

welcome back to this unit on thermodynamics and we will go through today about the criteria for spontaneous processes and we will introduce entropy and gibbs free energy just to recap what we have learned in last class and

so basically we have learnt that reaction enthalpy or enthalpy of reaction or heat of reaction is a total energy of the enthalpy of the product minus total enthalpy of reactants if i just plot in two axis x axis your reaction coordinate if this is your reactance and say here you have products corresponding energy level is this

so if this is h_p is the total enthalpy of the product and h_r is the total enthalpy of the reactants this is h in y axis x axis is reaction coordinator

so in this case we are writing h_r is total enthalpy of reactants and h_p is total enthalpy of products then in this case the reaction enthalpy of reaction $\Delta_r H$ is given by this difference and this is product minus reactance is a negative value

so this is exothermic reaction similarly if i have the other case where i have again reactants and products reaction coordinate in case i have product reactance at lower level

so h_r and products at higher level h_p

so the difference is this

so this difference is this is the product total enthalpy

so this in this case this is the enthalpy of reaction is greater than zero

so this is a endothermic reaction endothermic and this is exothermic reaction now as we explain that this we cannot always it we need to keep the reactants and products in a standard state for comparing the values

so we defined that standard heat of reaction length of the reaction where all the products and reactants are at their standard state is given by summation of the enthalpies of products minus summation of nth entries of reactants

so this is standard molar enthalpy of the products and this is standard molar enthalpy of the reactants

so if you multiplied by number of moles which are the stoichiometric coefficients in the balanced reaction this gives you the standard heat of reaction where the both the reactants and products in their standard state and a particular temperature t now we also showed later on that you can express this in terms of the heat of formation of products minus standard heat of formation for reactants and these values this heat of reaction heat of formation for products and reactants are available in literature and some are there in your book as i have taken from ncert book you can see this table in this case you can see those the heat of formation standard molar enthalpy of formation of heat of formation is at 298 k or 25 degree centigrade is given for several substances now sometimes for gaseous reaction if you do not have the values for this enthalpy of formation you can get the standard enthalpy of reaction for from bond enthalpies bond enthalpies of reactants minus total bond enthalpies this summation bond enthalpies of products in this case is reactants minus products and how it is arrived we have talked we have discussed in last class and this is for applicable for gaseous reactions

so if you know the bond enthalpies for compounds we can ah get $\Delta_r H$ naught standard enthalpy of reactions and some of the values are available in literature and this is somewhat shown ah given in your book

so we later on we continued on discussion and in this case as i said that this we are not talking about number of moles in the reaction its just balance equation

so this is the extensive quantity and the balance equations isometric coefficients are number of moles and if you reverse the reaction the value it will be negative of that then we continued and discussed other reactions like

heat of formation heat of formation standard heat of formation at a particular temperature that we talked about standard heat of transition and which consists which are many types like fusion vaporization sublimation and we talked about combustion we talked about atomization we talked about solution solution we talked about reaction enthalpy for ionization

so ionization enthalpy we also talked about electron gain enthalpy for electron gain and this all these are for one mole of substance ok

so these are all intensive quantities because here we are making sure that we are dealing with one mole of compound either is formation combustion vaporization all this is related to one mole of substance then we also talked about thermo chemical equation which is nothing but the actual reaction plus the reaction enthalpy of reaction standard enthalpy of reaction values then we talked about hess's law and we talked about bond heber cycle this we based this with the basis of these two ah was that ΔH naught or ΔH is a is an state function to it depends or it does not depend on the path

so these are basically what we discussed in last two classes now we go back and look at the first law again first law of thermodynamics which says that ah when one form of energy of energy is converted to another the total energy is conserved that is the first law of thermodynamics

so we have said that ΔU for isolated system is zero and ΔU for closed system q plus w and we discussed what are this term means closed system now what it means that if system is losing some energy say for example if system is losing some 10 joule of energy

so q system if i write as minus 10 joule because it is losing some energy then surroundings if i write q surroundings it will absorb the same amount of heat

so it will be plus 10 joule

so total q it will be zero

so basically no energy is created or destroyed here only 10 joule of energy got transferred to the surroundings this is what exactly the first law says it does not says first law does not says about followings whether this transfer i just mentioned whether the energy transfer will happen at all if it happen then which direction it will happen if it at all happen how long it will happen again if it is happen then how fast or what is the rest rate at which this energy transfer will happen

so basically these are four questions is not answered by first law

so what we will do today's discussion will able to answer us the first three questions but this is the rate at which energy transfer or reaction happened is not part of thermodynamics is part of kinetics ok which is not subject of this topic of this unit what we know we know that what do we know we know that some some process some process happens processes happen spontaneously for example i i just put at a bullet point like i have spreading of perfume

so i have sprayed some perfume one corner of the room what will happen you will get the smell after some time from the other parts of the room as well

so spreading of perfume this just example some spontaneous processes gas expand into vacuum if i release a gas into vacuum gas will immediately expand and occupy the total volume hot object if i keep a hot object in a surrounding which has lower temperature then the object will cool down and will take the temperature

so if i have a pan which i i is a hot pan like the temperature is high if you keep here then that heat it will basically give up some energy and it will take up the temperature of outside

so so this happens automatically a weight falls from an height from a height if i keep the pan up they leave it it will automatically or spontaneously fall below if i ignite ignite a fuel on ignis ignition ignition a fuel burns

spontaneously

so these are the sum of example i can name many other examples but these are the some examples where this spontaneous process happened and if you think of the reverse process like if i have a smell if i have a like in in this room has already have some perfume spreaded is not happen that automatically the perfume will come back and and concentrate on one of the corner of this room that is not happen like if i have a gas occupied in in a container then it will spontaneously not happen that some gas will come to one part of the container and make the other part vacuum

so that is not happen like if i keep this pen at the same temperature outside it will never happen that some would some heat will come and suddenly heat this pain and make it a higher temperature

so that is not happen

so those are the process we are talking about non-spontaneous happen like if this pen i have kept here it automatically goes up it will not happen

so some examples we just gave correspondence

so what is spontaneous process and this process happens irreversibly because as i said the reverse process will not happen spontaneously

so these spontaneous processes are irreversible process

so what is spontaneity then we are talking about spontaneous ah this is what spontaneous

so spontaneous process means

so spontaneous that the process has a tendency or we can call potential to occur without any assistance from external agency

so without any this any spontaneous process will happen naturally automatically like without any assistance from external agency what do you mean by external the assistance from external energy this term assistance from external energy means we are talking about some work having to be done work having to be done like some that the surroundings should do some work to bring it about

so this help or assistance we are talking means that without any work having to be done to bring this changes or bring this process being this happen

so so the non spontaneous process we talked about the reverse reactions or reverse processes we just gave example where we required to the process cannot happen here it happens or it is a tendency to happen but non spontaneous process will not happen

so will not happen without the help from external legacy without without assistance from external which means if i have to lift the pen from it to a height obviously i have to do some work on the surroundings if i have to like ah reduce the volume of this is a volume of the system if i have to reduce then i have to push the cylinder inside to bring it to new position

so that which means i have to do some work on the system

so basically non spontaneous process like decrease in volume in this case i have to apply some external assistance to do that

so spontaneous process in the irreversible process which can be i can also writes ah spontaneous process is an irreversible process which can only be reversed by doing work that is reverse is the non spontaneous process

so reverse process of spontaneous process is non spontaneous process

so now you should be knowing what is a sponsor spontaneous process and what is a non-spontaneous process now

so what should be the criteria for spontaneous process or spontaneity

so criteria for spontaneous processes if i go back and look at the some example like the temperature i i have kept this pane which has a higher temperature i kept it here after some time the temperature will decrease and will occupy or it will take the temperature of the surroundings which mean in this case energy is

decreasing

so this example we gave here energy is decreasing energy decreasing now if i have the pin which i leaving it it going down again energy is decreasing there are some spontaneous chemical reactions which are exothermic some example we can give these are one of the examples of spontaneous reactions which is exothermic so in this case also energy goes down

so the examples we have seen here till now this three example which means ah which shows that the spontaneous processes reduces energy but does it always true the spontaneous processes will in decrease the energy will give few more will few more examples

so in these examples we have seen the spontaneous processes decrease energy that is for these three examples we are seen but that is true for always we will see we will look at other other examples now this is also that this energy is decreasing for what this is decreasing for the system if i consider the plane as a system which was at higher temperature then i keep it here it will dissipate heat come to the temperature of surroundings then in case this case the system the pain is giving away some heat but the surroundings is gaining some energy as a heat because the energy cannot be created or destroyed which means that in this spontaneous process if somebody loses energy the other the surroundings is gaining energy

so energy is not that the universe is losing some energy that is not happening but the system is losing some energy in these examples but we look at some other example as well for example let me take a slab say iron slab and we have a two two sides one side i have at sixty degree centigrade and the other side i have a twenty degree centigrade there was a insulator insulating wall or non aeriability one in between i have this surrounded by adiabatic wall

so that is my initial state initial state now if i remove this the barrier insulate thermal insulator then what will happen there will be exchange of energy in from heat from this to the other side and i will have the entire slab as forty degree that is my final straight now because it is surrounded by adiabatic wall no energy is getting lost to the surroundings but in this case this part is losing energy and this part is gaining same amount of energy

so in this process i can always argue that this is a spontaneous process where heat is getting transformed from 60 degree to 20 degree centigrade but in this process one part is losing energy spontaneously but other part is also gaining energy spontaneously

so is if i look if you think this is a system then lc system is gaining energy spontaneously for a spontaneous process which means that i cannot only talk about energy as a criteria for i cannot talk about only energy decrease of energy or energy change as a criteria for as a criteria for spontaneity

so that is not i cannot tell that now i can give other examples where we are not changing the energy at all for example if i have a ideal gas kept it here in again two sides i have kept it this in a constant temperature bath at t both are at t this is ideal gas this side is vacuum

so initial state this side pressure is zero vacuum and this side some volume of gas is there v_1 and this side is v_2 now what will happen if i remove the barrier in between you will have the gas will the ideal gas will occupy the volume of total volume $v_1 + v_2$ and temperature will remain same this is the final state what is the change in or was the energy change in this process again this because this is a expansion against zero pressure or volume

so w should be zero i am talking about ideal gas constant temperature
so Δu is zero

so obviously q should be zero which means there is no change in heat or there is no exchange of energy as a heat happens in this process but what happened

spontaneously the gas expand from initial volume v_1 to final volume v_2

so in this case no energy change no heat energy change is involved but the gas expand spontaneously

so again energy cannot be energy change or heat energy change cannot be a criteria for spontaneity i will give you one more example where i have a gas two different gas separated by a boundary one side i have um this ah this gas blue gas violet gas and another side i have red red gas molecules now if i remove this my initial state at temperature t now if i remove the barrier again the now what will happen you will get the gas all over both the gas in the entire entire ah volume

so that will be my final state

so what happened it is the gases are mixing spontaneously if i consider these two are ideal gases then there will be no interaction between them

so which means there will be no change of energy related to this

so in again in this case also we are saying mixing is mixing of ideal gases are spontaneous or is spontaneous and in this case also the energy decrease of energy decrease of energy is not a criteria of spontaneity you cannot just link to spontaneity this condition

so then what what is happening if you look at this ah we can also look at some reactions chemical reactions where ah the reaction is endothermic for example i can note down one example where this is a spontaneous reaction but it is a endothermic reaction

so in this case energy is actually going up the systems energy is actually going up but this reaction is spontaneous again we go back and say that decrease of energy is not or energy alone cannot ah be a criteria for spontaneity then obviously what is criteria for spontaneity that question will come what is the criteria if you go back and look this processes and will see what is happening see in this case if i talk about spreading of perfume what is happening i have kept a perfume in a spray the perfume in a corner then spontaneously what is happening that it is the matter is getting dispersed in all over the room

so basically it is becoming more random i have this hot object i have said this hot pin i kept it here and it will dissipate heat energy to the surroundings what is happening the energy in this case is getting dispersed to the maximum possible volume and if i consider the system plus the surroundings it is giving it is getting the getting more the energy is getting more dispersed or most disordered or most randomization of the energy if i talk about this to example in this case the the particles constituting particles were moving at a faster speed if i take this is a ah gas containing at sixty degree centigrade the gas molecules will move faster and in this case the gas mole will grow slower but when you remove the barrier basically the energy will dissipate and randomize and you get a mixture of these two in this case gas matter it was restricted in this volume and as soon as i remove this barrier the gas particle will dispersed and occupy the same volume

so basically from a concentrated scenario it is becoming more random or more chaotic

so what we are now getting idea that in this all these spontaneous processes what is happening either the matter or energy is getting dispersed throughout the system and the system or the system plus surroundings together is getting more random more random is becoming whether in terms of matter or in terms of energy

so basically what we can tell that natural tendency or spontaneous tendencies is to get dispersed or randomize or say disordered become disorder become disorder

so that is the or become chaotic whatever you call

so basically this is the terms we can use interchangeably that natural tendency is the is that the matter or the energies will spontaneously guess randomize or become disorder or spread as much as possible basically disperse space mean we are talking about dispersion we just give it ah just for non technical examples like if you have a kid at home like if you have a small kid one or two years old then what will happen if you just give a bucket of toy or a toys give it to him or her small baby now after sometime you will find that the baby has scattered all the toys

so dispersed and randomized

so so she does not know he does not know what to do it is not that reverse that if those toys are scattered throughout the room that small baby will come and collect and put it there in one place which is naturally does not happen for example if i go into class which are the three sections like and each section has 100 strength approximately

so total strength is 300 each section section 1 is 106 and 200 section 3.

now first they and i have basically three places left side right side and and the back of the classroom and when i enter in the first class i ask this question tell me which section you belong to in one of the parts and then there i will find that this the students from section 1 section 2 section 3 will occupy the entire room entire classroom its not that section 1 student they do not know i am talking about the first day when they do not know each other there is no interaction between them once they know each other there will be interaction between them they will probably try to ah sit next to each other but in the first class when they do not know each other there is no interaction between them

so they will disperse ok

so you will have a classroom which has a random population of section 1 2 3.

so this is just a natural example that mixing or getting dispersed or randomization is a natural tendency and we can explain this by statistically by probability but ah you know this random states or random mixing is probably higher probability than ah where you have one section is one part and other sixteen other part but ah this ah you know explaining this from a statistical point of view is not part of this unit

so we know now that we have a natural tendency to disperse or ah randomize or so now what we have to do we have to quantify this randomness

so basically one will do you quantify this randomness now we introduce in this time we introduce a thermodynamic parameter entropy symbol is s capital s this is basically the quantity which represents the randomness in the system or surroundings

so if the value of s goes up we we know that the randomness extent of randomness goes up and if the value of s goes down then the extent of randomness go go down

so for any now we can write for any for any spontaneous processes process the value of entropy of system plus entropy of surroundings will increase or if i write Δs change in entropy of the system plus change in entropy of surroundings would be a positive value for a spontaneous processes and if i make a isolated system where surroundings is not interacted to the system for isolated system only Δs system will be positive

so this is what we are concluding or inferring from the experience we have noticed till now and when you summarize a ah experimental observations or natural phenomena in terms of a equation or in terms of any hypoth any statement we call that as a law law is nothing but its a summary of the experimentally

observed or naturally observed phenomena and we call this as a second law of thermodynamics where we say that for any spontaneous processes the entropy of the universe system plus surroundings will go up

so always the for because all the time spontaneous there are several spontaneous processes happening that means the entropy of the universe is always increasing because the spontaneous processes are happening just a few things about entropy entropy is extensive quantity if you double the quantity of mass it will double value of the double it is state function and

so ΔS is independent of path now how do you mathematically get this value of entropy

so we will try to now get we will try the value of S from some relations now what we have seen that if we add if we add some heat energy energy as a heat the molecules move faster if you talk about gas they move faster if you solid they will start vibrating ah with a higher oscillation amplitude towards the mean position

so basically we see that when you add some energy as heat entropy goes up

so when we talked about this pain which has a higher temperature we keep it here the heat disappears he dissipate and in this case the entropy of the surroundings which is gaining the energy as a heat will increasing with increase but the entropy of this pen which for which it is losing some energy on cooling it will this entropy will come down now we know that q only appears during a process means if i bring a system and surroundings or two object of different temperature then heat exchange happen and the magnitude of heat exchange we call q if there is no process going on we do not bring this quantity q which means q should be related related to change in entropy as i explained when this having higher temperature kept at in the surroundings it is losing energy that means the change in entropy is negative for the pain and change of entropy is positive for the surroundings

so basically if q is positive if i add some energy as a heat ΔS will be positive for either system or surroundings

so if i go back and look at the example which i have given earlier if i have two sides and this is surrounded by adiabatic wall this is at temperature t_1 and this is at temperature t_2 if i think this is a system this is surroundings then from experience we know if t_1 is greater than t_2 then some heat will the energy will flow as heat from system to surroundings

so q will be negative and ΔS system will be less than zero and q of surroundings higher and ΔS surroundings will be higher now we know that q for system or q for system plus q for surroundings is zero that we know from first law of thermodynamics we explained i just explained the beginning of today's lecture itself

so if ΔS is only related to q then obviously the decrease of entropy is exactly matched by the increase in the entropy

so if i think that ΔS is only related to if ΔS is only related to q then in this process of transfer which is happening spontaneously ΔS will be zero total ΔS for system plus surroundings which is not the criteria we know that to a spontaneous process happen ΔS total which is for system plus surroundings has to be positive number

so ΔS for system distance per surroundings has to be positive number now to if this has to be positive then ΔS system which is a negative quantity the magnitude of ΔS system has to be lower than the ΔS surroundings i am talking about this particular example ok ΔS system is negative and ΔS surrounding is positive

so if the magnitude of the positive number is higher than the magnitude of the negative number we will land up ΔS total greater than zero now how can i what

is the difference here the temperature is difference now you can look at that if i look at the temperature and if we can think that ΔS is inversely proportional to temperature then obviously this was at lower temperature to begin with

so the entropy gain will be higher for surroundings and the entropy loss for the system will be the magnitude of the entropy loss for the system will lower because T_1 is greater than T_2 and how long it will happen as long as the moment T_1 becomes T_2 then there will be no heat transfer there will be no process

so you will get a reach equilibrium

so we also know that if i add some amount of energy as a heat to a system we have a lower temperature then the increase of entropy will be of higher amount compared to if i add the same amount of heat energy at a higher temperature which means that we are talking about that entropy change is inversely related to the temperature

so we have found earlier that a entropy change of interval b is related to q if q is higher ΔS should be higher

so somewhat directly related to ΔS is directly related to q and now we found that ΔS is actually inversely related to q

so with these two in mind we will define a mathematically ΔS for the system ΔS_{rev} as q_{rev}/T q_{rev} is the change in energy energy transferred to system reversibly please keep this mind reversibly this is important and T is temperature in kelvin please also keep this mind this is not a centigrade finite something not it is always in kelvin

so q_{rev} is the energy transfer to the system reversibly and T is the temperature in kelvin just talk about few examples where entropy increases or intro we just look at some in examples and see whether what happens to entropy for the system like we will take a liquid say water is becoming a gas or vapor what happen in this case ΔS for system i am talking about liquid as a system

so dentist system is positive now if you talk about liquid becoming solid in this case ΔS system is less than zero negative now if i talk about water as a liquid then you know that liquid to vapor water to water vapor or water to ice may happen deep may happen spontaneously depend on the temperature here if i talk about say 25 degree centigrade say 125 degree centigrade then water will become water vapor spontaneously if i talk about minus 25 degree centigrade then water will become i spontaneously now in this case the entropy of water is increasing and in this case entropy of water is decreasing now what what are two ice is an endothermic process and water to sorry water to ice is a exothermic process and water to vaporization is a endothermic process now in this case because exothermic process some amount of heat is coming out to the surroundings

so though in this case the systems is going down but the surroundings entropy is increasing even more in magnitude

so the total entropy for change for system plus surroundings is is positive similarly in this case this endothermic process

so surroundings is losing some heat to the system

so in this case the entropy change entropy increase for system is higher compared to decrease in entropy of the surroundings

so basically the temperature which determines which is the direction for spontaneous processes in this case there are other examples like we talk about increasing increasing the temperature of a solid from say 10 degree k to 120 k at lower temperature the the constituent particle will move and oscillate about their equilibrium position at a lower extent whereas the higher temperature it will move and oscillate to the their mean position as a higher extent

so it will become disorder more which means entropy will increase
so ΔS would be positive for the system in this case example if you talk
about say one bicarbonate sodium bicarbonate solid is dissociated
so because of solid to gas formation here also entropy increases entropy is
positive there could be some other example as well now in this case we are
talking about spontaneity $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$ for a spontaneous process now we cannot always look for surroundings
because some cases the system is a open system or closed system
so we will try to get some parameter which will be only focusing on for system
so that now we can determine the spontaneity based on a property only for
system and that will talk about in the next class will not next class i will try
to focus on only the system and try to get some property which will
determine the spontaneous process based on its value only of the system you