactions and the energy change of different systems we can understand when some processes are feasible and why some processes are not feasible on a quantitative manner.

After that we go into the depths of phase equilibrium thermodynamics as I have already mentioned earlier first we will be dealing with single phase single component the simplest type of systems. We can also deal with single phase multi-component systems where the compositions does not change as the process proceeds.

So both of them will have the same treatment and we are going to deal with them then we are going to deal with single component 2 phase systems then multi-component 2 phase or multiphase systems. So with this I end up this particular class, thank you very much.