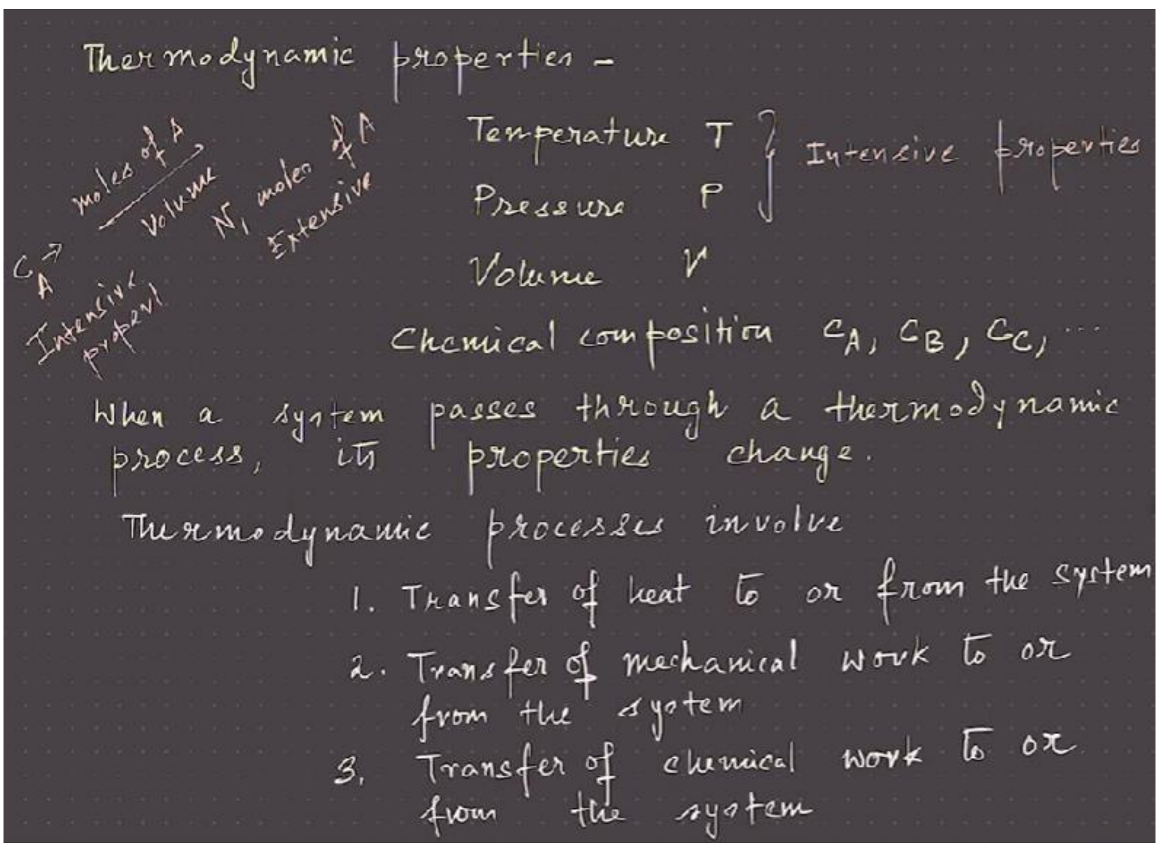
**Thermodynamics And Kinetics of Materials**

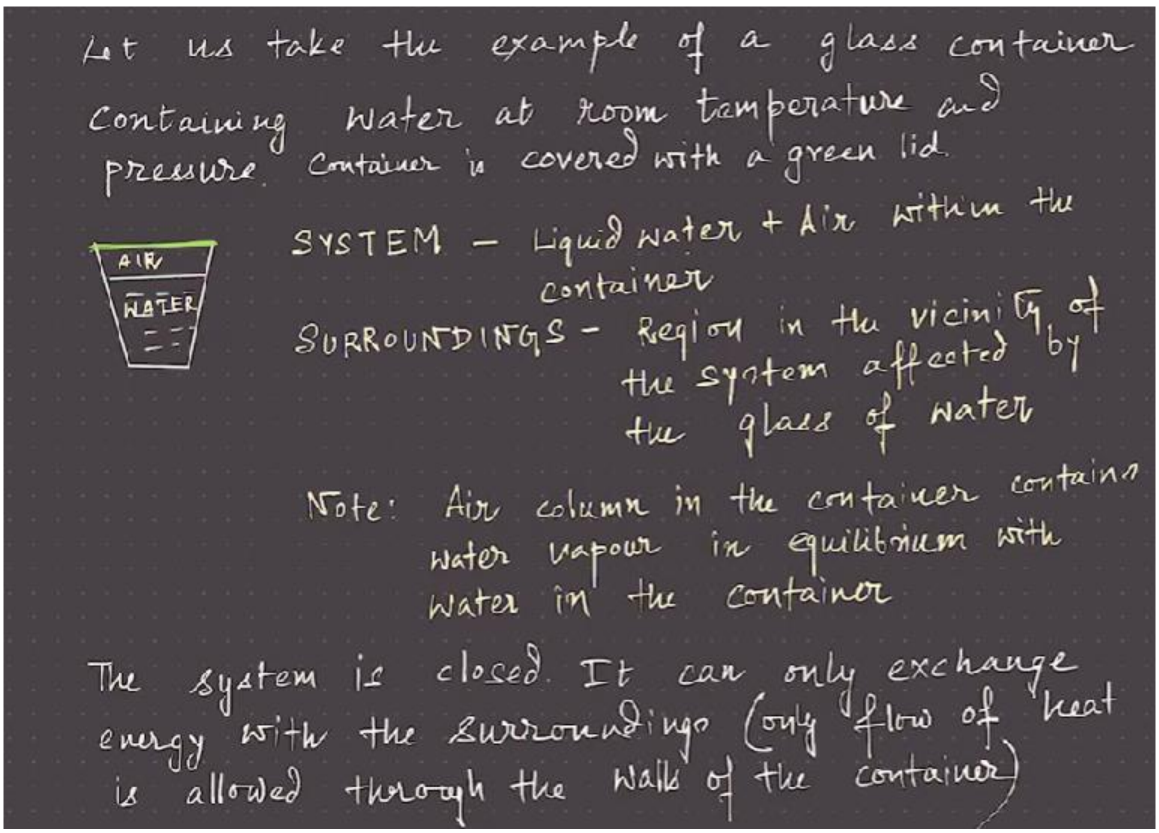
**Prof. Saswata Bhattacharya**
**Dept of Materials Science and Metallurgical Engineering,**
**IIT Hyderabad**

**Lecture 3**
**Energy, Heat and Work - II - Part 2**

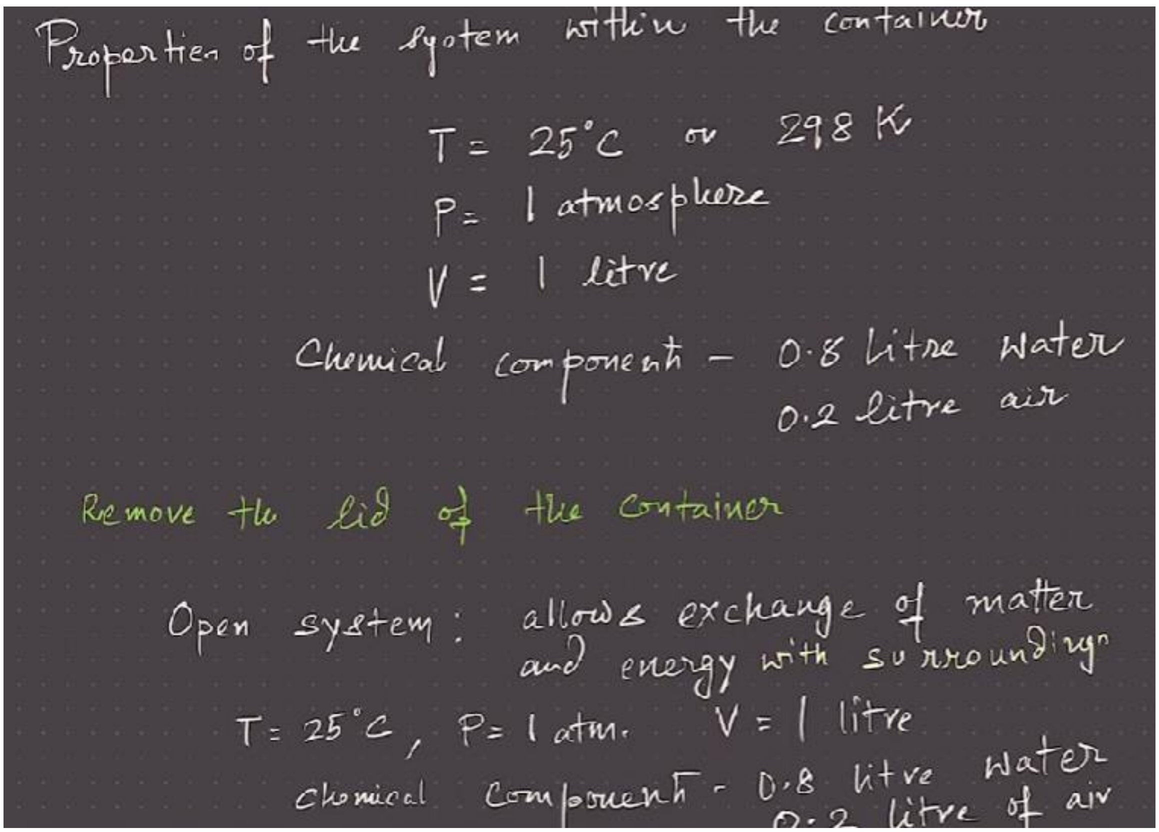
The thermodynamic properties also you can also think of like the temperature of the system, we can specify the pressure and as I told we can specify volume, then we can describe chemical composition in terms of $C_A$, $C_B$, $C_C$ which is the concentration which is like moles per unit volume or in terms of $N_A$, which is nothing but mole number, please note that here is something is a food for thought basically you can try to understand this these are all extensive properties.



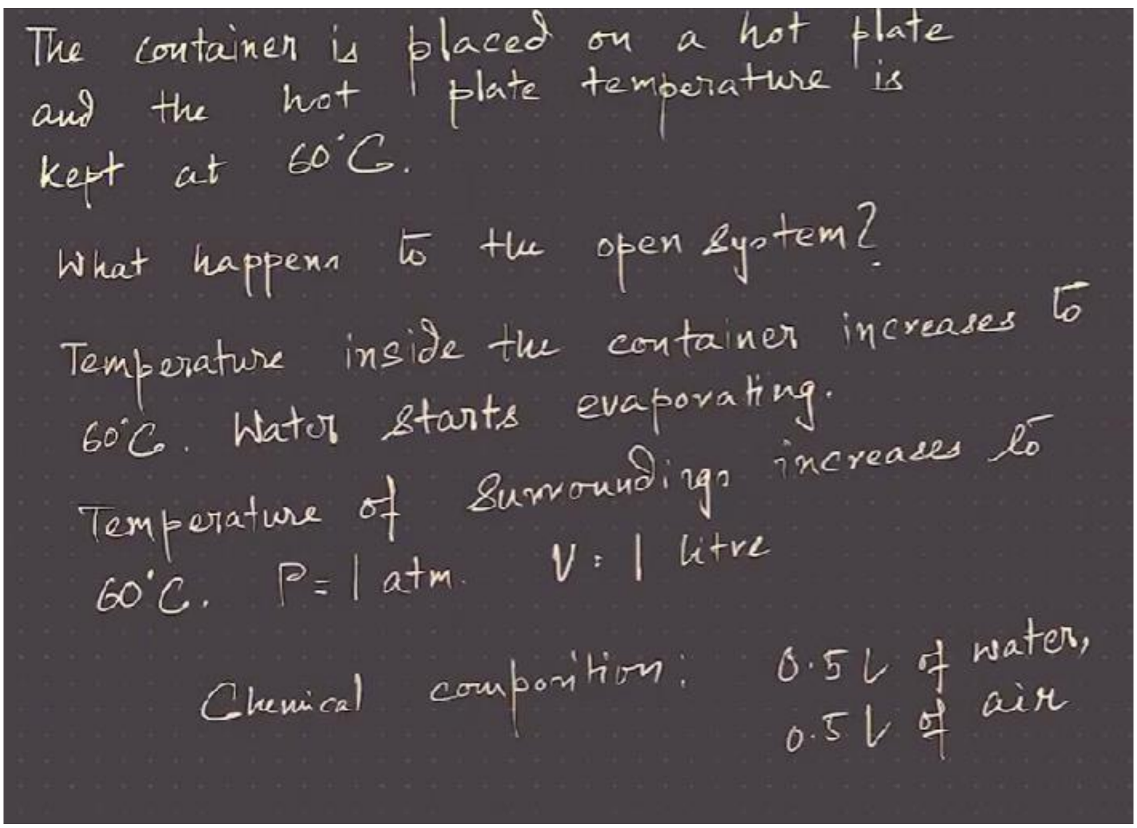

On the other hand the properties that we are describing here like temperature T, then pressure P these are all intensive. Similarly chemical composition in terms of, so if I tell in terms of C where C denotes it's like you know $C_A$ is it like moles of A per unit volume right so in that case your $C_A$, so $C_A$, $C_B$, $C_C$ takes an intensive property. On the other hand if I would have told $N_A$ means $N_1$ moles of A that's like a mole number then it's an extensive property, it is additive it depends on the external system but here it is an intensive property right. So this is something that you should be very careful about so we can describe a system in terms of intensive and extensive properties but you will see that describing in terms of extensive properties has its own advantage somewhere and you will see that there is a relation between them and this conjugate relations and all these things will be discussed. Now we know that what are the different thermodynamic processes right we have already described some of these processes like heat input, so transfer of heat from or to the system or from the system right we are extracting heat from the system or transfer of mechanical work again to the system or from the system again another work is transfer of chemical work to or from the system right so these are possible.



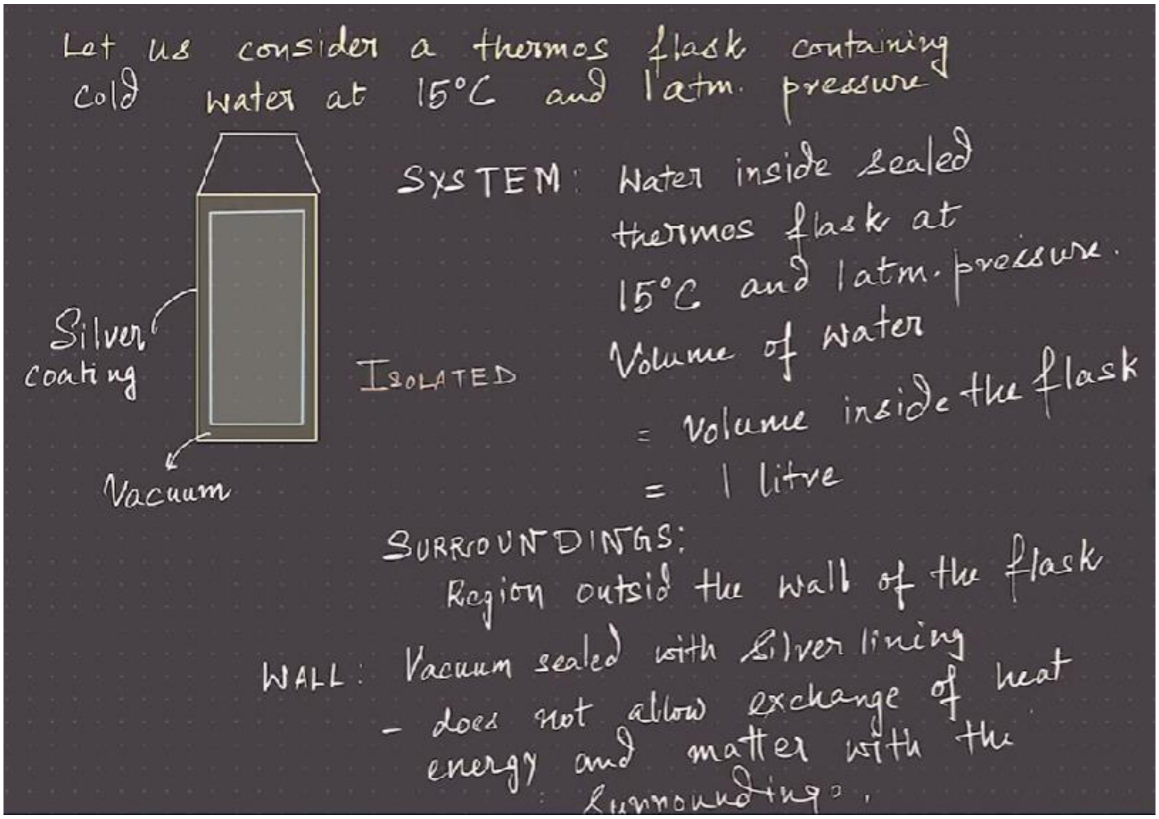

Now think of this, now what type of systems are possible now I am basically classifying the systems right this is something very important because if I can classify I can also modify the first law or the differential form of the first law to take care of which will basically according to the nature of the system right so for example if I take a glass container which contains some water at room temperature and pressure and it is covered with a green lid right it is covered with a green lid right there is a green lid and it is a glass container it contains some water it also contains some air right. Now if you look at that this system under consideration is basically liquid water plus air within the container which is kept at room temperature and pressure. Now the surroundings is the region in the vicinity of the system that is affected by this glass of water right affected by the glass of water for example because of this glass of water may be the surrounding is slightly that means going towards the temperature which is like the same temperature as water and all and so it is definitely going to be affected means that this is the region in the vicinity of this glass of water that is the surroundings. Now you have this air column which contains water vapor right this air column will contain some water vapor that is in equilibrium with water in the container right that is what is required.



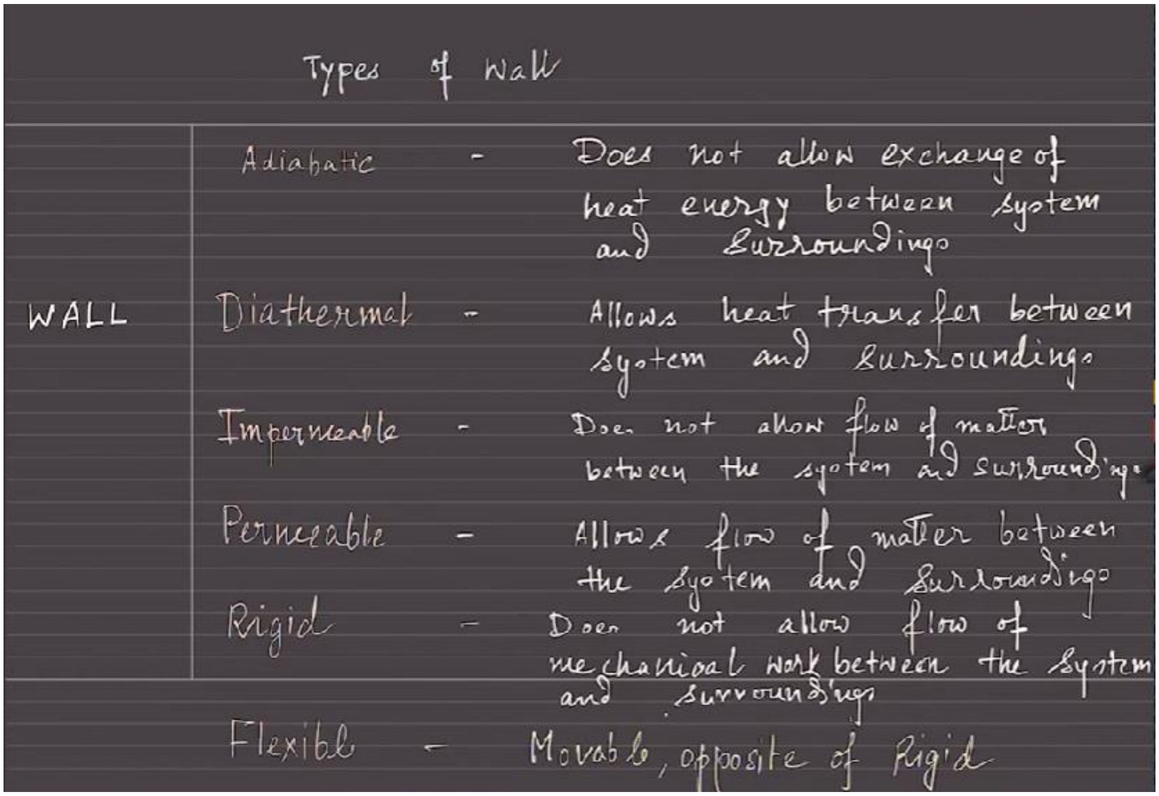

Now this system is called closed system because it can only exchange energy right there can be flow of heat right say for example the surroundings is hot hotter than this glass of water which is kept at room temperature then it will flow from the surroundings into this glass of water right that is permeable right or if outside is at so that is this is one possibility another possibility is that heat is basically extracted out from the system by the surroundings right it is extracted out by the surroundings right all these are possible or heat is input from the surroundings to the system. So it is like heat flux happening from water means there is a heat transfer happening from hot from this water container to outside which is permeable right or from outside into water that is also permeable so energy can always be transferred however you cannot because it is closed right it is closed with a lid the lid water cannot evaporate right water has this air column the air column cannot escape so all of these cannot happen so there is no transfer of matter to the walls of this container but because there is a it is covered with a lid and all but it can exchange energy to the surroundings so this is called a closed system. Now say for example as I told you that properties of the system in the container was like $25^{o}C$ or 290K pressure was 1 atmosphere and say the volume was 1 $^{o}$ right so the so see in one litre we had let us say like 0.8 litres of water and 0.2 litres of air now only thing that will influence the so temperature was $2^{o}C$ and say outside the temperature was 30 $^{o}C$ then this water we can get warm and then it can adjust and somehow it can find a balance where the water inside the container and the surrounding can be at the same temperature right so that is possible.



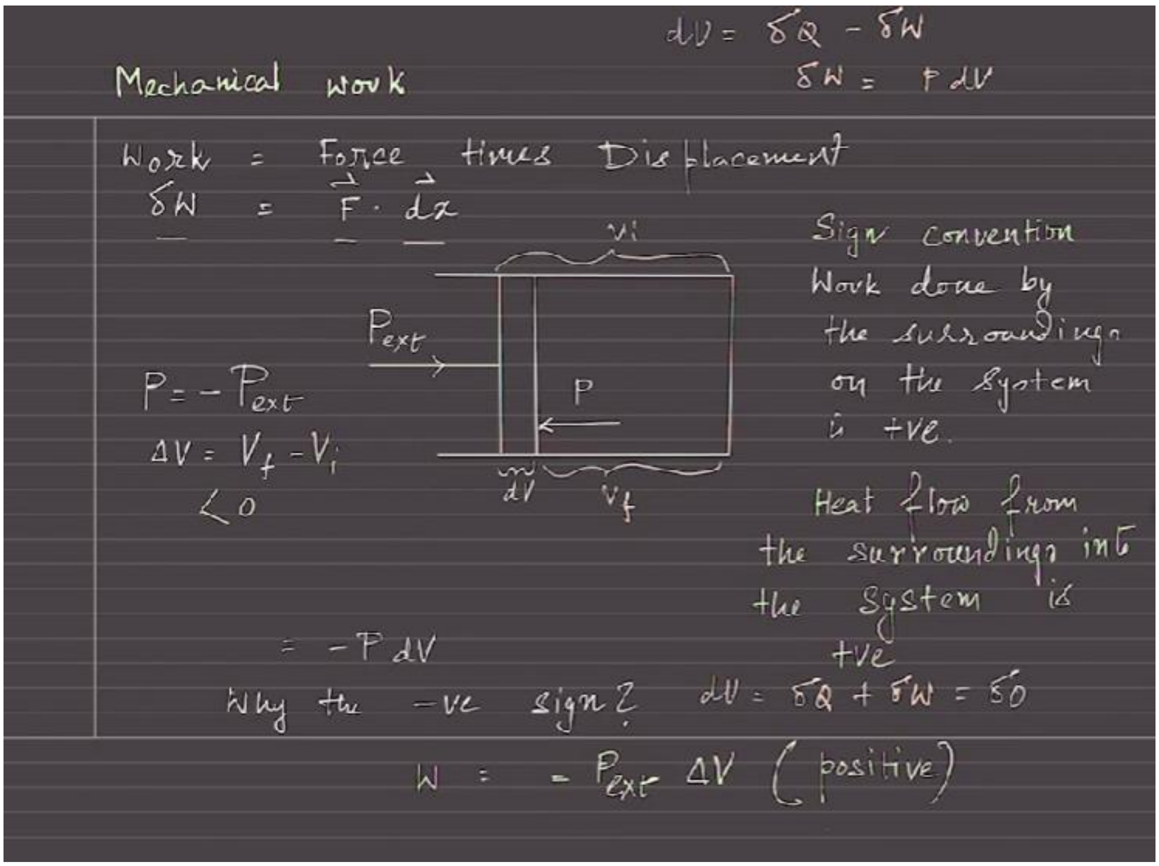

Now if I remove the lid of this container I remove the lid of this container and I allow 10 what happens I start I allow exchange of matter and energy with the surroundings now I have p at p was $25^{o}C$ p was 1 atmosphere p was 1 litre and chemical components is like 0.8 litres of water and 0.2 litres of air now what I did I took this container okay which is open because the lid is removed and I put it in a hot plate right with the skip test some 60$^{o}$C what will happen what happens to the open system the temperature inside the container will start increasing until it reaches 60$^{o}$ and water will start evaporating right it is not going to boil but it is going to evaporate there will be some evaporation right so temperature surrounding so will also increase too this will be greater 60 degree Celsius the water will have like the temperature of 60$^{o}$C there will be some evaporation and after some time after a long time say for few days or maybe 1 or 2 days I see that the chemical composition now what is there right inside the container is like 0.5 litres of water and 0.5 litres of air that means 0.3 litres of water have evaporated right that is possible right so this is something that we will see in case of open system so open system allows the transfer of matter and energy there is yet another system which is called an isolated system so think of an a thermoflask thermoflask you have seen lot of us use thermoflask right in hot weather we use thermoflask we keep our water cold and in cold weather we often carry tea or coffee the thermoflask right even hot water right sometimes people carry warm water in thermoflask right now say for example in a very hot summer day in Hyderabad I have kept this thermoflask means filled this thermoflask with cold water at 15$^{o}$C and want to have a cold atmosphere pressure now I go to my office and I see that it is still cold and I can enjoy this cold water right when I am drinking so this so why is it cold because in hot weather in Hyderabad the temperature can goes up to like 40$^{o}$C right so why is it that this water inside this thermoflask sealed thermoflask remains at 15$^{o}$C you have a vacuum right there is a vacuum in thermos there is a good technology there is a very nice technology here so you have a vacuum seal and also a silver lining so that you can prevent heat loss by radiation and this vacuum basically does not allow any heat loss by conduction so basically it is vacuum sealed with a silver lining and therefore it does not allow any exchange of energy right it does not allow any heat exchange of heat energy between the system is the thermoflask right the water inside the thermoflask and the surroundings right water inside the thermoflask cannot interact with the surroundings so as a result it remains at 15$^{o}$C it remains isolated from the surroundings and it is also closed right the thermoflask will keep it closed unless if we drink water we will remove the lid and we will drink but other than that by the way and this exact time when you are drinking basically is the time when there will be some exchange of energy and exchange of matter right but other than that as long as you are keeping this water intact there and it is sealed and there is a lid that is given if the cap is closed there is no exchange of matter or energy whatsoever so as a result so basically this vacuum seal with silver lining does not allow any heat energy and again it is also closed so it does not mean there is a lid and it is closed and all so it does not allow any exchange of matter so with this as a result by the way there were earthen pots previously where we used to store water and these earthen pots you know there is like there will be pores in earthen pots and we will see that this water is evaporating and we will see a very interesting thing this evaporation causes cooling right that is the principle so you will see that the water inside the earthen pots will be like quite cool and I will in fact this is something that I will ask later that why does that happen and what is this type of system so we will often have these questions like what type of system is it? Is it an isolated system? Is it a closed system? Is it an open system?



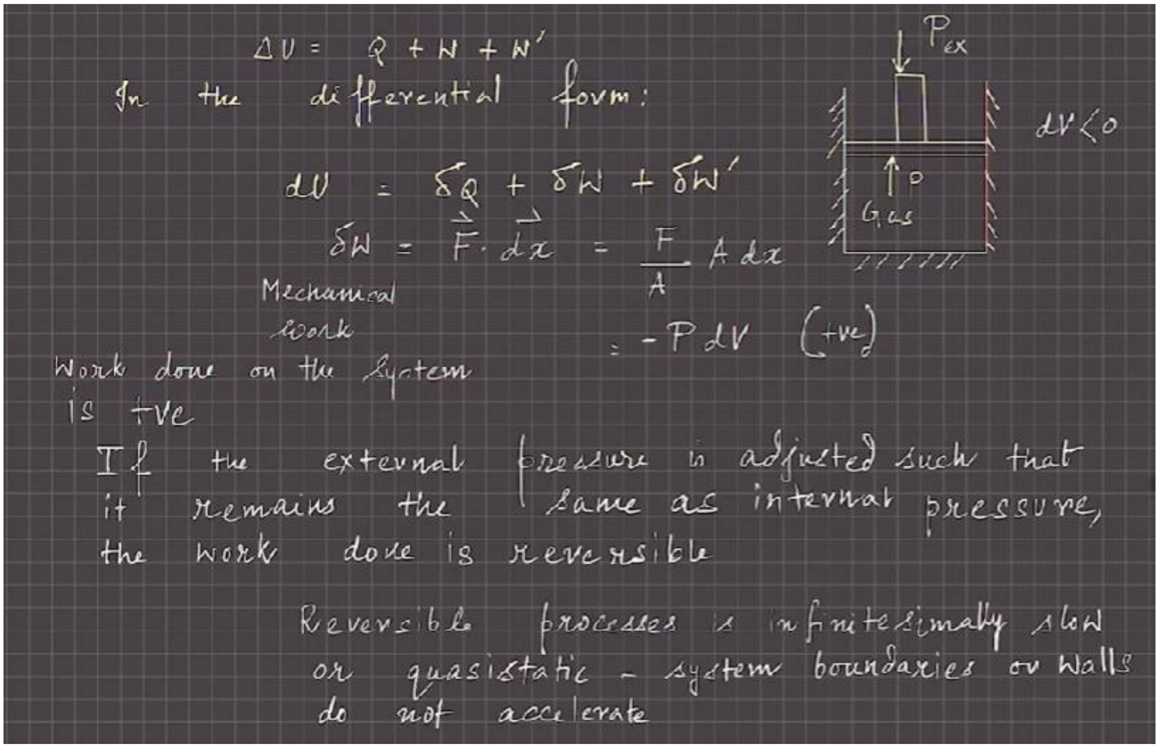

So open system means it allows for transfer of energy it allows for transfer of matter it allows for transfer of energy as well as matter when it is a closed system it only allows transfer of energy between the system and surroundings but it does not allow transfer of matter and finally you also have this isolated system where the wall is such that it does not allow the wall basically this vacuum seal coated with silver this wall basically does not allow in exchange of energy between the system and surroundings it does not also seal that is there all over it does not allow exchange of matter with the surroundings so these keys are called an isolated so these systems are called isolated systems so this is an isolated system so as I told you this is like open system then you have this closed system which has this leg and then there is this isolated system does not allow is a matter of energy this one right and now you have this different types of walls like for example



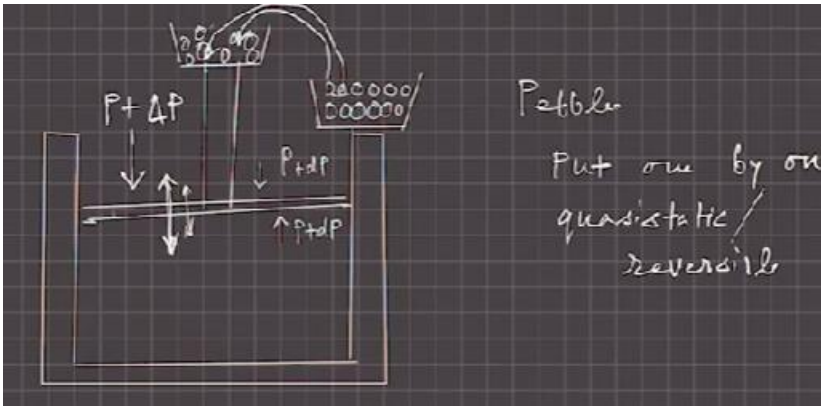

if I have an adiabatic wall which is that thermos plus wall basically it does not allow exchange of heat energy between the system and surroundings right opposite of adiabatic will be diathermal diathermal allows you transfer between the system and surroundings similarly I can have matter transfer between the system and surroundings if the wall is permeable however if it is impermeable it does not allow like for example I have closed with an impermeable lid the container is impermeable everything is impermeable then it does not allow flow of matter between the system and surroundings right that is called impermeable now if it is permeable namely that we have a that the wall is like a permeable the wall is permeable for example the body of a earthen pitcher. so those are permeable so it allows water to escape right so basically it allows matter to transfer or flow from system to surroundings or surroundings to system right and then there is also another part that we are looking at mechanical work say think of mechanical work when we think of mechanical work we think of a piston we think of a container and we think of like moving the piston down on taking the piston up right we think of such a setting right in such cases say for example the wall is rigid if a system is there whose wall is rigid then you cannot the rigid wall will not allow flow of mechanical work on the between the system and surroundings the same idea happens if I have say we are talking about system and surroundings but I can think of like two subsystems or a composite system which contains of many many subsystems which is separated by this different types of walls right and we can look at these walls we can relax some conditions we can make these walls adiabatic or diaphragmatic we can think of these walls to be permeable we can make them more impermeable we can also make these walls rigid, rigid means it is not allowed any readjustment of volume it is not allowed any flow of mechanical work in the system surroundings on the other hand if it is flexible then it is movable which is basically opposite of rigid then your system can go down or go up and as a result basically you can perform mechanical work on the system ok when the system walls are say when the walls between the system and surroundings are flexible right so we will now discuss a little bit about the mechanical work right in mechanical work basically as



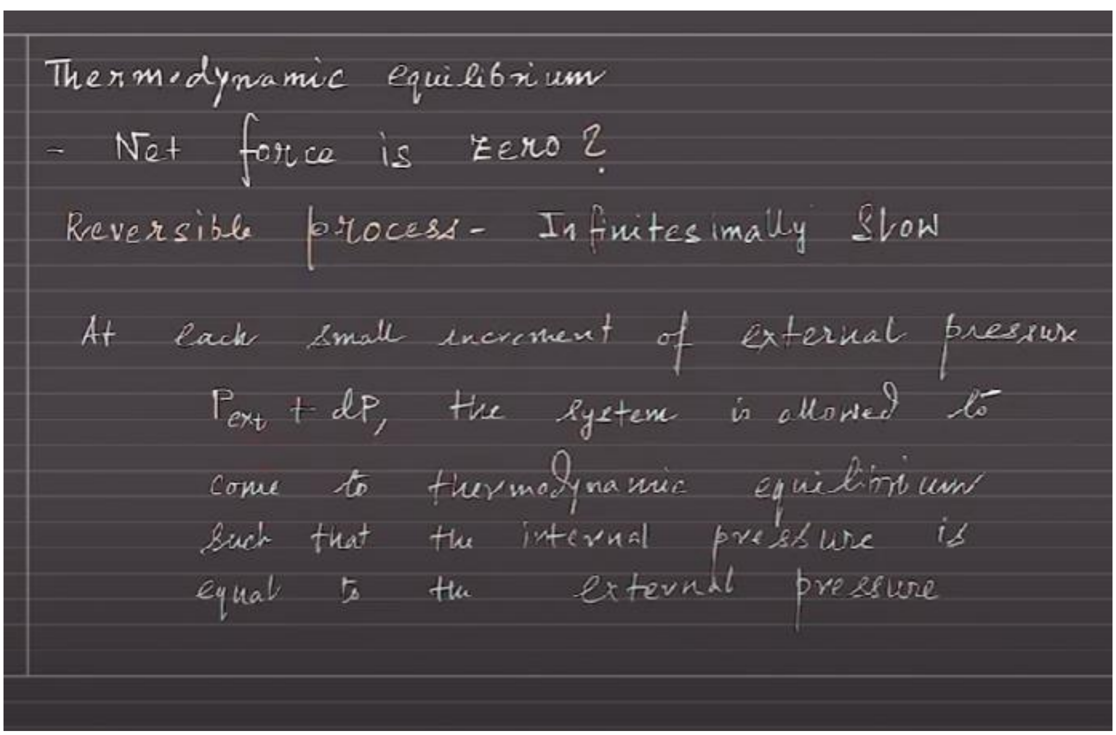

we know work is nothing but force times displacement and force is a vector and displacement is also a vector and if I take a dot product of it what I get is 1 right $\delta w$ right if I do as displacement infinitesimal or differential displacement dx and I have a force then f times dx is $\delta w$ right it is again a differential but it is an inexact differential right and the sign convention what we told is what done by the surroundings on the system is positive right now if you think of this lets think of this piston so you have this external pressure remember the pressure that you are exerting ok is in a process the process that you are applying is like you are exerting pressure in such a way that it is almost like a quasi-static increment of pressure so every time you apply pressure you allow the piston to equilibrate so that the internal pressure and the external pressure equilibrates and again you increase the external pressure times infinitesimal power that is what you are doing now if you see if I am considering this external pressure then what is happening you initially if you initially now I had an external pressure and say for example my volume is changing in such a way that $\Delta V$ is negative that means my initial volume my initial volume was $V_i$ and my final volume is like $V_f$ then basically $V_f$ is less than $V_i$ that means $V_f$ minus $V_i$ or $\Delta V$ is less than zero now in that case what done on the system side say you are applying pressure right as a result your volume is decreasing or reducing now volume dv is negative I have to put a minus in front of p so that minus p dv becomes positive right because dv itself is negative so if I put a minus sign then my sign convention works right minus p dv now some people write say du equals to $\delta q$ minus $\delta w$ in their case they are telling $\delta q$ that is heating is positive but $\delta$work done by the system is positive work done on the system is not right if work done by the system is positive now think of this internal pressure is increasing the volume because it is acting against the external pressure it is increasing the volume from say $V_f$ to $V_i$ so $\delta$means basically if you are looking at the internal pressure which is doing work on the surroundings then basically we are trying to move the system such that $\Delta V$ is positive if $\Delta V$ is positive but minus $\delta w$ so it is minus $\delta w$ right that is because work done by the system is positive work done on the system is negative now work done by the system is positive now if work done by the system is positive if $\Delta V$ is positive then p has to be positive right so basically here also if I have to write $\delta w$ in this case where we have this different convention it will be basically given by p dv here it will be given by minus p dv right so ultimately when I write p dv then my du is $\delta q$ minus $\delta w$ but the way we have written it is like du equals to $\delta q$ plus $\delta w$ and $\delta w$ in our case also because the volume is decreasing which is $\Delta V$ is negative so minus so we have to put minus in front of p external right to make the work done positive so this will be $\delta q$ minus e right so this is the angle now again dv that means volume dv is also an exact differential so volume is a state function right volume is a state function because dv is an exact differential so as you can see in the differential form the first law for closed system can be written as du equals to $\delta q$ plus $\delta w$ plus $\delta w$ right and as you can see $\delta w$ is f dx which is basically f by a into adx adx is nothing but the dv right adx is change in volume and there is a minus p dv because $\delta w$ has to be positive according to our sample function or the system is positive now remember when this type of experiment is going on that we are doing mechanical work this external pressure is adjusted in such a way that the process remains quasi-catalytic and it remains the same as the internal pressure means every time I am incrementing the external pressure there is an increase in the there is an increment in the external pressure by a small amount we allow the system to be vibrate in such a way locally that it has to remain the same as the internal pressure right in such a case the work that we are doing it is a very infinitesimal process I am pressing the piston and then I am holding it so basically I will give an example here so my drawing is not that great but I can still tell you the angle so you have this chamber right and then I have to split it with a piston right split it with a piston we have this chamber and what we are doing is I have put a small container and I have also put another small container here in this container I have kept a lot of pebbles right I have kept a lot of stones or some pebbles small stones and here I have kept nothing now what I am doing is I am taking one pebble and putting it here as soon as I put one pebble here there is a small external pressure that happens right there is a like like like I am adding some some things are P plus T now for one pebble now once it happens happens so slowly the internal pressure exactly becomes like P plus T right it is almost like equilibrium at each step again.



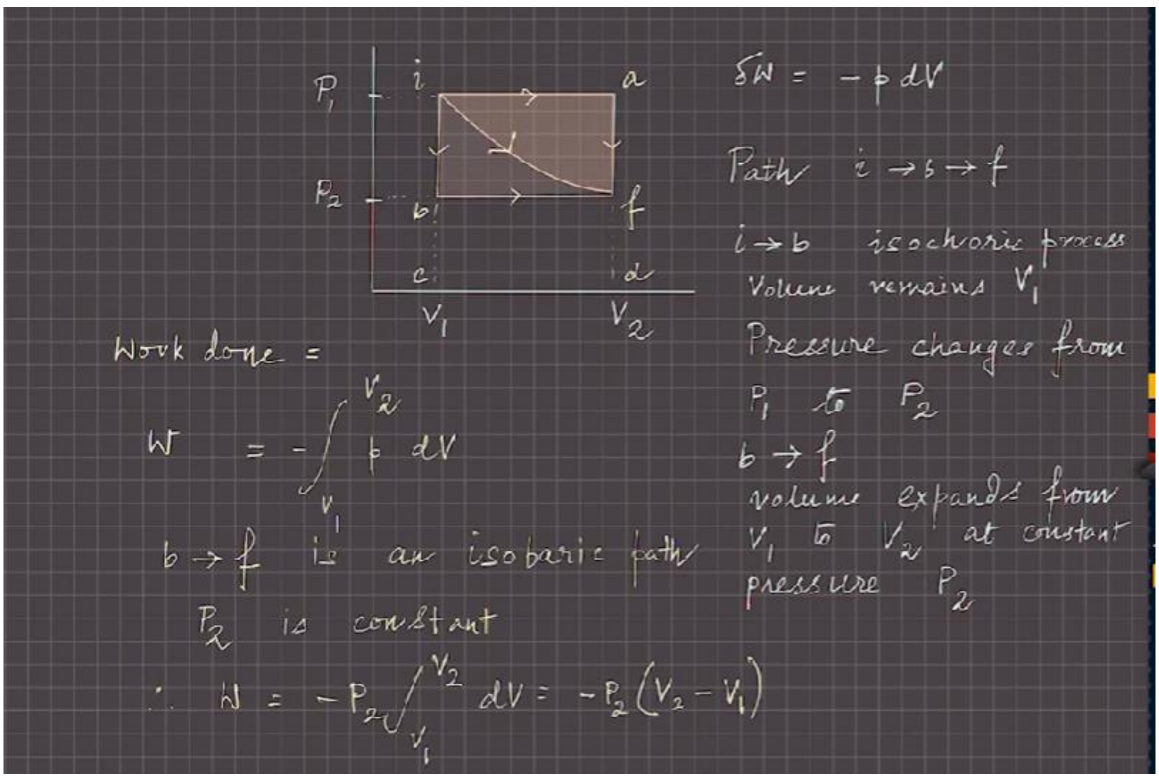

I put the second one and so on and so forth now this is one experiment that I am thinking another experiment another is instead of doing that I take all of these pebbles I take all of these pebbles right I have like all of these pebbles I put all of them together I put all of them together then what will happen suddenly the pressure will go up it will not allow to equilibrate right suddenly the pressure will increase right say E plus some increase like δP now you are not giving time you have put all the pebbles together so you are not giving time for the internal pressure to adjust right the internal pressure to equilibrate with the external pressure so basically there will be some sort of a shaking motion right so it will be like a two and two motion of this piston so it will be like it will shake and then it will also shake about its mean position it will go on doing that it will like vibrate about its mean and then finally it will settle to that increased pressure by the time it will settle maybe the internal pressure also will be equal but in the process in the intermediate times you basically see that this entire piston is like going up and down it is like vibrating about its mean and it is like wobbling and at that point so there is some sort of a disturbance that you can easily feel and that is a non-equivalent process



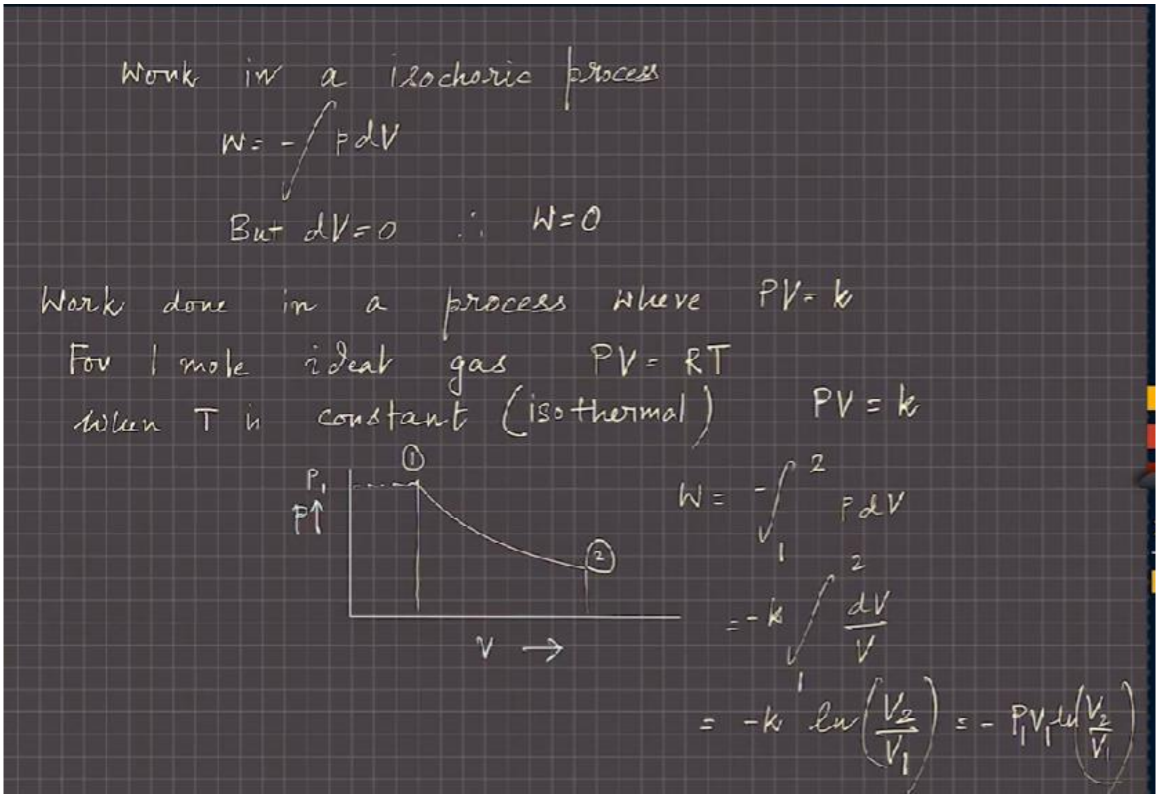

on the other hand or irreversible process right you put all the pebbles together you have suddenly increased the pressure and as a result the piston is going down but when it is coming down it is coming with some jerks right it is coming with some jerks it is basically trying to vibrate about its mean and then finally settle down to its final position on the other hand the other experiment where we put cable with these pebbles one by one when I am putting pebbles one by one then every time there is a small increment in pressure that there is enough time or enough time is given to the internal pressure to readjust so that the small increment in pressure from the external can be exactly countered by the increase in the internal pressure right that is the so if you feel this so it is like pebbles and you have this plunger of the piston



and you have on the plunger you have this empty container so pebbles put one by one so it is like quasi-static and the process is reversible because again if I put it one by one then slowly the piston head will increase right the volume will expand right that is like putting it one by one or removing it one by one so we have a quasi-static resistor process because we are allowing enough time for the system to adjust the internal pressure so that can counter the rise in external pressure so that is the thing so it is adjusted in such a way it is like you are doing like P plus TP type of an experiment right so it is always remain the same as the internal pressure right that means the work done in this case is reversible, reversible processes are most these are theoretical right these are infinitesimally low or quasi-static that is system bodies or walls will never accelerate right they will come so slowly that you will feel like it is always static it is almost static that is what it is so what does thermodynamic equilibrium mean very simply this means

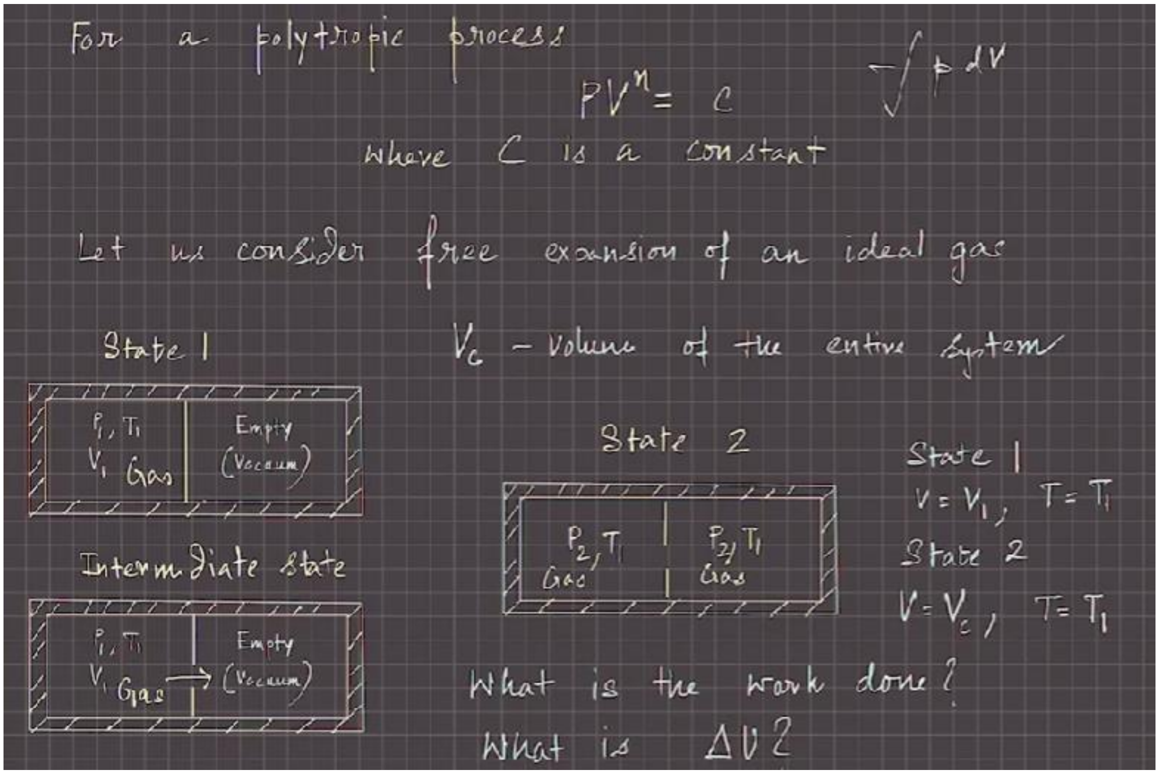



say for example I can take the example of mechanical equilibrium, mechanical equilibrium means if I have mechanical equilibrium that means the sum of forces on that particular body right if a body is in mechanical equilibrium with the surroundings so basically there is no net force on the body right all the net forces are not right so a reversible process so if that means the piston although it is slowly there is some slow increment at each step there is a, a thermodynamic equilibrium that is achieved and that kind of equilibrium is nothing but mechanical equilibrium which tells the net force on the piston head is zero right so as I told at each small increment of external pressure P x down plus TP right at each small increment P x down plus TP the system is allowed to come from equilibrium or mechanical equilibrium such that internal pressure is equal to external pressure that is right right now again δW is a path function we have already discussed this and you can take different paths say for example I can go from I to P to F

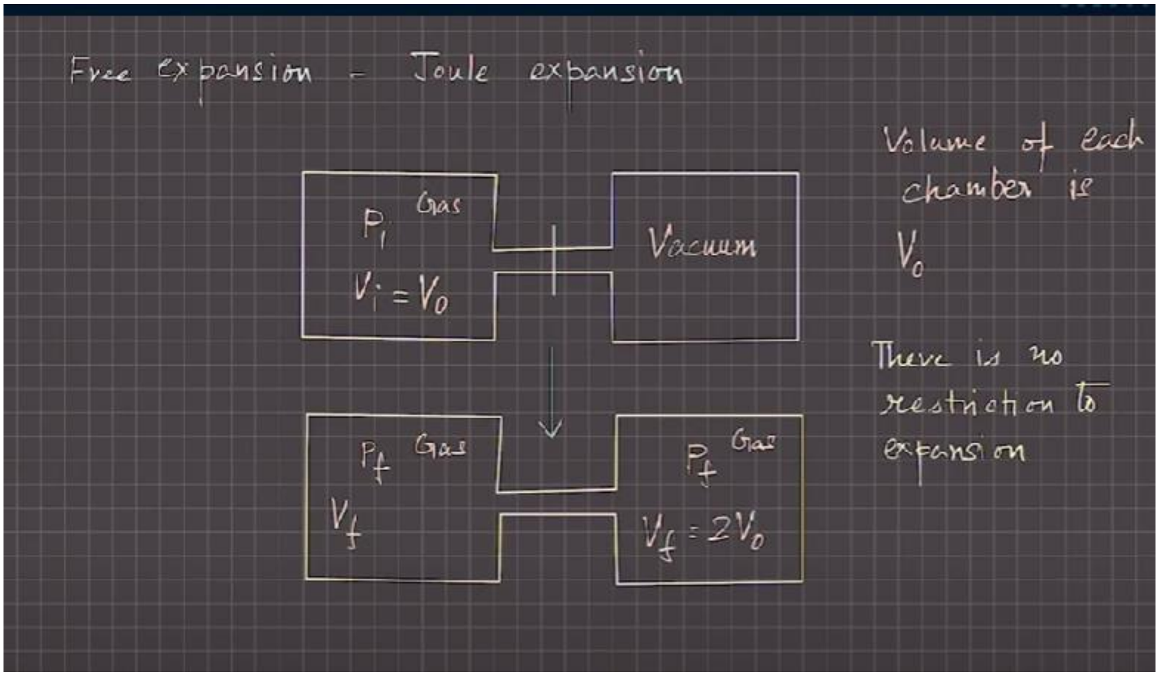



or I can go from I to F directly so I to P is an isochoric process where the volume is constant and then pressure changes from $P_1$ to $P_2$ then there is $V_2$ right $P_2$ F is like pressure is not changing right so in the isochoric process pressure is changing from $P_1$ to $P_2$ right it is decreasing and then you go from V to F where the volume is expanding at concentration of $P_1$ right now if I look at the quadrant in this case it is minus P dV and integral from $V_1$ to $V_2$ right it is like that it is at constant pressure we are telling it is happening from $V_1$ to $V_2$ at constant pressure, at this constant pressure so say for example $V_2$ F is an isochoric process and since it is an isochoric process that means basically the $P_2$ is constant and as a result as a result you can easily integrate because you can take out P from this integral right P because P is a constant and W just becomes minus $P_2$ times the integral of dV from $V_1$ to $V_2$ right so this is like minus $P_2$ dV minus $V_2$ so it becomes very very easy right because the isochoric is not there now in an isochoric process when there is no volume change basically which is W equals minus $P_2$ dV dV equals to zero so for isochoric process what that is going to be same now if we are thinking of an isothermal process where work done for example P becomes $P_k$ and if you are looking at say for example one mole of hydrogen gas then P equals to NRT because T equals to T right and T is a constant which is an isothermal condition and right

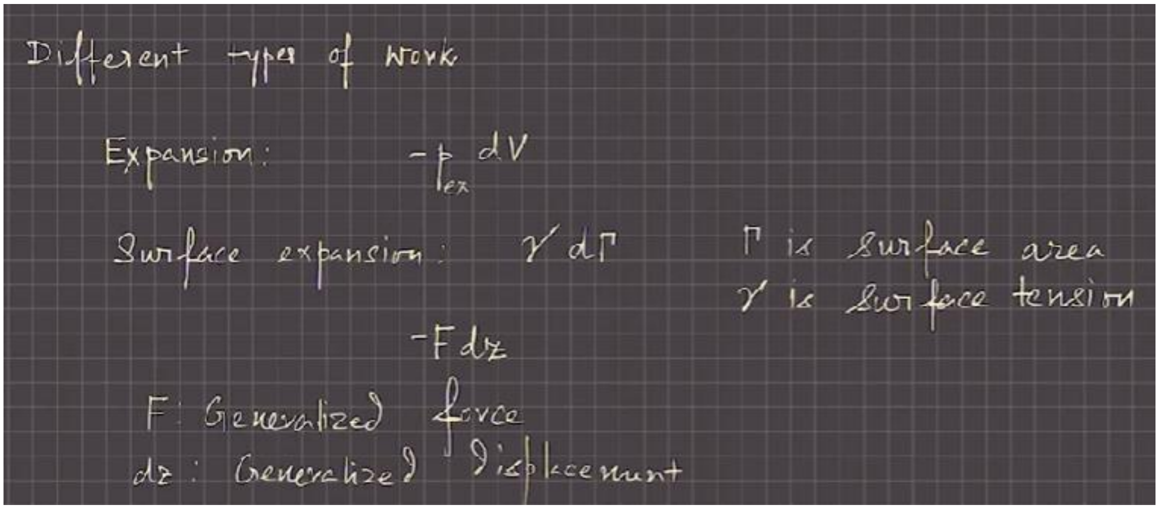
T is constant means isothermal condition in this case I am integrating C from one to two and I am using W equals to or $\delta W$ is equal to minus one to two PdV and P is basically PdV is constant that means PdV is constant so basically I can tell PdV equals to




k so if that is so then P is basically k by V so as you can see here so minus k and by V so dV by V is ln V and then again there is an integral from one to two so it is like minus k ln $V_2$ by $V_2$ right and k is nothing but you can write k so you have this state where you have $P_1$ here you have $P_1$ here you have $P_1$ here and say you have P right so it becomes like minus $P_1$ $V_1$ and then $V_2$ by $V_1$ so again if it is a polytrophic process it is like PdV to the power N equals to constant then basically then you can find out once you have done again you have to do this integral minus PdV and you can use this relation like it is like constant by $V_N$ and then you can try to do that now consider a very interesting problem of pre-expansion of an ideal gas so if you have an ideal so you have an ideal gas so this is a state one so if you look at the state one you have an ideal gas at temperature $P_1$ pressure $P_1$ volume $V_1$ and the other side of this composite system so this is a composite system see this has one system one another is system two right so these are like two subsystems of a full composite system which is separated by a wall the wall is such that the gas initially the wall is such that the gas cannot pass through right the gas cannot pass through the wall right using impermeable and out and we have maintained the right side to be empty that means basically it has it is vacuum right means it's like it gets vacuum inside and it's empty now if you look at the intermediate state if i create a small orifice or an opening immediately the gas will start filling up the empty chamber and finally you will achieve this state two where your pressure has readjusted such that pressure is all over the same the temperatures react to $P_1$ and everywhere you have basically the same gas right so basically the gas has just without any pressure whatsoever from outside the gases just completely fill the entire chamber right in the entire chamber.




so now in the entire chamber at every point the temperature is tuned the pressure is $P_2$ right but what will be can you tell me what will be the work done i can give you a hint the work done in this process because it's a free expansion there is no pressure which is acting on the membrane or which is acting against the membrane so pressure is basically zero so it will PDB as you know so this is only work done will be zero now the work is zero what will be δU please find out right the same free expansion experiment was performed by joule right it's also called joule expansion right where you have a gas and you had vacuum on the other side of the chamber and finally the volume of each chamber is like V naught and there is no restriction to the expansion and what happens is as soon as you release this valve you have PF on both sides and then you have the final volume right so the final volume can be like you know will be like so you had $V_i$ equal to $V_0$ and vacuum but now it will be like the $V_f$ will be like $2V_0$ right so it will be like the total volume will be $2V_0$ now there are different types of quarts like for example we are talking about expansion or contraction right expansion e is like minus P it's not V or pdv right which is like gamma pressure working on the surroundings and then you can have surface expansion right which where gamma is the surface area and sorry this big guy this surface area and this one this small gamma is the surface tension so it is like gamma d so this is also I can capital gamma you can check that so basically if you have a force let's call a generalized force it can be a chemical driving force it can be a surface tension force or it can be an expansion or whatever like mechanical expansion or contraction so in all these cases you can have a generalized force and then you have a generalized displacement so it is basically the way we are writing it whatever way like it is PdV or whatever gamma d gamma but mainly one thing we have to understand is that f is a generalized force dz is a generalized displacement so it works for any type of this will work for any type of work .




so if I know what is the generalized displacement if I know what is the generalized force I can include many different types of work including electrical work, curing some magnetic work right so okay then so today's lecture is so I hope that you have enjoyed the lecture and if you have any any any questions or doubts please feel free to post and send us send my TA and us emails