welcome back to our discussion on this unit on thermodynamics and in this today's lecture third lecture which is in this unit we will talk about enthalpy and heat capacity and then determination of internal in in internal energy change and enthalpy change for different processes but before that i just wanted to revise some part which i covered in second lecture which are shown here in blue color you know the total energy of a body e can be represented as k plus v plus u where k is the macroscopic kinetic energy and v is a macroscopic potential energies of the body k happens due to the motion of body through space and v potency energy because of presence of field that acts on the body and you is we discussed in last class that use the internal energy of the body due to molecular motions and intermolecular interactions

so change in total energy could be represented as change of each of these energies and if we talk about absence of any varying external field acting on system which means delta v is 0 and system is at rest delta k 8 0 which is the case we talk about in chemistry chemical reactions and different chemical processes this is the scenario then total energy change would be represented by change in internal energy and if the system does not interact with surroundings at all there is no exchange of energy between system and surroundings then which is the case for an isolated system then the first law says which is basically the conservation of energy which says that energy cannot be created or energy cannot be destroyed

so delta e is constant for isolated system when the system does not interact with surroundings or does not exchange any energy between system and surroundings deltas e the internal energy should be constant

so delta u should be zero ok

so this is the mathematical description of first law of thermodynamics that for an isolated system change in internal energy is zero now what is the internal energy we discussed in last lecture as well internal energy is the energy of within the body which is due to the molecular motions and intermolecular reactions in intermolecular interactions between the molecules present in a system

so and also you know the internal energy or we described in last class its a extensive quantity

so if you increase the more amount of if you add more amount of substance in a system obviously internal energy will increase

so for a cis closed system where we are talking about there is no change in amount or no change in composition in the system internal energy can be given by the following term this translational motion of the molecules energy due to translational motion of the molecules rotational energy vibrational energy electronic energy and intermolecular the energy due to inter molecular interactions between molecules and you rest we described this is the rest mass energy of the electrons and nuclei is given by m rest c square this is the velocity of light which is a constant term and as we cannot get this experimentally measured

so this absolute as you discussed in the last lecture as well the absolute value of u cannot be measured we can only measure the change in internal energy experimentally these terms are either some of these terms could be constant for some cases but most cases either they are in most cases they are function of temperature these terms depend on temperature only and the second term intermolecular the the energy due to intermolecular interactions will depend on the distance between the molecules which will depends upon temperature and volume or you can say temperature and pressure as well

so the first term is dependent this first four terms depend on temperature second terms dependent on temperature and pressure or temperature volume and this is a constant term

so we can write for a closed system entropic and sorry internal energy can be represented as a function of volume or temperature or function of pressure and temperature now if we consider ideal gas or a perfect gas then you know that there is no intermolecular interactions between molecules in case of an ideal gas of a or a perfect gas then this term will not be it will be zero

so the internal energy of an ideal gas would be only dependent on temperature for a closed system of course

so for an ideal gas closed system internal energy will depend only on temperature

so if we fix temperature and we change the volume or we change the pressure the internal energy of the ideal gas will not change please ah keep it this in his mind that internal energy of an ideal gas in a closed system only depend on temperature

so u is a external extensive quantity extensive property and obviously because it is a state function if you come back to the original state then change will be zero

so the cyclic for cyclic process change in inter energy is zero and change in internal energy between two states initial state and final state is not dependent on path is basically depending only on the thermodynamic state of the initial state and the final state

so how can you change the value of inter energy of a closed system obviously by exchanging energy with surroundings now what are the different ways we can exchange energy with surroundings we talked about there are basically two ways one by work exchange or by heat exchange now work could be of different types but in our ah or this unit will be restricting ourself only to the pressure volume work or which also called expansion work or mechanical work

so basically we now know that internal energy can be altered in a cis closed system in energy con can be altered by work or by heat exchange between system and surroundings

so if you in a closed system if you want to write the first law of thermodynamics in a general form then we will write the change in internal energy in a closed system is given by q plus w what is q q is the increase in the energy of the system remember we are talking about increase in the energy of the system due to thermal exchange through diathermal wall and w is the increase in the energy of the system due to mechanical exchange or expansion work through non rigid wall obviously if it is rigid wall there will be no movement of the walls no volume change and then w will be zero

so in both case q and w we are talking about increase in energy ok

so the sign and w and q are positive if system gains some energy or the increase there is a increase in energy of the system and they are negative if system loses some energy or there is a decrease in energy of the system please remember that w and q are positive if the system gains some energy and negative if they loses some energy

so when the surrounding does some work in the system which happens in compression case it is w is greater than zero because system gains some energy and the system does some work on surroundings then its which happens in case of expansion then system loses some energy w should be negative similarly when a system receives some energy from heat from as a heat from surroundings then q is positive and system loses some energy to the surroundings then q is zero q is greater than less than zero is negative

so look for the some questions which are there in your ah book express express the change in internal energy of the system when no heat is absorbed by the system from surroundings but work w is done on the system and what type of wall

does the system have now in this case node heater heat is absorbed
 so q is zero w is this is the magnitude w is the magnitude of the work is done on the system that means system gains this w amount of energy
 so delta u in this case would be q plus w from first law and in this case w is positive because work is done on the system and what type of cis wall this is this is a no heat is absorbed
 so its a adiabatic wall and because there is a work done
 so it will be a non rigid wall
 so assuming that is a closed system there is is it is also a non permeable not permeable wall the second question no work is done on the system
 so obviously w is zero but q is the amount of is taken out not this term taken out from the system and given to the surrounding
 so in this case system is losing some energy and magnitude is q here
 so from first law in first law in the main equation we had q was increase
 so in this case because it is decreasing we will write w minus q which is minus q in this case no work is done on the system
 so in this case w q is q is the magnitude and because heat is taken out of system system will lose some energy
 so instead of increase it will decrease
 so it will be a minus q value and the type of wall would be obviously non adiabatic because heat is getting exchange or diathermal and it is a rigid wall because no work is done in the third question w is the amount of work done by the system work done by the system which means system is losing some energy
 so it will be minus w and q is the amount of heat supplied to the system that means system is gaining energy
 so in this case w would be q minus w where w is the amount of work done by the system when system is doing the work that means is losing some energy and q is the amount of heat supplied to the system
 so it will be the positive number and obviously this is a closed system because work is getting done and volume is getting change
 so generally we talk about volume in case of closed system especially in the gaseous system we move to the second question you just see for each process state whether q w and w is positive zero or negative
 so this process is given you have to tell whether what is the sign of q w and del u
 so that will clarify this one more time
 so combustion in a sealed container with a rigid and adiabatic wall now when you are talking about rigid wall that means w is zero adiabatic wall q is zero obviously del u is zero in this case combustion of benzene in a sealed container that is immersed in a water bath at twenty five degree centigrade has a rigid thermally conducting wall its a it has a thermally conducting wall
 so which allows energy exchange is a heat and because combustion of benzene is a exothermic reaction heat gets generates which goes out of the system to the surroundings which is the water bath
 so in this case system is losing some energy as a heat
 so q would be negative rigid
 so w would be zero
 so del e would be q plus w
 so would be negative as well c adiabatic expansion of a non ideal gas into vacuum adiabatic k is zero its expansion into vacuum expansion into vacuum we know w is 0 and del u is 0.

 so if i had expansion of the non ideal gas other than vacuum some again some constant external pressure then because of expansion w would have been negative

and del u would have been negative
 so i hope by this time you you are very clear about the sign of w q and w in any processes
 so next we will move to work and in last and and as i said the beginning of this lecture that work could be of ah two types one is basically the what commonly what we are describing the expansion work the mechanical work or the pv work and any other work like electrical work or magnetic work we call together as a non expansion or additional work but in this unit will be only talking about pv work and mechanic or or mechanical work or work of expansion
 so if nothing is mentioned about the work you have to assume that its a pva work its a pv work on or you can just if no nothing is means as i said nothing is mentioned everything that is the pv work and we talked about the how to calculate those in in last lecture that for a reversible process is given by this expression and because p external is infinitesimally close to the pressure of the system and for irreversible process we write we have the expression where w is the p external sorry p is p e x is the external pressure final volume initial volume that we discussed in last lecture expansion against constant pressure you can
 so it is minus p delta v v two minus v one or v final minus v initial free expansion expansion against constant opposing pressure is p external is zero
 so w is zero and for your reversible isothermal process for ideal gas we have seen that ah this is the expression for work now i quickly ask a question and let's see whether you can ah solve this
 so that will be my question 3 in this lecture
 so i will take ideal gas enclosed system and we consider a reversible process
 so what you have to do you have to calculate ah the change in or calculate the work involved in this process and you have to schematically draw the area which will corresponds to the work
 so this is the initial state some temperature t its a isothermal condition to 1 pascal 10 meter q is the volume and that temperature t
 so in this case that is my first part
 so if i want to get w you know ideal gas reversible process isothermal condition
 so i can write nrt ln v final which is 10 meter cube by 1 meter cube and which will energy is equivalent to pv for ideal gas
 so ln 10 which will give us minus 10 into 1 and let us write 10 a meter cube into 2.
303 or minus 23.
303 joules and if i want to draw schematically in this graph if this x axis is volume and y axis is pressure then if this is your 10 pascal and this is say one pascal and this is your one meter cube and this is your ten meter cube then you have this area corresponds to your work now in the second part of this this question we will write we will do the same thing instead of a reverse isothermal way we will do it in two parts like i will take ten pascal one meter cube t and then first do a isochoric constant volume process take it to some other temperature and then do a isobaric constant pressure process and take to get the phi this this initial state and final state is same as in the last example here this initial state is and final state is same in this case but in earlier i did a reversible isothermal way in this case we are doing in two step isochoric and isobaric then what will be the work done in this case total work would be the work done in this two step and first step is a constant volume process
 so it will be zero and in second case it will be minus p v two minus v one which is 0 minus i can remove 0 1 pascal 10 minus 1 meter cube gives me 9 z you can see this is a expansion process volume is going from one to ten meter cubes

and because the expansion process system is losing some energy

so in all the cases you are getting a negative value for your work now if i draw this in in p v scale

so this is your higher pressure to same volume isochoric condition you are getting to lower pressure and then you are increasing to the volume

so this area would be your work

so in third case i can do the other way round ten p a one meter cube now i do the i just reverse the step earlier in ah in last example i did it isochoric isobaric now in this case i am doing isobaric and iso followed by isochoric

so in this case again w would be w one plus w two and this case minus ten p a ten minus one meter cube plus this is isochoric process

so that would be zero which gives ninety joule and if i want to draw this pressure volume curve

so you start from here isobaric process

so do is go to ah intermediate state and then bring the pressure down

so this your first process second process this is one two

so this would be your this area would be your work done in this case

so basically if you compare the three the three ones we just discussed

so basically you are doing ah we are doing the same change from initial state 1 to state 2 but we are getting different value of work done which shows that work done between two states is a path function it does not only depend on the two states but it depends how you are carrying out the changes just for your as a home part of homework you can do this solve this problem where you do the same change irreversible way in one step and then two step and then in infinite number step which is basically a reversible process and you also calculate the work done in forward direction and work done in backward direction and you will see that again the the value of work will be different as you change the process

so that you can do in your yourself at home

so next we will talk about enthalpy and we started talking about enthalpy in ah last class we defined mathematically enthalpy as u plus p v these are all a state variable u p v

so h is also a state variable or state function or state property whatever you call u is extensive quantity it depends on the size of the system or mass of the system

so i h would be also extensive quantity and again as the value of u cannot be deter absolute value of u cannot be experimentally determined

so absolute value of h also absolute value of h also cannot be cannot be determined experimentally and again because its a state variable

so delta h the value of delta h between state 1 and state 2 or initial state to final state will only depend on the value of delta h will only depends on the initial and final states now we know that from first law we from first law of thermodynamics we know first law that del u is given by q plus w for closed system of course we now if you talk a process which is at a process which is happening at constant volume

so just like p one t one v to say p two t two and v

so doing a change at constant volume and if as you doing at constant volume obviously the w would be 0 then del u would be the change which is happening at constant the heat change which is happening at constant volume now if the process is for a process at constant pressure we can write generally like t one v one p two t two v two and p in this case we have seen in last class that q p the ch heat exchange can be written as q p is equal to del h

so q v is a process is as constant volume then q is equals to del u and if the process is constant pressure then it is the q is equals to the del h enthalpy change now if we consider a constant pressure process again and then del h we know from definition del u plus constant pressure

so we can write p del v and for we know that for liquid ah for liquid or say solid now this change in volume is ah negligibly small or very small del v is very small for a sparse process

so in this case we can consider that del v is negligibly small

so we can consider del v zero

so del h is equals to del u for solid and liquid ok these are very close not exactly same but because the volume is very small

so this we can consider these are almost close to this but for gas for gaseous the the reactions of the process involve gases

so the reactions or processes which involved processes involving gaseous substances or gases we had shown that in last lecture the del u is del n g r t now we in that deriving this we consider that the gaseous are ideal ok this we had considered

so we will just move to next problem and then just will ah to it will be question five

so it consider a process a process where we talking about okay this problem is given here

so the molar enthalpy change of vaporization of water at one bar and 100 degree centigrade is 41 kilo joule per mole calculate the internal energy when this to 1 and 2 and assume the water vapor is a perfect gas this is from your textbook

so if you note down

so this is basically a vaporization process and one mole of it is given one mole of water is vaporized at one bar at hundred degree centigrade

so h two liquid to h2o gas at one bar hundred degree centigrade and we are talking one mole here one mole and in this case it is given del h for this vaporization process we can write del vaporization h is 41 kilo joule per mole now again this is a positive number because for vaporization we have to add some or supply some heat to the system

so the system actually gains some energy that is the reason it is a positive number

so we can get the other value del u ah from the expression we learned just now plus del n g r t or del u is del h minus del n g r t we talking about one mole of substance one mole of water

so this value 41 kj per mole that is a molar into one mole of substance minus again one mole delta n g is change of one mole ignoring the volume of liquid

so basically one mole of gas is produced into r value is eight point three one four joule per mole per kelvin into three seventy three hundred degree centigrade we are considering three seventy three k in in solving ah physical chemistry problem you must be very careful about ah the units and if you put units appropriately you will get your final answer exactly the way you want because del u which basically you are talking about energy change

so it should give you energy number

so in this case it is giving you a energy

so for and because you are doing it for one mole you can write it that delta u for vaporization is 37.

9 kilo joule per mole but this is your answer 37.

9 kilojoule is the change in value of change in internal energy for vaporizing one mole of liquid to one mole of gas

so in the second problem ah you have one mole of water is converted twice

so we can write in

so that's second one

so two o solid again this is one mole this is one mole and generally it is done at ah generally this ah we are considering this is a constant this is done this transition is done at constant pressure

so constant pressure condition is what we are assuming

so del h can be considered at del u plus p del v and as we consider as we talked earlier that because of ah solid and liquid the volume change is we are considering is negligibly small

so in this case we will have del u is close to w which is 41 kilo joule for 1 mole of gas

so you can write del u as you can do 41 kilo joule per mole as well but your answer is 41 kilo joule

so we talked about enthalpy we talked about to work with dr internal energy and we now will talk about how to calculate the heat part the q in your first law now heat exchange happen um exchange of heat energy happens because of or heat exchange happens between system and surroundings because of temperature difference between system and surroundings because of temperature difference that we all know we understand that if there is a temperature difference between system and surroundings if they are brought in contact through a non adiabatic wall heat exchange will happen and heat will move from higher temperature to lower temperature and we all we know that this heat is proportional to the temperature difference of system and surroundings and if we consider small change then we can write d q which is the small value and which is we can write small this is d q is for small value of q and d t is a small value of very small value of a temperature difference

so for

so what is the proportionality constant we have this proportionality constant as c capital c

so for the entire process we can get q summation of integration of t one t two d t if c is constant if c is constant in temperature range between t one and t two then we can take this out of integral then it will be c del t which is giving giving us the same value c del t ok

so that is only you can write in case c is not dependent on the temperature which will for in this unit or in your case we will consider the c is independent of the temperature range we are talking about

so we now know that q is c del t this c is called heat capacity of the substance we are talking about this is remember this is where this c is capital letter or upper case whatever you call that is for the entire substance obviously if you have more substance this value will go up

so this is a extensive quantity now we can also write q as if we divide by number of moles and write c is n c m where c m is c by n molar heat capacity then n is the number of moles then in this case molar heat capacity would be a intensive quantity we can also express in terms of mass and small c where c is capital c divided by m and m is mass and this case c is remember we are talking about c is small later or lower case and we are calling this as specific heat capacity now what is how you can what is the difference now the heat exchange can happen ah can happen or can be carried out in two ways one at a constant pressure other could be a constant volume now if as we said have you seen earlier if the process is if a process is at constant v like the example we had earlier p one t one v two p 2 t 2 v then we know del u is q v as w is 0

so del u would be given by cv del t similarly if the process is process of our interest is at constant pressure as we have seen earlier then del h is q p

so del h would be given by c p del t but if you have a general case we have say a process we have a general process all three are changing say i have p 1 v 1 t 1 2 p 2 v 2 t 2 then how do you get this del h and del u now because del h and del u both are are state variable they do not depend on the path

so we can break down the process institute step for example if i want to get d u i'll let me break this to this process into two step t one to v one t two and some other temperature p three and then

so this is at constant v and we do it next is constant t t two v two and p two

so where we are reaching from state one if the call state 1 to state 2 we are going state 1 to state 2 but in 2 steps now

so what will be del u then del u would be del delu in the first step plus delhi in the second step now if you consider a simple case of an ideal gas now what do you know the ideal gas u is only function of temperature

so if temperature is fixed then delhi would be zero which means for the second step where temperature is constant delu would be zero

so del u second process would be zero as temperature is fixed remember we are talking about ideal gas please do not generalize this this is only applicable for ideal gas and daily one the constant volume process as we discussed earlier it will be given by cv dt

so del u will be given by del one a first process and second process

so cv del t plus 0 cv del t

so we can write del u is cv del t that is only for ideal gases ideal gas do not this expression is only valid for ideal gas please do not confuse is a general expression and cv is we are talking about heat capacity at constant volume ok similarly we can think of general process and we can break down to a constant pressure and constant temperature process and we can get again del h is cp dt for ideal gas if we can write one more time delta u is c v del t these are for ideal gas this is not for general example ok this generally is applicable now how c p and c v are related how they are related means which is what is the relationship between them if we consider two process say we take a cylinder and first we consider this a piston first we consider that this is a fixed

so the volume does not changes and we have supply some heat which will because we are supplying some heat it will increase the energy and temperature will go up

so here whatever heat is supplied here this will increase the internal energy which will increase the temperature of this of the system but if we do the process at constant pressure we write the same thing but in this case this is not fixed this is movable ok

so this is movable or non rigid then if you have supply heat volume will expand the gas the volume of the gas will expand and a result there will be volume expansion and if volume expansion happens you know that system is losing some energy or it is doing some work on the surroundings and

so it is losing some energy by doing work

so this is a constant pressure process this is a constant pressure we have applied and this is a constant volume process

so now you can compare that in this case constant pressure process whatever energy you have supplied as a heat it is it is increasing it is used to utilize to increase the internal energy or temperature of the system plus some of which are getting lost as doing work on the surroundings but here whatever you are adding as a heat then all it like getting utilized to increase the temperature

so you can now compare because in this case if you want to increase same temperature del t in both cases you have to supply more heat here

so q has to be more in this case compared to constant volume case because part of the queue which is getting in is getting lost as the system is doing some expansion work on the surroundings

so c p is greater than c v and this is true mainly for gaseous substances gases because in case of gas the volume change is significant and as we have talked earlier also that for solids and liquids for solids and liquid generally ah the volume change del v is negligibly small so c p is nearly same as c v

so this is the case for solid and liquid but and but but if you true sense in true sense if you do not neglect the small volume change then cp would be greater than cv with exception where with exception where volume reduces or decreases on heating if there are cases like water between zero degree centigrade to four degree centigrade on increasing or on heating that volume decreases then you can get c v less than c p but most and almost every cases c p is greater than c v case is also exception cb is equals to cv like that the when the volume goes through minimum

so thats four degree centigrade water at one atmospheric pressure

so these are exception where c p is equals to c v most cases or on every cases with just few exception where c p is greater than ah c v but in practically for solids and liquid cp is almost close to cv but for gases for gaseous substances we always have cp greater than c v now for ideal gas we will talk about ideal gas that is the simplest case we are always talking ah we can get del h is equal to del u plus del pv del u plus del n r t now for ideal case we know del h is cp del t del u is cv del t and in this case nr del t

so we can write from this c p minus c v is n r for ideal case or c p m we talk about molar heat capacity c v m could be v n minus r

so these are expressions for your ideal ideal gas now what will do we will go back and look at few questions to ah clarify ah just to see clear your ideas and will write ah say for each of the following processes the just write a following process and you have to get me the sign of q w ah del u and del h

so i will write the process and you have to tell me ah the sign

so one first would be reversible melting of benzene at one atmospheric pressure and normal melting point

so you tell me what is the value of q w del u and del h the melting process requires heat in the system

so q must be greater than zero this is a constant pressure process at one atmospheric pressure

so q is q p which is equals to del h

so del h equals to zero now in this case on melting volume increases

so del v is positive even though it is very small but it increases expand

so w would be minus p del v del v is positive

so w would be negative in this case and del u is q plus w now as i said this is a solid

so w is negligibly small compared to q

so you can ignore q in this case

so at q is positive del u should be positive

so that is the first question example in the second example we will do the same thing but for ice reversible melting of ice at one atmospheric pressure zero degree centigrade again you have to find sine of q again for melting you have to supply heat

so q is greater than zero and is a constant pressure process

so q p is del h greater than zero now in this case on melting at zero degree centigrade what atmosphere actually volume drops

so in this case w is minus p del v

so w should be a positive number because the volume comes down volume decreases

so del u is a positive the w is a positive quantity but very small as we talk about solid and liquid

so because of very small

so we can consider del u is equal to q plus w and this is small

so the sign of w should be del u should be same as q

so del u should be greater than zero we will talk about the third example

reversible isothermal expansion of an ideal gas now isothermal reversible expansion when you talk about expansion del v is greater than zero
so w is less than zero ideal gas isothermal
so del t is zero and when del t is zero we know for ideal gas del e del h is zero del u is zero del u is zero which is q plus w and w is less than zero
so q must have to be greater than zero
so what will do we will ah stop in this class ah now ah will i give you few more ah this type of problem in the next class and next class we will talk about how to determine the ah values of del h and del u experimentally and then we will talk about ah del h for different processes you