welcome back to this unit on
thermodynamics and as we have seen in last lecture that we have talked about criteria for spontaneous processes and it   introduced the concept of entropy and today we
will introduce the concept of gibbs free energy   now just to recap what we learned in last lecture
we learned that you know some processes are spontaneous and some are non spontaneous spontaneous processes are the process   when the process has a say process which
has a right and that thing has fonte nias process means that the process has a tendency or potential to occur without any external assistance now we gave you examples of several spontaneous processes   and if you have noticed that we are using the
terms tendency or potential whatever in some processes are thermodynamically spontaneous
because you know they are they can do or   care that the process can be carried out without
help of any external assistance but their raters   rate are
 so slow that you know with a small time
frame or a normal time frame you probably will not   be able to see any significant process happening
so in that case apparently the process is not   spontaneously happening but they the process has a
tendency to occur without any external assistance   now the reverse process of spontaneous reverse of
any process which reverse of spontaneous process is a non spontaneous process which
require work need to be done from outside   to carry out the process and we gave you example
also now we talked about what are the criteria for   the spontaneous processes and
we found out that decrease decrease in energy of the system is not a criteria for a process to happen spontaneously now we are only talking about energy of the system
because we know that the total entropy of system   plus surroundings cannot decrease you cannot
change the in energy of system plus surroundings
 so we are talking about only look at the system
that decrease in energy of the system cannot be   a criteria for a spontaneous process and we
gave you several examples like endothermic   process where the energy ah exothermic process
were actually the energy um system loses energy it might have smallness but in in in case of
endothermic processes where system gains energy   still the process can happen spontaneously
we talked about many endothermic processes   in the last class
 so what we found out after
ah deliberation that you know increase in increase in randomness or disorder or chaos whatever you can call
meaning the meaning you should know the meaning   disorder of system plus surroundings which sometimes call totally these
two together is called universe
 so increase in randomness or disorderness

of or disorder whatever you call disorder of system plus surroundings should increase in a spontaneous process so we quantified this degree of randomness or disorder in a system as s which is entropy we define it as a entropy which is is extensive quantity state function so del value of delta s does not depend on path depends on path now we have also seen that if we increase so if we add some energy in the system if we just talk about system then if we add some energy so q is greater than zero then entropy of the system increases so delta is system positive and we also have discussed that if the same amount of same amount of q is added at lower temperature then the change in entropy is greater than the same amount of energies ah added to the system at a higher temperature this is what we observed which means we have discussed last time that delta s should be inversely related to one over t so or with temperature so this is what we discussed earlier that if you increases if you add some energy to the system systems entropy increases and if you add that same amount of energy at lower temperature then the increase in entropy more than if you add the same amount of energy at higher temperature then we went on and found and said the relationship between this q and temperature with del s and we wrote this q reversible by t now for system we can write del s system cis q reversible for cis and temperature of system for surroundings i can write dental surroundings is q reversible surroundings by t surroundings now because surroundings is very large for a system surroundings is always very large so whatever energy is added to the system always happens reversibly so it does not matter whether the process which is undergoing in the system is reversible or not if there is a heat exchange between system and surroundings whether this surroundings loses some energy or gain some energy surroundings will always do deposit from surroundings point of view the heat exchange is always a reversible process because if you add some 100 calorie or 100 joule to the surroundings it does not matter surroundings is so large that whatever amount of heat you take out or you add it it happens ah reversibly so in if you talk about a process where q is so we can write this as minus q of system because we know from first law as we discussed in the last class also that surroundings energy change is exactly opposite to the systems

so minus of q surround system and if we consider that the system
and surroundings are at thermal equilibrium if system and surroundings are at thermal equilibrium this happen when
they are separated by a non adiabatic or diathermal one then obviously
when they reach equilibrium the temperature of system and temperature of surroundings would be equal at equilibrium then obviously we can write the surroundings
is same as t system
so this we can write when system and surroundings is separated by a
non adiabatic wall and at equilibrium of course system and surroundings will be equilibrium which
means 60 surroundings will be same as t system
so i can write del s surroundings as this now
what we will do from next time onwards for system will omit this term this superscript
for system will remove this superscript and for surroundings we will keep the surroundings and for total we will write t total as a superscript
so if i write delta s
or q or t then you will assume that these are for system now if i want to specifically mention
delta s for surroundings or t for surroundings then i will write delta s surroundings or
t surroundings these are for surroundings and if i write total say del s total t o t
which means it will be delta s system i am not writing system plus dentist surroundings
so this is the convention is followed if there is no superscript on any of these
thermodynamic terms then you will understand that these are meant for system and if we specifically
talk about total or for surroundings then the superscript of surroundings or total is
added
so one more time if there is no superscript subscript is added to any of this term then you
can assume that we want to we are talking about this for the system
so if i now write
here we can just write delta s system is q reversible by t i have removed the system terms
and delta s surrounding should be minus q i am removing system term and then t ok
so i will come
back and rewrite this in the next page
so delta is surroundings is minus q by t and delta s which is then transfer
system u q reversible by t q reversible means it is the exchange of heat energy in a reversible
process if i will come back and describe this ah little more in a minute we will talk about for
surroundings if i talk about a adiabatic wall then obviously this will be t surroundings
but what will be the value of q q is zero because for any adiabatic
process you know key is zero then delta s surroundings is zero
so for any adiabatic
process or if system and surroundings are separated by a adiabatic wall then

delta s surroundings would be always zero
please remember for any adiabatic process no matter what is the process because there is no
heat change q is zero delta surroundings would be zero always
so we will now
go back and look about system or focus on system now what is
q reversible q reversible is if the process from state one if i
i have something like p one v one t one to some other p two t two v two say i have these two
states this is state one and this is test two now actual process can bring about this change in any way in you know obviously this
spontaneous process spontaneous process will be a irreversible process as we mentioned in
the last lecture that all the processes we see in happening spontaneously in real time
they are all irreversible process
so in practice the change from state 1 to state 2 will happen
irreversibly but what we have to find out we have to find out from the given condition from given information we have to find out what is state one and state two now that is what we need to find
out at beginning from the given information and once we find out state one and state two then
you have to imagine any possible reversible path between one and two and for that you can find
out q reversible and you can get del s from q reversible by t we will go back and look at that a simple example we had talked in last
class that we have say state one we have we are talking about say they hm
expansion of ideal gas adiabatic process adiabatic thats this simple process
so i have this
side this is adiabatic
so it is surrounded by adiabatic wall
so no heat exchange is
possible now this side volume is v one and this is v v two now at the beginning we assume that this is p is
equal to zero and this is some pressure p p one and this is some temperature t one
so that state one and then what we were doing in
state two we are removing this barrier between this part and this part
so what will happen
obviously the gas which is the ideal gas we can take a specific i mean
sort of free expansion here we can write free expansion because we are talking about p x zero to zero external pressure is zero
so what will happen now the volume would be
v one plus v two what will be temperature pressure will be different
so it will p two what will be temperature now remember this is q
is equal to zero this process q is equal to zero w is equal to zero expansion into vacuum free
expansion
so del u must be zero and as soon as d u is zero we are talking about ideal gas you know
del t is zero
so here also it will be t one ok
so now i got state two where i know what is p
p one p two and v one what is the volume total volume v one plus v two

so this is the first work you have to do you have to just find the process given the process in this is this is given free expansion of ideal gas in adiabatically so in this case you have found out that what are the two steps now q is zero so delta s surroundings is obviously zero as i said earlier that adiabatic process you will see dendrite surroundings is zero now this is actual for surroundings one more time it is the actual q which matters for surroundings the actual please consider the actual q here the actual q is zero so when you one more time writing surroundings is minus q by t this q is the actual q involved in the process ok but in the systems case it will be q reversible by t ok where you have to imagine that from state 1 to state 2 the process happened reversibly in this case this free exam expansion it actually happened irreversibly but now you have to imagine that system has gone from state 1 to state 2 reversibly and then you have found out what is q reversible now what is w in reversible expansion a volume v one to v one plus v two is given by minus n r t l n v one plus v two by v one the original this is thus my state so original volume was v one new volume is v one plus v two so i can write final volume v one plus v two by initial volume is v one minus inner t because its a reversible we are talking about reversible so i can write w reversible del u is zero in this case because there is no temperature change so obviously q would be minus of w so nrt n v one plus v two by v one so del s system this is q reversible system is q reversible divided by t be equals to n r l n b one plus v two by v one please remember what i did i just again repeating the actual process is not a reversible process it actually free expansion so its irreversible process so by knowledge of the actual process i found out what is the initial state and what is the final state and what is the actual q involved actual q we have used for calculating delay surroundings but for system once you know state 1 and state 2 you have to imagine a process reversible process from state 1 to state 2.

so i would imagine now that a gas having initial state of p one t one v one has expanded to state two where temperature is t one pressure is p two some other pressure and volume is v one plus v two so this is the process so now i i put w reversible is this and because we know del u is zero isothermal expansion ah adiabatic process ah ideal gas so del u is zero so q reverse will be minus f w so this and delta s system would be or we can write just write delta s it will be q reverse one by t so this is v one plus v two now you can see that this is always positive as long as v one plus v two is greater than v one delta s system would be greater than zero and delta surroundings is already zero so total would be depend upon delta s system so in this case you can see this is a spontaneous process and delta s total system plus surroundings is turned out to be processes so any expansion process of gas will result into a total entropy change positive in total positive interchange so that is why it is a spontaneous process so again one more time i will explain for surroundings you have to get the actual q in the process and then use this formula for system you have to find out what is state 1 and state 2 from the given information and once you get state 1 and state 2 you have to imagine a reversible path between state one and state two and then you have to find out q reversible in that process and from then apply this formula to get the systems entropy change now we revisit our criteria for spontaneity criteria for spontaneity criteria for spontaneity is delta s total is greater than zero which means dentist system plus delta s surroundings is greater than zero we are not writing anything on system now and what is delta surroundings is minus q by t surroundings greater than zero now if i apply first condition where i think system and surroundings are in thermal equilibrium then t surroundings is same as t system or just t for um we we do not want to write system so just t then i can write this turns out to be delta s minus q a by t greater than zero now we apply our second condition where pressure is constant in this process pressure is constant so q is q p and we know q p is del h then we can write del s minus del h by t is greater than zero on rearranging we can write del h minus t den s less than zero now we will put third condition now a third restriction where temperature is constant if temperature is constant then we can write this as del h minus del t s less than zero or h minus ts less than 0.

so what did we do in this page we knew by this time we know what is the criteria for spontaneity but in this case criteria has both entropy change for system

and surroundings
but we do not want to always deal with   surroundings is always difficult to
handle with
surroundings
so you want to get some conditions   where we will only look at the system
values
corresponds to system but that will not come   for free we have to apply or we
have to put some
restrictions to get some value only for a criteria   for we can get some
criteria for spontaneity only
for system and this is what three restriction we   have applied from this case
and we got finally
this value now this is all for system
so there   is no term which is related to surroundings here
but to achieve this conditions we have to put   three restrictions system pla
surroundings are in thermal equilibrium   pressure is constant and temperature
is constant
but in most cases what happened we deal in   practically we deal with systems or
any process
happening in in diathermal wall non adiabatic wall   in that case equilibrium
condition will always be
where system plus surroundings are at equilibrium
so this is this condense is ah this
condition ah condition is often met
so we generally mention this con condition
most of the times
so we only ah talk about   pressure constant and temperature constant so   from
now onwards i will just omit this condition
because this is assumed to be happening for   when the system is not
adiabatically um surrounded
and as you know if this surrounded by adiabatic   density surroundings entropy
change is anyway
zero
so we will deal with only system if if system   is surrounded by adiabatic wall
if it is not
surrounded by adiabatic wall non adiabatic world   then automatically at
equilibrium we will get the
thermal equilibrium between system and surrounding
so temperature the system will be same as
temperature the surroundings hence we we consider   this is a given condition
so we will mainly deal
with pressure constant and temperature constant
so we know what is the criteria for
spontaneity that del of h minus change in   h minus t s is less than zero and
condition
it will put only on constant temperature   and constant pressure
so that is the
conditions now to make it simpler   we mathematically define a new term
g as h minus t s
so we can write   delta g less than zero at constant t n p
so this is the conditions for spontaneity delta g is less than zero
so g will should
decrease in any process which is happening   at constant temperature is process
for this

process to happen spontaneously what is g g is we call at gibbs energy gibbs energy or s called gives free energy this is again extensive quantity extensive parameter parameter state function
so del s value of del g will not depend on
path like other thermodynamic parameters now g is called free energy because i am not going in detail the value of g is
is signifies the actually is the available available energy to or free to to do non expansion work non expansion work non pv
work or we call other work or additional work additional work like electrical work magnetic work those work
so you will see its significance when you study electrochemistry
so that is why this term free
energy comes
so this is the part of the energy of a system which is free to do non expansion work
or additional work
so the term free comes that is why it is sometimes used gives free energy now at
equilibrium if the process has reached equilibrium we know we have seen earlier that total entropy
total is zero when at equilibrium
so in this case for system it will turn out to be delta g is zero
at constant temperature and pressure for system in equilibrium
so this is the process
condition for condition for spontaneity and this is the condition
for condition for equilibrium
so clear now we have from the main conditions which we got it
from our experience that total entropy of the system should increase in
a spontaneous process we landed up expression only for system where the gibbs free energy of the system should decrease at constant temperature and pressure to have a
spontaneous process happening and if delta g is 0 at constant temperature and process pressure then
the system has reached equilibrium
so g is minimum when the g will have a minima minimum value
when the system will reach equilibrium similarly the entropy of the universe is always
increasing or maximizing when we talk about ah the spontaneous processes
so we will go
back and write delta g is equal to delta um h minus t s
so if i consider a constant temperature process constant temperature process then we can write simply del g is into del
h minus t del s this is we are talking about constant temperatures please mind it
so for a
chemical reaction um for a chemical reaction we can write similarly standard gibbs free energy for reaction delta g naught is equal to standard enthalpy of
reaction minus t standard entropy of reaction
so this expression we can write at constant
temperature at constant temperature now this will um from this we can if the lot of cases
these values are known
so from we can just ah analyze this expression to find out the type

of reaction which will become spontaneous and in this case temperature will play a lot of ah
important role just to go back and see what the possibilities are
so the
possibilities are will make a table
so these are the possible
expressions combinations where standard enthalpy of reaction is less than
zero negative and this is positive remember what is the expression delta g is den h minus
t del s if this is negative delta is positive then del g must be a negative term irrespective
of what is the temperature and we know when this becomes negative at
constant temperature and pressure this process become spontaneous
so this is spontaneous at all temperature all temperature now if i get the other condition
this is negative and this is also negative then temperature this is negative this is negative
so this term is negative and this is actually positive term
so depending upon temperature
value of temperature the sign of del g will determine get determined
so if temperature is low
this term will dominate
so it will become negative
so this is 0 at low temperature and
this is positive at higher temperature high temperature now this is relative low and
higher relative
so this will be if this is the case where both standard enthalpy of reaction
and tender entropy of reaction are negative then it is likely that the process of the
reaction will happen spontaneously at low temperature and it is likely that it will be non
spontaneous it will not happen at high temperature we can now consider the other one where both
are positive then the situation will reverse then it will be positive at low temperature
and negative at high temperature
so in this case will likely to have a
spontaneous reaction at higher temperature and if we get the situation reverse of
the first one where delta h is positive and delta s is negative then this is a positive
term and this is also a positive term because this is negative quantity then it will be
positive
so in this case this is spontaneous for or at all temperature in this case this is spontaneous and this is
spontaneous this is non-spontaneous this is non-spontaneous and at
any temperature at temperature which del z standard in become 0 or del g become 0 that is when at constant t and p that is
why we reached we will reach equilibrium
so if we consider one ah sim j any
chemical reaction a plus b to c plus d then the criteria for equilibrium
criteria for this reaction to reach

equilibrium criteria for reaching equilibrium would be delta g for the reaction is zero ok
so once it reach or g minimize in this reaction it will become
ah it will reach a equilibrium situation now we can show that ah this is linked to
ah at equilibrium you can directly write it can be shown that at like node this is 0
equals to the standard gives free energy change in the reaction plus r t l n k where
delta r g naught is the standard gives energy change in the reaction and k is equilibrium constant at that temperature where it
is happening reached equilibrium at t
so if you know
so any case if we if we know
the any of the terms will be able to find out the other term if we just go through a
problem then it will be probably able to see
so where say in a case where delta z 0 is given is given this is from your book
delta naught the standard gibbs free energy change is given as 13.
6
kilo joule per mole at 298 k then the equilibrium constant we can find out from this expression we can find out equilibrium constant from this expression which is ah
minus dot divided by rt ln sorry to just rt log we have taken
so 2.
303 rt
so you
can just solve this equation to find out the value of equilibrium constant now we i think this is what we need to cover
in terms of ah topics we have covered and now i think i should go back whatever time
is remaining i will just look at few problems ah quickly and see whether you are just to revise your knowledge ah one more time
so just just you know as i will
not be repeating or revising this last portion i just wanted to go back and revise it one more
time ah because this is likely to the last lecture in this unit
so in this case we from the condition
of space spontaneity which is delta s total or entropy change for universe should be positive
we landed ah landed to a condition which is only related to system where delta g should be
negative at constant temperature and pressure and delta g is is a mathematical description
of this quantity h minus ts g which is a which is called gibbs free gives free energy or gives energy is extensive quantity state function
so the entity will not depend
on path and we talked about ah delta g at constant temperature is del h minus t del s and from that we found out that these are the ah possible options so if you we assume these are all happening at constant temperature and pressure and
these values are not changing in that if if we change the temperature
so which

means this will this will happen at small and this will happen if if the reaction enthalpy
standard reaction enthalpy is negative and entropy is positive then it will happen spontaneously at all temperature and we
discuss the other possible conditions
so now i think i have about ah 15 or 10 15 minutes
so i will just quickly go through few of the questions which is there in your
book and i will stop as soon as the times ends these are from your book
so this multiple choice
question it says thermodynamic state function is a quantity used to determine heat change
whose value is independent of path you should determine pressure volume which is value depend
on temperature but we know the thermodynamic state function does not depend on path
so this
would be your answer to for the process to occur under adiabatic condition q is 0 adiabatic
condition w is 0 there is no volume change delta t 0 the initial temperature and final temperature is
same it does not mean this is isothermal process delta p is 0 does not mean there is isobaric
process it just says the initial temp pressure and final pressure is constant but adiabatic
condition always will have q is equal to zero the third question is the enthalpies of an element
in the standard state now this question is little ambiguous i think the question should be framed
like this the standard entrant is a formation ok is this term is missing this should be
standard enthalpies of formation of element in the reference state that is zero but this is ah none
of this answer could be ah right answer for this particular question though some of will suggest
that it is zero but it is not zero enthalpy of all element india standard state is its
not always zero its not in fact zero because we we know what is standard state standard
test for liquid and gas
so liquid and gas is corresponds to a pure pure state pure pressure
is one bar and a particular temperature t
so all elements if you look talking about liquid and
gas any pure element will not have um enthalpy is zero at one bar pressure or at any
temperature for ga
so liquid and solid solid and liquid for gas we have two additional
criteria that the gas would be ideally in this ah in this pressure which is not possible
so it was
for gas it is a fixed tcs state
so i think this is not ah not neither of this is a right answer but
i think this question should be frame the standard the formation of all the

elements in the
standard state will move to the next question it says del h some values is given find
the value of del h combustion of methane   combustion methane is just burning of methane
and you are getting ch2 plus co2 plus h2o you can balance this may be this and this this
is gas this is gas this is gas and this is liquid
so in this case delta n gas is
equals to 1 minus 3
so minus 2.
this is one ah post and before it is three moles
so delta n minus is minus two
so del h would be del u plus delta n g r t
so del e would be delta u
minus twice r t which means del h would be greater than del u no matter what
is the value it could be negative or plus but   this should be always greater than ah del u if
del n g is minus if it is a positive quantity   then del h should be sorry in
this case del h yes del a should be because some
there is equal to del u minus something
so del u del a should be less than
so del h is del
u minus something
so del e should be less than del   u if this is a positive quantity then del a should
be greater than del u ok
so you have to just look   for this expression find out del del n g and from
that you can find out what is the ah relationship   in this case it says some energy is produced
once the energy is possible produced   to have a positive entropy so
in this case if you talk about   think about constant temperature and pressure
then q is equivalent to del h
so del h is some energy is released
so del
h is negative exothermic process   and positive entropy change
so del s is positive
so now you can go back and look for find out ah   you yourself can find out what is the temperature
low or high where this should be negative the next question is from your book again and
this is 701 heat is absorbed by the system when   some heat is absorbed by the system q is
positive
so this is seven zero one joule   and three ninety four work is
done by the system when work   is done by the system system loses some energy
so w is minus three ninety four joule
so the internal energy should be summation of
these two quantity q plus w you can do later on   this is calculate the enthalpy change of freezing
of one mole of water at ten degree cent ice at   ice to this
so you have three process
one ten degree centigrade water to   zero degree centigrade water and then

freezing
water to ice at zero degree centigrade and then   0 degree centigrade ice to minus 10
degree centigrade ice
 so this is a three process where you can just total total enthalpy
change you can add up the enthalpy change for   all the three processes and if we consider
these are independent of temperature in the   the 10 degree gap we have then we can
find out ah in this case ah c p c p of   h two liquid and we are talking about one mole
 so n is one it will be cp multiplied by del t in this
case del h in this case its fusion   fusion means melting
 so this will be a reverse of
melting
 so it will be minus six point zero three   kilo joule per mole and similarly it will
be c p ah h two solid into t
 so you can add   this three term to get the value for the
total enthalpy change for this reaction
 so here it says the enthalpy change of
formation of ah the four quantities are given   and you want to find the value of
del h r now we know del h are ah is   equals given by ah summation of a i and
delta h formation ah of of reactant products minus b i for reactants
 so in this case all the values are
given for now remember these values are for one   mole the definition enthalpy of formation
standard enthalpy of formation for one mole
 so whenever there is three mole tree mole
you have to multiply it by three and then   just use these expressions to find out ah the
change of a total entropy in this case ah the   enthalpy change is given for this reaction so
what is the standard enthalpy of formation of   now these are the ah there is no temperature given
so i even assume 298 k is given is as temperature   of this process and in 298 k the reference state
of nitrogen element is nitrogen gas and hydrogen   is hydrogen gas
 so this is fine
 so this reaction
is formation of ammonia from their reference state   but mind it yeah its two
 so its two mole
but the formation is for one mole so   ah in this case ah the enthalpy of formation
would be half of this reaction ah half of this   value because you are forming two moles
what you need to find out for one mole   from this reference state so
this value will be just half of the case and this is i think we can apply the
hesse law using this ah formation reaction in this
case you should mention i think ah c c l liquid this should be a liquid
 so delta
evaporation will be c c n for liquid   and you i think i have uh just gave example

of this type of ah calculations from his law
so from which you can get the expression from the
calc the value of del hr of this
so one fourth of that value would be the bond enthalpy i do not
have time
so i have to stop ah i think i had many more questions to discuss but
unfortunately
because of time i am not going to do
so what i will do i will ah stop here and just say that i
hope you enjoyed this course on thermodynamics and in case you have any
question any doubt your
your feel you are free to do
so you just send me an email or contact me i will be happy to
answer your questions and my contact informations are available in the website
of chemistry
department of iit kharagpur
so good luck you