

ok welcome back we will start the lecture two in this unit on thermodynamics and just to repeat what we ah just recall what we discussed in the first lecture you know i showed you that these are the topics which i intend to cover in first two lecture we have covered the essential concept and definition and we talked about heat energy work and energy which will basically continue little bit more and internal energy and in lecture two probably i'll talk about first law of thermodynamics calculation of work heat different processes enthalpy and and other things which is listed here last class we talked about system surroundings and boundaries world we talked about different systems open system closed system isolated systems and we talked about different types of boundaries rigid non-rigid movable impermeable or pierceable adiabatic or non-adiabatic and we talked about that if you have a movable boundary then exchange of energy as a work is possible between system and surroundings if it is permeable then exchange of materials can take place between system and surroundings if it is impermeable then its a closed system and if it is a non adiabatic or diathermal boundary then ah energy exchange can possible between system and surroundings as a heat and you also describe that a system surrounded by rigid impermeable and adiabatic wall is an isolated system then we also discuss how to define the system state of a system is basically by defining ah the or specifying the values of small number of microscopic variables which are properties or parameters of system like pressure temperature and all those things we discussed intensive properties and extensive properties i am not going to go in details anymore and we talked about homogeneous system heterogeneous systems phase processes which is basically from one state to another state and we talked about isothermal isobaric isochoric processes cyclic processes now we did not talk about we we talked about that in this unit we will talk about or in this course we will talk about mainly equilibrium processes or the system which are in equilibrium now what do you mean by equilibrium obviously the first question most of the student answer is that if the the values of the properties of the system does not change with time then we call that system as attained equilibrium now that is a partially true i will just show you how that is partially true that definition of equilibrium is applicable or true for an isolated system

so for an isolated system if the values of the macroscopic properties do not change with time then we call that system has reached equilibrium and the values are equilibrium values for the system now for a non isolated system two conditions need to be satisfied one the microscopy obviously the macroscopic properties should not change in time secondly if we remove or if we disconnect the system from surroundings then there should be no change in the values of the thermodynamic properties of the system i will just give you a small example you probably realize i have a say long rod iron rod and one side this is connected in a large pool of water which is kept at say 25 degree centigrade and the other side you have a large pool of water which is kept at say 40 degree 35 degree centigrade is a large pool ok and we are assuming that no no heat is exchanged between this rod and the surroundings now what will happen after sometime after enough time what will be the temperature in this iron rod this side would be 25 degree and this side would be 35 degree and there will be a gradient of temperature increasing from 25 to 35 degree centigrade which will not change with time if we keep this intact there will be no change in temperature obviously pressure volume are associated with this there will be no change in in the value of those

so we can we call this as equilibrium no we cannot call because if we remove the contact of surroundings like if you disconnect this part if you disconnect this part immediately the temperature will now come back and it will have a

average or steady value of 30 degree throughout the rod

so we need to have for a non isolated system as i said that you need to fulfill two conditions macroscopic properties do not change with time and removal of system from contact with surroundings causes no change in properties of system if the first one is fulfilled in this case a point a is fulfilled then we call the example i gave in just now we call this system is in a steady state ok not in equilibrium

so there is a little difference between a steady system is in static state and in thermodynamic equilibrium

so you should be clear about what is equilibrium e what is the equilibrium because we will be dealing only with equilibrium systems in this course ok

so now we will go back the discussion we were having on internal energy ah we talked about ah internal energy and inter as i said internal energy is the energy within the system

so what are the energies where from a system get energy within the system is from the molecules which it has the system has ah in the system now the molecules can have lot of different types of energy and especially for gas and liquid we can ah distinguish them in the in terms of molecular ah translational energy rotational energy vibrational energy electronic energy and we also have the relative relativistic rest mass energy which is m raised u c square which is basically the mass m rest is the mass of the electrons and nucleus which is at rest which is not possible to get that's the reason u cannot be determined absolute value of u cannot be determined and this is a constant this term is constant

so if you get the difference between u between two states then this term will cancel out

so we can get the difference between ah the values of u in two ah two states and another terms we have the potential energy of interaction between the molecules now if you talk about ideal gas the potential energy between interaction and of interaction between energies how much because the definition of ideal gas is that it does not have any volume or the molecules do not interact with each other

so basically this term the potential energy term because of the interaction between molecules do not appear

so value of which is zero for ideal gas

so ideal gas this should be zero and i am not going in detail about the first four terms this as i said this is a constant and this is zero for ideal gas and these terms the values are mainly dependent on temperature you know they are either constant or dependent on temperature

so you if i talk about general system you would be function of temperature and obviously distance between the molecules which is governed by either volume or p and obviously u is an extensive quantity

so if you increase the amount of substance you will also increase

so you need to give the moles of the component present in the system and if you want to get the difference between two states then is the function of the volume and if we talk about the closed system then there will be no change in ah this number

so we can just write as a function of temperature and pressure or temperature and volume

so whatever ideal gas ideal gas because this term is zero and this is constant so Δu for ideal gas only depends on temperature is only function of temperature or u of ideal gas only function of temperature instead of Δu we can write u as a function of temperature for ideal gas

so if you change the state of say if we change the volume of ideal gas without

changing temperature then there is no change in internal energy for the for ideal gas if we change pressure of ideal gas without changing temperature there is no change in the value of u

so basically if we keep the temperature of ideal gas fixed obviously in a closed system without changing the amount of substance if we consider closed system where we are not changing the composition and the amount of substance gas present then the value of internal energy of an ideal gas only depends on temperature as and temp if temperature is fixed there is no change in internal energy

so just keep in mind that u for a closed system for ideal gas only depends on the temperature the inter energy value of inter energy only depends on temperature now we have seen in last lecture that energy can be exchanged between system and surroundings either by doing work or by exchange of heat between system and surroundings and we also had seen earlier that the total energy change we can equate to change in internal energy for the systems which we normally deals with where the macros change in macroscopic kinetic energy and change in microscopic potential energy is zero

so total energy change is given by only the change in internal energy and what are the two ways we can change we can change by the by exchange of energy between system and surroundings as heat energy which we will write as q and the other one is by doing work ok

so that we will write as w

so we can write Δu is q plus w where q is the increase in energy due to heat exchange q is the increase in energy in the system due to exchange of heat between system and surroundings similarly w is the increase in energy of the system because of the mechanical exchange between system and surroundings if we have volume constant volume is fixed if volume is fixed then w is zero because there is as i said earlier this there is no change in volume then there will be no energy exchange as work

so w will be zero

so in that case we can write Δu would be q_v where v is q_b means that heat exchange under constant volume and if we talking about the adiabatic process a process which is happening in a system which is surrounded by adiabatic wall adiabatic process in this case there is no heat exchange between system and surroundings which that case daily would be w we call adiabatic now if there is no exchange of heat and no exchange of work between a system and surroundings which happens in an isolated system an isolated system as you remember we described that it is surrounded by rigid wall which means no change in volume no work w is zero and it is surrounded by a adiabatic wall

so q is zero

so for an isolated system w is zero q is zero hence Δu would be q plus w which is also zero

so this is the mathematical expression of ah first law of thermodynamics where it says that for an isolated system isolated closed system we are talking about no change in composition or amount of sustain substance most cases will be dealing with closed system as i said

so in case i forget sometimes you have to remember that in this case the the internal energy can be changed by the heat exchange the work section and also metal exchange if we add more substance from outside obviously the internal energy will increase but obviously we are not considering the case where there is a material exchange between system and surroundings we are dealing with closed system most cases

so for a closed system or closed ah iso isolated system obviously closed system does not matter it is indeed a closed system

so there is no matter exchange of matter is possible
so for an isolated system Δu is 0.

so that is the mathematical description of first law of thermodynamics which says that for an isolated system there is no change in internal energy and for any general process Δu is q plus w we talking about closed system in this case

so one more thing this is a one more time this is a generic expression of first law of thermodynamics where the change in internal energy is given by q plus w where q is the increase q is the increase in energy of the system due to heat exchange between system and surroundings across a non adiabatic wall similarly w is w is increase in energy of the system due to exchange of energy as work between system and surroundings across a non rigid wall obviously for an isolated system both q and w is zero

so for an isolated system Δu is zero here we do not need to mess closed system because isolated systems are indeed all the isolated system are indeed closed system

so this is the mathematical expressions of a first law of thermodynamics because thermodynamics you know first law of thermodynamics is basically obtained for your experimental evidences which says that energy cannot be created or lost in in transformation from one form to another

so we had seen Δu is equal to Δw in the systems we are talking about
so as the energy cannot be created or lost

so in a process Δu can be only you know Δu can be change or in inter energy of the system can be changed by processes which we mention now

so this is what is a mathematical description of the first law of thermodynamics

so we will now look at how to calculate work and just take a simple system where we are taking a cylinder

so this is pressure y axis and x axis we plot volume and this is the system and this is the initial volume if we this volume which corresponds to this value v_i which is initial volume then we compress we apply a external pressure p_x if it is higher than the inside pressure then this will move in till the internal pressure is same as external pressure

so we can have a final volume sorry lets say it has come up to this

so this is the final volume v_f and the volume change is given by this area

so this is the area which is the change in the volume

so that is the initial state where the cylinder has this much volume which is shown here in this graph and it has a final volume where it is shown as v_f now if the area of this piston is a then obviously the force given by the piston is given by pressure into area which is p_{external} into a the distance move it has moved distance if this is say l then work done could be force into distance which is given by p_{external} into a into l now this a and l is nothing but the change in volume Δv

so $p_{\text{external}} \Delta v$ or $p_{\text{external}} (v_f - v_i)$ if i place this is this pressure corresponds to p_{external} then this area will be equivalent to the work due to this compression this is the area which is shown in this rectangle now here what happened the volume of the system has reduced

so the surroundings has done some work on the system and what happened to the system energy increased or decrease

so in this case systems energy has increased now if something increase the energy increase means the change in energy has to be a positive number but in this case $v_f - v_i$ Δv is a negative number

so to balance this we put a negative sign here

so this negative sign is written or brought in this expression just to balance this remember what we talked about in earlier page that w is the increase in energy now if system is working on this surround sorry the surroundings is working on the system which means the energy of the system is increasing we should reflect in our equation

so during compression surroundings work on system as a result the energy of system goes up

so the value of w must be a positive number now to make this number positive we are putting a negative sign in this expression and it will be fixed all the time so there is no more change in this expression

so for a compression when surroundings work on system and system gain some energy the Δv value is negative

so w is w is positive number

so system gains some energy if system does work on surroundings during an expansion if you doing an expansion where the volume is increased in that case system is doing work on surroundings which means system is losing some energy

so w should be a negative number

so Δv is a positive in that case for expansion which means w should be negative which which will come negative

so for compression Δv is negative because v_{final} is less than v_{initial} and in this compression case surroundings does work on system as a result the energy of system goes up or increases which indicates that w should be a positive number because there is increase ok

so if we write the expression w is equal to minus $p_{\text{ext}} \times \Delta v$ because Δv is a negative

so this will turn out to be a positive number ok for compression for expansion Δv is positive

so w is v minus $p \times \Delta v$

so positive number negative sign

so negative number

so now we are clear that why the negative sign was brought in and it will be there in all all our expression

so we can write Δu as q plus w instead of w we can write minus $p_{\text{ext}} \times \Delta v$ and in this case we are talking about ml we just talked about one step process where the volume was decreased in one one step that is why the sign p_{ext} the the value of p_{ext} is kept here ok

so this is one step process we mention here and

so this this is the expression for your work now if we go back and do the same in multiple step like if we just do it in pictorially pressure and this is the initial volume and we decreased we keep the p_{external} here and as a result the volume get decreased and then again the pressure is increased volume gets decreased further again if i increase the volume is decreased

so this is the final volume v_f where we are doing in three different steps first step we change increase the pressure to p_1 which is higher than the internal pressure and then we change the further increase the pressure p_2 and then we made the pressure p_3 where p_3 is higher than p_2 and p_2 higher than p_1 and p_1 obviously higher than the internal pressure

so this is the area which represents the work now if i do in infinite number of steps from this v_i to this final volume here and pressure this final pressure is here then we can have

so here we are doing in multiple step we have in the last page we had shown one step in this case we are talking about three step and in this case we are talking about infinite number of steps where we are doing a continuous changes in pressure and volume now just just look at be careful one thing though i have

drawn a line here ideally there should not be a line because you do not when i draw the line in between that means you are fixing the pressure for these points which is not true i have changed the pressure to this value which corresponds to this this was my initial stage pressure here and then i change it here and then further i change it to here and then finally chamber

so i should get only three points and there should not be a continuous line in between but this has just shown to you just to show that the area which will be corresponds to the work done or the value of w corresponds to

so in this case what we know that the the area the area under this curve the three value for w are different when you are doing one step or two step or three step which means the value of w depends on i am going from same volume v_f to v_1 and same final pressure but we are getting three different value of the work

so which means w depends on path which has been adopted for going from state 1 to state 2 or initial state to final state now we know $w = \Delta u + q$ and u is a state function because its only depends on pressure temperature volume and the amount of substance in the system

so u is a state function

so if w is a path function then q also must be a path function in this case ok now in the case this case where we are changing the pressure continuously in infinitesimally small quantity

so that we can draw a continuous line between the initial state and the final state this process is called a reversible process and the first two case where we change we brought the change from state one to state two in one step or in a discrete two three step those are called those are called irreversible changes irreversible processes in the third example where we just drawn a continuous line between the in initial state and final state specified all the ah states in between equilibrium states in between that is a reversible process

so what is the reversible process reversible is process is a process is a process where system is always in finite c mainly close to equilibrium you know an infinite small change in condition can reverse the process to restore both system and to the initial state

so basically if we changing from one state to another space if we are changing the volume of a um i have a i have a cylinder ah if i draw a cylinder here this is $p_e x$ and inside is p now if $p_e x$ minus p is infinite similarly small then the change if p_x is a lower if p_x the p_x is infinitesimally lower than p then this piston will go up infinitesimally small now if you want to increase the volume definite amount of volume of this system then this will take almost infinite time because the steps which is taking its in in financial in finite symmetry slow steps

so it is a reversible processor in finite seemingly slow process

so it will take almost infinite time

so in the it is it is just in reality it is a it not possible

so it is basically an idealized process we require the concept of reversible process for several calculations ah and to derive several thermodynamic parameters and in this case if the change is infinitesimally small then if we can go back and write the expression for work done and if i write the expression for dw which is just talking about is very infinite similarly small change in pressure work then i can write $-p_e x dv$ where the change in volume is infinitesimally small and as p_x is almost same as p because they are different different than each other is infinitesimally small we can write instead of $p_e x$ we can write just p

so this is for reversible process

so if i want to get the work done for the entire process i have to integrate from state 1 to state 2 to get the total value for the work done going from

state 1 to state 2 in a reversible process in a reversible process process and we talked we knew ah when we talked about irreversible process

so this is the value for work done for irreversible process if i just extend to an ideal gas case in ideal gas p is equal to $n r t$ by v

so w would be v_1 to v_2 $n r t$ by v dv

so for if i talk about isothermal process heuristic discussion for isothermal process then t is constant i can take t out of the integral

so w would be $n r t$ v_1 by v_2 or initial to final dv by v or $n r t \ln \frac{v_2}{v_1}$

so for isothermal reversible process of an ideal gas w would be given by minus sign means the minus sign here

so minus minus $n r t \ln \frac{v_2}{v_1}$ again for compression just to recheck for compression as v_2 is less than v_1 w will be positive number and for expansion as v_2 is greater than v_1 w would be negative number

so during expansion system loses energy and

so is actually energy decreases and for compression the energy of the system increases

so w is positive for free expansion what is free expansion when the means p_{ext} is zero external pressure is zero

so the expansion is happening in vacuum

so expansion when expansion of a gas happens ah in vacuum

so p_{ext} is zero then we call it free expansion

so w would be $p_{ext} \Delta v$

so zero for if we do in an isothermal process now any isothermal process ideal gas any isothermal process for an ideal gas as i discussed in length Δu should be equals to zero again isothermal process ideal gas Δu will be zero now if Δu is zero w is zero

so q is also zero

so for free expansion of an ideal gas isothermally will lead q is equal to w is equal to zero ah Δu is equal to zero and for free any free expansion all the time no matter what is the process isothermal or ideal gas w would be equals to zero now in this case also this is also an isothermal process ideal gas which means Δu would be zero hence q would be minus w which is given by this expression

so we talked about isothermal reversible process of ideal gas and free expansion if we talk about adiabatic process now all the adiabatic process as soon as you hear the adiabatic process you will know that q is zero the moment the process is adiabatic which means there is no exchange of heat between system and surroundings

so q is 0 which means Δu is w adiabatic and when we talk about isochoric process isochoric process means Δv is zero Δv is zero which means w is zero which means Δu is q b now though w and q are both path function in this two case in case of adiabatic process and in case of isochoric process in adiabatic process w is equals to Δu

so in this case w is no longer a path function similarly in this case q for the process which happens at constant volume is equals to Δu and Δu is a state variable or state function which means q in this case does not depend on path

so q in this case is a state function

so remember that not all cases w and q are path functions there are cases where w and q could be a state function as well

so we talked about adiabatic process isochoric process now if we do about the isobaric processes like constant pressure process

so Δu is q plus w i can write q_p because a constant pressure process and no matter what is whether it is a reversible process or irreversible process p can

be taken out of integral because it is a fix then integral v is $v_2 - v_1$

so in this case no matter it does not matter whether process is in reversible process or irreversible process the value of w would be same $p \Delta v$ or $v_2 - v_1$ similarly we in this side also we can write $u_2 - e_1$ now you can rearrange this to write this is as $q_2 - p_1 + v_2 - e_1 - p_1 v_1$ now this term $u_1 + p_1 v_1$ we are defining a new thermodynamic parameter h as $u + p v$ this is the mathematical definition of h h is named as enthalpy from greek word enthalp p means to work for heat content now you can look at h you will see that this is only depend related to $u + p v$ all these terms are state variable which means h is also a state variable that means the value of Δh which only depends on the h_1 and h_2 it does not depend on the path or the process it has been taken from going to state one and state two $h_2 - h_1$

so is i just trying to say that because h is related to $u + p v$ which are who are the terms which are state variables

so h should be state variable it should not depend on the path of the system

so now i can write q_p here as i can write one more time q_p we have written $h_2 - h_1$ as h is equal to $u + p v$ we can write q_p is equal to $h_2 - h_1$ or Δh

so for constant pressure process at this is the exchange of heat between system and surrounding at constant pressure process which is the heat absorbed by the system heat absorbed or increase in energy due to heat exchange it absorb simply cannot absorb by the system at constant p for exothermic process heat gets evolved

so Δh

so system loses energy as heat goes out from the system to surroundings

so Δh is negative for endothermic process where heat is comes in the system from surroundings in that case Δh is positive greater than zero for most of the cases like because $p v$ you know you can write Δh as $\Delta u + \Delta p v$ now for liquid and solid this this is not a high number significantly high number

so for liquid and solids solids you know Δh value almost or less almost similar to the value of Δu but for gas obviously they are significantly different for gas we can write if we take two gases almost you know two condition where we write v_a if you talk about say reaction and product

so v_a is the reactant n_a is the number of moles of reactant similarly v_b is the volume of volume of volume of products n_b is volume of number of moles of then we can if we consider these are almost ideal gases then we can write v_b is $\frac{n_b R T}{p}$ v_a is $\frac{n_a R T}{p}$ v_b is equal to $n_b R T$ then $\Delta p v$ is your $p v_b - p v_a$ $R T$ so $p v_b - p v_a$ gas $R T$

so in this case $\Delta h = \Delta u + \Delta p v$

so in a chemical reaction gaseous chemical reaction almost if we assume the gases to be ideal almost gaseous nature then we can have this relation between Δh and Δu where Δn_g is the change in the number of moles of almost gases in the reaction this is almost where we are talking about gaseous reaction and change in the $\ln g$ is the change in number of moles of gases now we will just try to discuss little bit of almost heat i think time may not permit today

so what we will do in next class almost we will try almost first thing as to quantify the exchange of almost heat between system and surroundings as a result of temperature difference and in that we will bring the concept of heat capacity almost and we will take the rest of the discussion from there

so in next lecture we will start from quantifying almost or or basic sodium the equation for heat exchange between system and surroundings you