Chemical Principles II
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Conditions for Spontaneity

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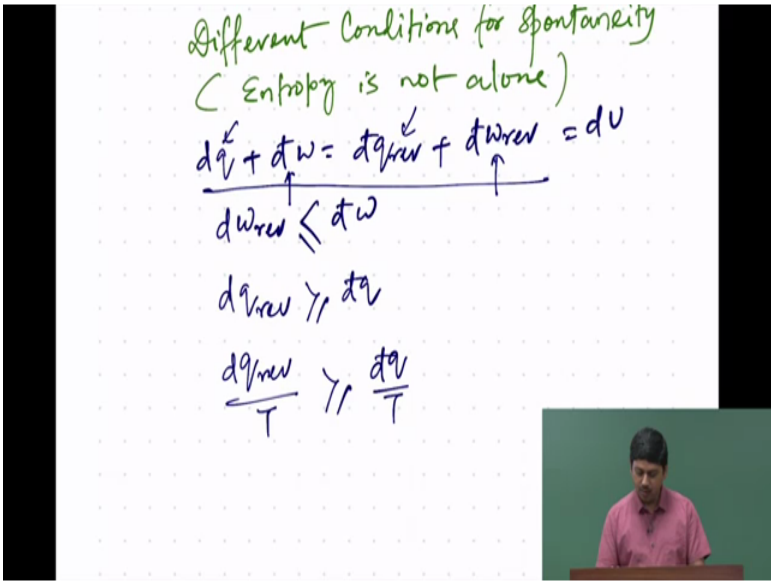


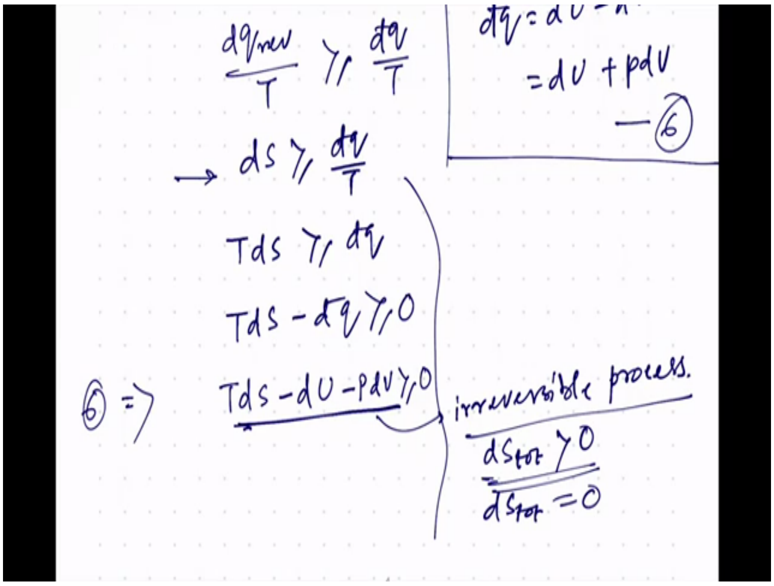
Different Conditions for Spontaneity
(Entropy is not alone)

$$dq + dw = dq_{rev} + dw_{rev} = dU$$

$$dw_{rev} \leq dw$$

$$dq_{rev} \geq dq$$

$$\frac{dq_{rev}}{T} \geq \frac{dq}{T}$$



$$\frac{dq_{rev}}{T} \geq \frac{dq}{T}$$

$$\rightarrow dS \geq \frac{dq}{T}$$

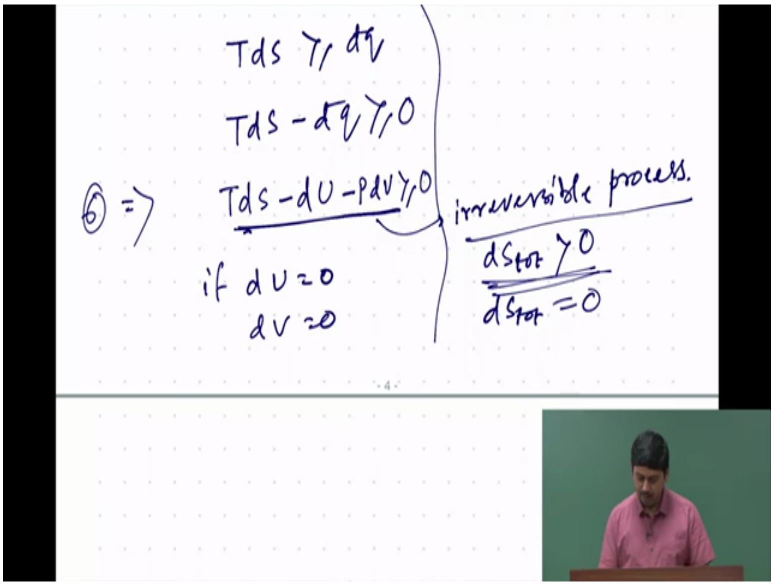
$$TdS \geq dq$$

$$TdS - dq \geq 0$$

⑥ $\Rightarrow$ $TdS - dU - pdV \geq 0$

$dq = dU -$
$= dU + pdV$ — ⑥

irreversible process.
$dS_{tot} > 0$
$dS_{tot} = 0$



$TdS \geq dq$

$TdS - dq \geq 0$

⑥ $\Rightarrow$ $TdS - dU - PdV \geq 0$

if $dU = 0$

$dV = 0$

irreversible process.

$dS_{tot} > 0$

$dS_{tot} = 0$

So now we are going to talk about the conditions of spontaneity of a particular process, so different conditions for spontaneity, so you want to just emphasize that entropy is not alone is the criteria I will just remind you still is that it is still the criteria when you talk about an isolated system or talk about the system plus surrounding but eventually we will see that is giving you different criteria when you look at only the system.

So again we start from the derivation that dq plus dw is nothing but dq reversible plus dw reversible, we because both of them are equal to dU, so therefore so then that case we know that dw reversible so work done on the system, so whenever we talk about only dw remember we emphasize that it is work done on the system not by the system minus dw will be work done by the system.

So work done on the system is minimal so therefore it has to be less than dw or less than equal to, so equal to sign denotes that when work done is done in a reversible manner then of course that it equal otherwise they are unequal. Now if you look at this particular equation if this guy is less than this guy then this has to be more than that, so therefore we can write that dq reversible is greater equal to dq and when you divide by the temperature we can write that because reversible is just one path, so dq does not have that cut thing dq reversible by T is greater equal to dq by T and dq reversible by T we know to be ds which is greater than dq by T.

So therefore TdS is greater equal to dq or TdS minus dq greater equal to 0 and we know that dU is dq plus dw, so therefore dq is dU minus dw and dw is minus PdV, so therefore it is plus PdV. So the TdS minus dU, so from this equation from 6 we get and we substitute dq value from 6 actually, so minus dU minus PdV greater equal to 0, so you see that so that is what we get as the condition first spontaneity because you see that wherever this condition holds equal to 0 then the this is the condition for equilibrium whereas if it is greater than then it is the condition for spontaneity, ok.

So now coming back, so now we see that the reason that this greater equal to 0 is so here we know that this condition whenever it is whenever this quantity is greater than 0 that denotes an irreversible process because we talked we talked about that right we talked about equality sign being reversible and inequality sign being the irreversible and we know for irreversible process the overall ds total is always greater than 0.

So therefore if this is the condition for spontaneity then this is also the conditions for spontaneity when it is greater than 0, if it is equal to 0 then we are talking about an equilibrium process so therefore the equality sign will hold for the equilibrium process. So therefore for inequal inequality we will go for a spontaneous process and equality will go for an equilibrium process by using this particular argument that ds tot greater than 0 for an irreversible process, we will show later a similar one directly from the entropy it itself.

So now that we have here what are the things that we can observe we can see that immediately that if u d u equal to 0 that means there is no change and dV equal to 0 then from this equation.

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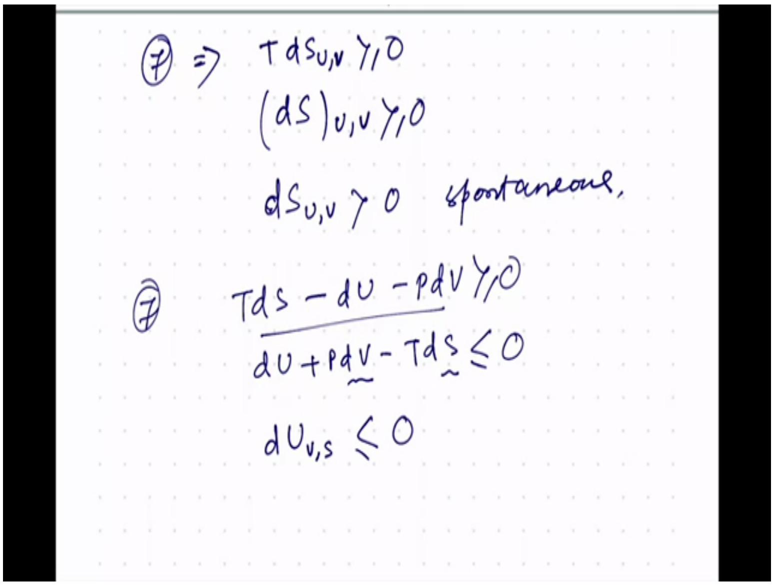


⑦ $\Rightarrow T\,dS_{U,V} \geq 0$

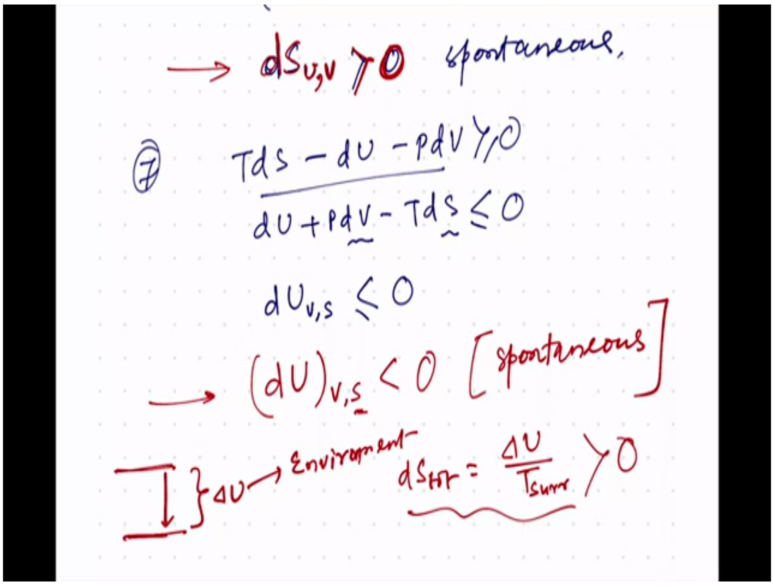
$(dS)_{U,V} \geq 0$

$dS_{U,V} > 0$ spontaneous,

⑦ $T\,dS \underline{- dU - P\,dV} \geq 0$

$dU + P\,\underset{\sim}{dV} - T\,d\underset{\sim}{S} \leq 0$

$dU_{V,S} \leq 0$



$\rightarrow dS_{U,V} \geq 0$ spontaneous,

⑦ $TdS - dU - PdV \geq 0$

$dU + PdV - TdS \leq 0$

$dU_{V,S} \leq 0$

$\rightarrow (dU)_{V,S} < 0$ [spontaneous]

$\}\Delta U \rightarrow$ Environment

$dS_{surr} = \frac{\Delta U}{T_{surr}} > 0$

So let us say that let us call that equation number 7, so from 7 we immediately get that TdS at a constant U and V it is greater equal to 0 or dS for constant U and V it greater equal to 0.

So for condition for spontaneity is wherever there is a change at a constant U and V greater than 0 then the plus process is spontaneous whenever it is equal to 0 the process is in equilibrium remember here we are talking about the changes for the system. Now again from 7 we can use the particular expression in 7 as TdS minus dU minus PdV greater equal to 0 now taking all the terms to the other side we can get dU plus PdV minus TdS less equal to 0 and now we can take V and s as constant and you can write dU for constant V and s is less equal to 0.

So therefore now the conditions for spontaneity is that whenever dU for a constant entropy and volume if it is less than 0 then the best process will be spontaneous, so the above expression for example this one dS U and V greater than 0 for a constant U and V, so if V is constant then there is no work done and if U also is constant then there is no change in the internal energy, so even if the entropy changes and the then you can say that that dS U V denotes the change in entropy when the energy of the system is constant and there is no work done in that system for that kind of situation we already know that entropy has to be positive for the process to happen spontaneously and that is what the whole thing about system plus surroundings entropy will increase or isolated system entropy will increase.

So this is intuitive and this we understand however what does this mean? This means that if I talk about an (iso) entropic situation for example an adiabatic process expansion or contraction but volume is fixed, so there is no work done, so it is neither expansion nor contraction process and entropy is not changing for the system, the energy is decreasing what does it mean?

So it means that there is no work done and there is no change in the entropy of the system that means dq reversible for the system is 0 which essentially means that the change in the internal energy which is that means the systems energy let us say the energy of the system was here it is going below and this is the amount of energy that is released to the environment and that release of energy to the environment as a heat increases the entropy of the environment.

So therefore if you now sum them up you get 0 from the system entropy, entropy change of the system is 0, entropy change of the surrounding is the change in the delta U of the system divided by the temperature of the surrounding and that is the amount of entropy that is overall changing and there for overall system plus surroundings entropy is changing by that much amount.

So d S taught in this particular case above is delta U by T of surrounding and that therefore is a continuous process because that is a positive quantity it is positive because temperature is positive and delta U is also positive because delta U is negative for the system that means it is positive for the surrounding it is going out and say surrounding is getting the delta U. So although you might think that you know system will try to lower down it is energy however it is nothing but a consequence of the fact that surrounding wants to increase it is entropy, ok.

So that is what we should remember now continuing further we can see that now let us consider both S and P as constant.

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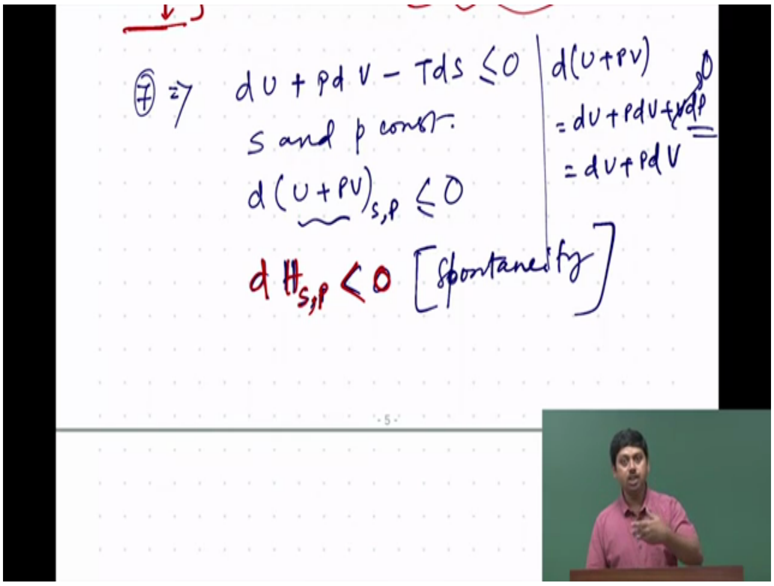


$⑦ \Rightarrow dU + PdV - TdS \leq 0$

S and P const.

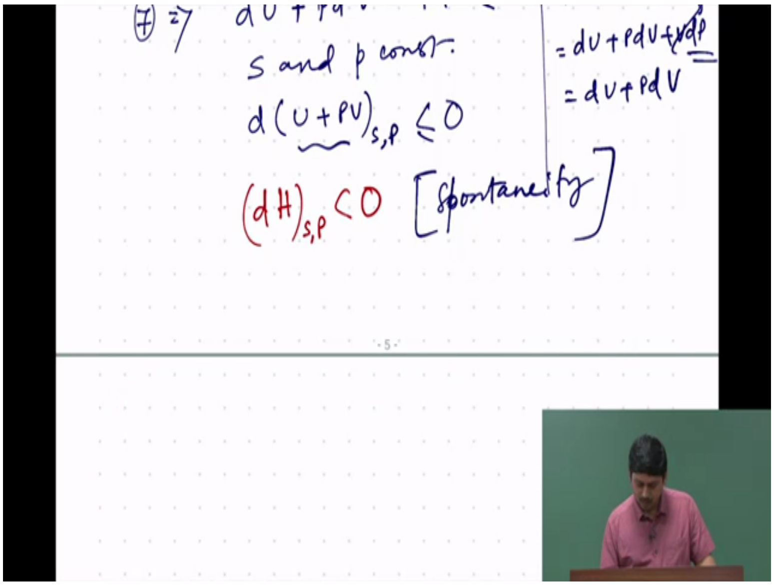
$d(\underset{\sim}{U+PV})_{S,P} \leq 0$

$dH_{S,P} < 0$ [Spontaneity]

$d(U+PV)$

$= dU + PdV + \overset{0}{\cancel{VdP}}$

$= dU + PdV$



$⑦ \Rightarrow$

S and P const.

$d(\underset{\sim}{U+PV})_{S,P} \leq 0$

$(dH)_{S,P} < 0$ [Spontaneity]

$= dU + PdV + \overset{0}{\cancel{VdP}}$

$= dU + PdV$

So if you do that we can write this same equation from equation 7 again dU plus PdV minus TdS less equal to 0, now let us take S and P constant, so what we get? We get d U plus PV. So if I write the U plus PV it essentially means that we have to differentiate both as a dU plus PdV plus VdP now if P is constant then we get dU plus PdV. So dU plus PdV I can write as this when my pressure is constant or this quantity becomes 0.

So I can write that and so my S and P are constant so that will be less than 0, so therefore d H at the constant S and P is less equal to 0 for spontaneity and of course equal to 0 for equilibrium process and just write that in a red colour. So again as you can see that instead of doing the experiment at a constant volume if I choose to do that at a constant pressure then

then I have to consider enthalpy as the determining factor whether the process will be spontaneous or not.

In this case also the argument is same that it is not that the system is trying to lower the entropy rather it is the entropy of the surrounding that is increasing because yet also the entropy of the system remains 0, so only thing is that the change in the enthalpy of the system which of course is caused by both lowering the energy and the work, so therefore both of that together it is giving out the effective heat or effective change in energy of the surrounding positive change and that is giving rise to positive change in the entropy of the surrounding del H at a constant s and P is less than 0.

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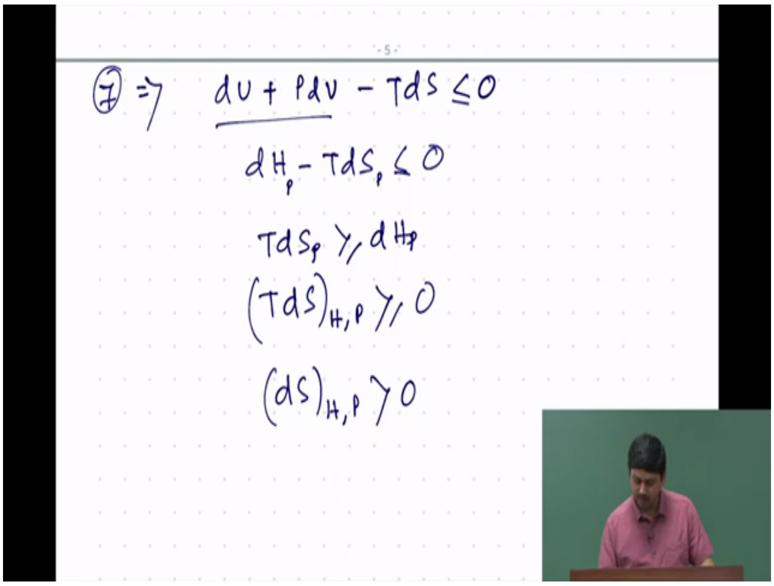

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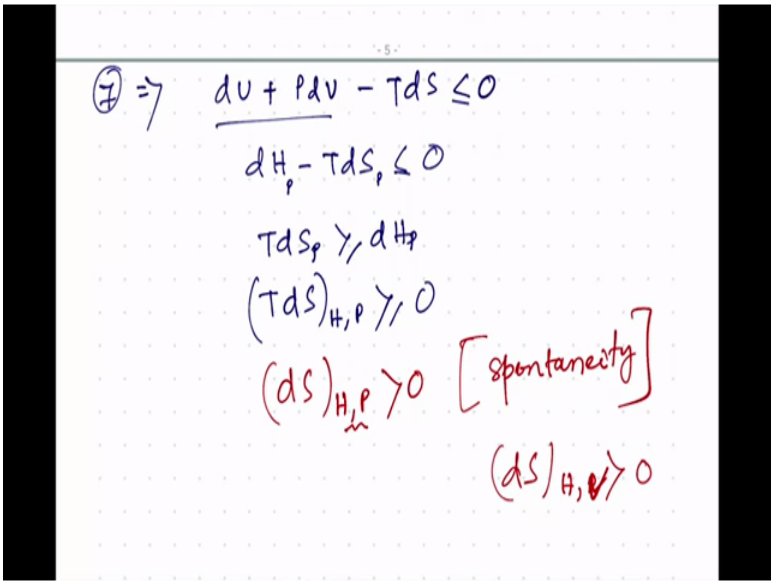
$$⑦ \Rightarrow \underline{dU + PdV} - TdS \leq 0$$

$$dH_P - TdS_P \leq 0$$

$$TdS_P \geq dH_P$$

$$(TdS)_{H,P} \geq 0$$

$$(dS)_{H,P} > 0$$



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$$⑦ \Rightarrow \underline{dU + PdV} - TdS \leq 0$$

$$dH_P - TdS_P \leq 0$$

$$TdS_P \geq dH_P$$

$$(TdS)_{H,P} \geq 0$$

$$(dS)_{H,P} > 0 \quad [\text{spontaneity}]$$

$$(dS)_{H,V} > 0$$

Let us again write the equation 7 and we write dU plus PdV minus TdS less than equal to 0 for from earlier equation now we know that this is nothing but dH minus TdS plus is equal to 0 and of course when whenever our pressure is constant, so therefore we can we can write that TdS is greater equal to dH P and we can write that TdS for both H and P has to be greater equal to 0 for therefore for spontaneity T is a fixed quantity, so therefore spontaneity dS at a constant H and P has to be greater than 0, I will just write it in the red colour dS at a constant H and P has to be greater than 0 for spontaneity.

So you see a dS at constant U and V needs to be greater than 0 and dS at constant H and P needs to be greater than 0 do not mix them together do not mix H with V or U with P because then it will not be spontaneous. So if I say that can you say that this will be (spaont) this is as conditional spontaneity or not it may not because that is that will not fit into the thing. So therefore remember that these are very important parameters to mention these subscripts do not ignore them do not ignore the subscript and do not mix the subscripts because they automatically arrive at when we do this, ok.

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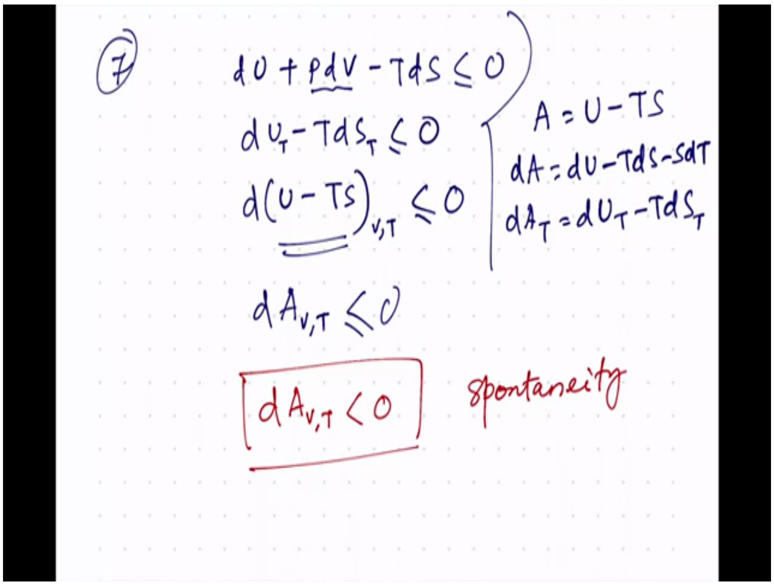


⑦ $dU + \underbrace{PdV} - TdS \leq 0$

$dU_T - TdS_T \leq 0$

$d(\underline{\underline{U - TS}})_{V,T} \leq 0$

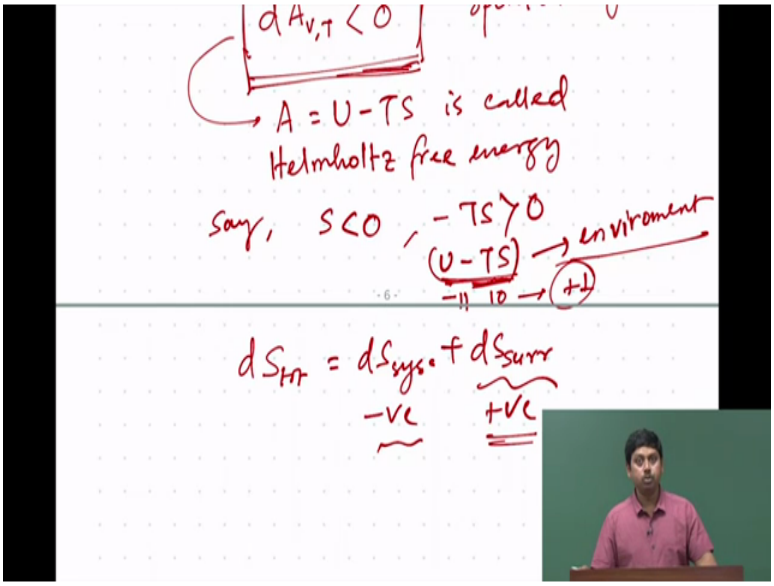
$dA_{V,T} \leq 0$

$\boxed{dA_{V,T} < 0}$ spontaneity

$A = U - TS$

$dA = dU - TdS - SdT$

$dA_T = dU_T - TdS_T$



$\boxed{dA_{V,T} < 0}$

$A = U - TS$ is called Helmholtz free energy

Say, $S < 0$, $-TS > 0$

$(U-TS) \rightarrow$ environment

$-11 \quad 10 \rightarrow (+1)$

$$dS_{tot} = \underset{-ve}{dS_{sys.}} + \underset{+ve}{dS_{surr}}$$

Now coming back again from seven we write dU plus PdV minus TdS less equal to 0, now we can take the V as a constant and we can write TdS less than equal to 0 and we can take the T also as a constant because why we need to have the T as a constant will say tell you and we can write U minus TS when we say both V and T as a constant as less equal to 0. So let us define a quantity called quantity A as U minus TS now when we take the derivative dA you get dU minus TdS minus SdT, so when you take T constant then you can write dU T minus TdS T and that is what it is here because we took it taken T to be constant and then we took V to be constant to get remove of that term.

So therefore now we can say that dA for a constant V and T less equal to 0 or for condition of spontaneity dA V T is less than 0 is the condition for spontaneity this quantity A which is U minus TS is called Helmholtz free energy, you may not have heard this name till now you may have heard of a different free energy call gives free energy will come back come to that as well but this is called free energy for a reason the definition we are defining as a new thermodynamic potential as U minus TS and you will see just like U just like S, A is also a thermodynamic potential and the state function it does not depend on path or anything and you can see that obviously will not depend on path because U is a state function, T is a state function and S is a state function, T is a variable but it depends on the state only right.

So therefore U TS all depends on the state only so therefore A also depend on the state and it is also a state function and it is then why it is called the free energy then that that is what we need to understand and that is what we are going to see. So before we do that we will just little bit talk about this condition that why it has to be negative for a spontaneous process let us understand a little bit more.

So here we see that A is U minus TS, so either you know for a constant S you need to be less than 0 and that I have discussed that how that means that the entropy of the surrounding will be positive quantity because U is going there. However even if S is not 0 then what essentially it means that that let us say S is no negative quantity a little bit you know let us say S is negative, so therefore if S is negative then minus TS will be a positive quantity and U has to be more negative than the TS in order for a positive U to go to the surrounding what i mean by that is that?

Let us say S is less than 0, so minus TS is greater than 0 now you minus TS is the net effective energy that is going to go to the environment, so therefore if minus TS is a positive quantity U has to be more negative than that positive quantity. So let us say minus TS is plus 10 so U has to be 10 or less let us say minus 11 in order for this quantity to become negative and if that happens this minus 1 of energy will go to the environment as plus 1 and will contribute to the entropy of the environment and that will however remember, so that that has to be again that entropy has to be more than the yeah so and that then only we will get an effective entropy of the system plus surrounding to be higher greater than 0 and therefore the process will be spontaneous.

So not only that and not only like unlike other (ca) earlier cases when S was 0 it was just the energy itself was fine U less than 0 was would be a spontaneous process because S of the system entropy of the system was 0 but here entropy of the system is non-zero, so it can be positive then it will of course boost the surrounding entropy as well because the it will contribute in the overall total entropy as a in a positive manner but if let us say we are talking about del S tot right.

So del S tot is del S system plus del S surrounding now if this is negative this quantity has to be positive more positive than the negative quantity see this more positive means that the U the change in the energy of the system has to be more negative than the positive part contributed by TS of the system, if TS becomes as negative, so that is what it means that what is the A is giving you that an effective measure an effective amount of energy that can be used.

So the change in the internal energy of the system U is wasted a little bit in the entropy you can think of that that way, so U have some now ten rupees you are giving you have to give out some you know in TS you have to give out some 2 rupees as a tax or something and then the net eight rupees that you have is going to be effective, so that is what that is what the free energy means that how much available energy is there to be converted to work.

So we can said see that by you know doing a derivation also a little bit.

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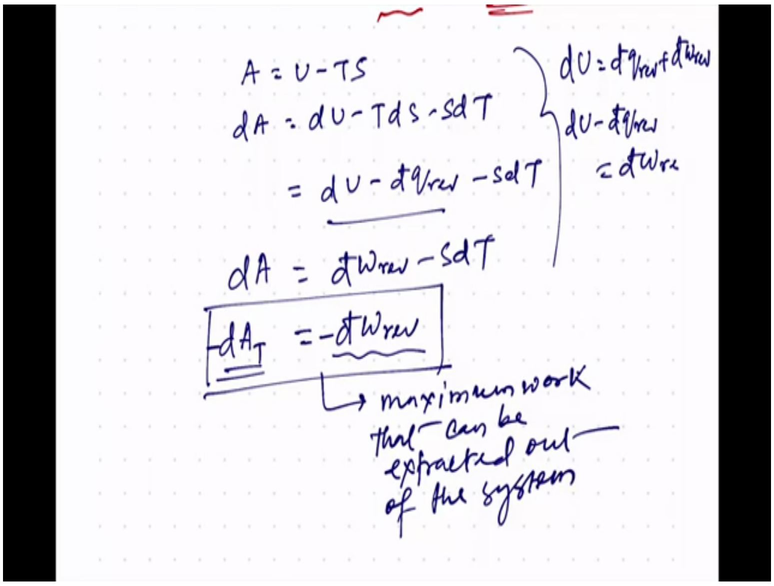

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$= \underline{dU - đq_{rev}} - SdT$$

$$dA = đW_{rev} - SdT$$

$$\boxed{-\underline{dA_T} = -đW_{rev}}$$

→ maximum work that can be extracted out of the system

$$dU = đq_{rev} + đW_{rev}$$

$$dU - đq_{rev} = đW_{rev}$$

So you know that A is U minus TS and dA is dU minus TdS minus SdT and TdS is nothing but dq reversible minus SdT and dU minus dq I will just remind you again dU equal to dq reversible plus dw reversible, so therefore dU minus dq reversible is nothing but dw reversible, so this is dw reversible minus SdT. Now that means at a constant temperature at which actually we define A is nothing but dw reversible.

So this says that and reversible work as you know is work done by the system in a reversible process is maximum. So if you put a minus 1 that is the work done by the system that is maximum, so therefore the you know change in the free energy denotes the maximum work that can be extracted out of the system it is a free energy that is available in order for you know doing the work because anything you know some amount of the work anyway you have to waste in the entropy which is not going to give you any work, work is you can say an ordered form of change of energy whereas entropy is not an ordered form it says the random motions will give you an energy which is not useful.

So dA is a measure of the available maximum work that is possible, ok. So now we are going to do the statistical approach a little bit because we have learned the statistical approach of thermodynamics.

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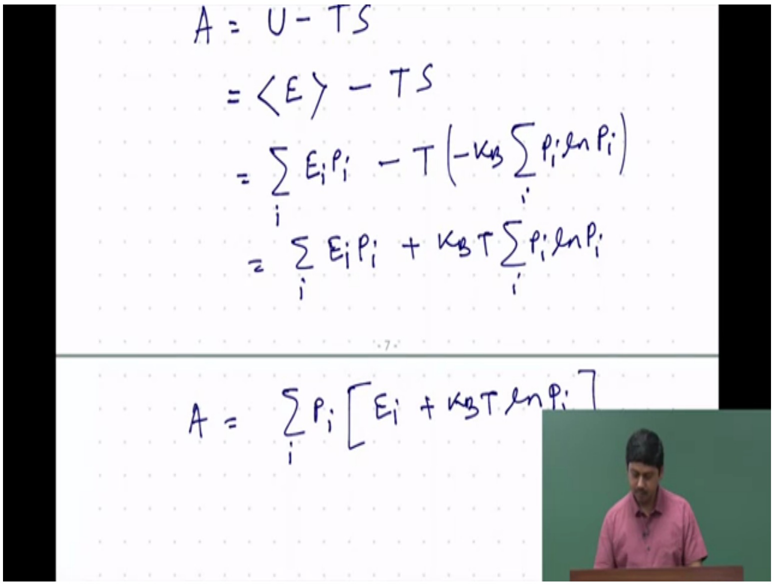
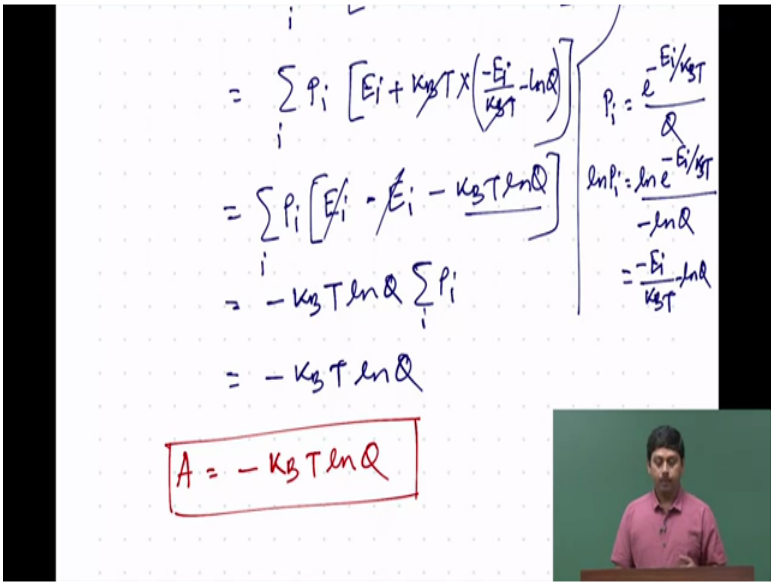


$$A = U - TS$$
$$= \langle E \rangle - TS$$
$$= \sum_i E_i P_i - T\left(-k_B \sum_i P_i \ln P_i\right)$$
$$= \sum_i E_i P_i + k_B T \sum_i P_i \ln P_i$$

$$A = \sum_i P_i \left[E_i + k_B T \ln P_i\right]$$



$$= \sum_i P_i \left[E_i + k_B T \times \left(\frac{-E_i}{k_B T} - \ln Q\right)\right]$$
$$= \sum_i P_i \left[\cancel{E_i} - \cancel{E_i} - k_B T \ln Q\right]$$
$$= -k_B T \ln Q \sum_i P_i$$
$$= -k_B T \ln Q$$

$$\boxed{A = -k_B T \ln Q}$$

$$P_i = \frac{e^{-E_i/k_B T}}{Q}$$
$$\ln P_i = \ln e^{-E_i/k_B T} - \ln Q$$
$$= \frac{-E_i}{k_B T} - \ln Q$$

So we are going to now talk about the statistical approach of Helmholtz free energy and you know the by definition S is nothing but U minus TS and U is U TS A they are all macroscopic variables that means we are talking about a bulk system, a system of one mole of particles and things like that and we have emphasized that anything that is measurable in a macroscopic sense is nothing but an average quantity.

So this U is nothing but an average energy E even er interchangeably used so I am just writing as e minus TS and what is e? We have defined e average energy as E i P i well i is the number of possible states and S by definition was minus k B P i ln P i. Now we will just simplify it a little bit E i P i minus minus will become plus K B T P i ln P i continuing further we get A equal to i take P i common and we get E i lus K B T ln P i ok.

So now we get P i, now what is ln P I we will have to do it little bit on the side to show you, so P i is e to the power minus E i by K B T by partition function Q that is the probability P i right. So now ln of P i is ln of this quantity e to the power minus E i by K B T minus ln of Q. Now ln of any exponential quantity is that quantity itself so that is nothing but minus E i by K B T minus ln Q we can write that plus K B T into minus E i by K B T minus ln Q.

So P i E i plus then K B T K B T will cancel no it is not yeah of course will cancel and give you E i and this K B T inside will give you minus K B T ln Q and this will be minus this cancels now Q is a constant quantity K B T is also a constant quantity, so let us take it outside of the sum, so K B T ln Q sum over P i and you know that sum of all probability is nothing but 1, so we get K B T ln Q.

So therefore in statistical mechanics Helmholtz free energy A is written as minus K B T ln Q. So if you know partition function of the system you are going to know and the Helmholtz free energy of the system as well, so and and from Helmholtz free energy of the system you can also get a lot of other quantities.

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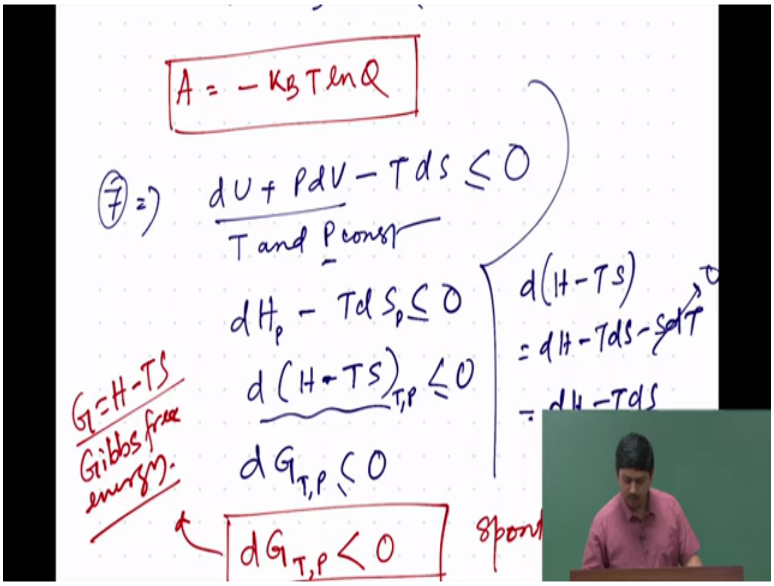


$$\boxed{A = -K_B T \ln Q}$$

⑦ ⇒ $dU + PdV - TdS \le 0$

T and P const

$dH_P - TdS_P \le 0$

$d(H - TS)_{T,P} \le 0$

$dG_{T,P} \le 0$

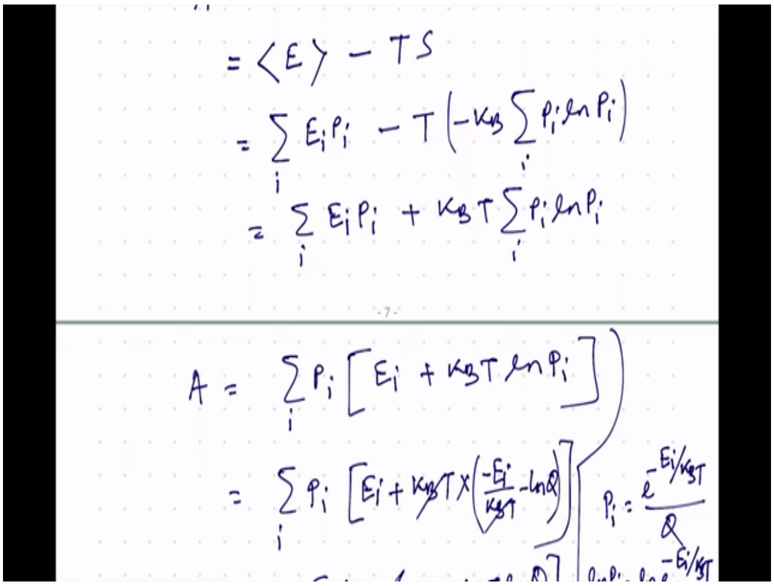
$\boxed{dG_{T,P} < 0}$ Spon

G = H - TS Gibbs free energy.

$d(H - TS)$

$= dH - TdS - \cancel{SdT}^{0}$

$= dH - TdS$



$$= \langle E \rangle - TS$$

$$= \sum_i E_i P_i - T\left(-k_B \sum_i P_i \ln P_i\right)$$

$$= \sum_i E_i P_i + k_B T \sum_i P_i \ln P_i$$

$$A = \sum_i P_i \left[E_i + k_B T \ln P_i\right]$$

$$= \sum_i P_i \left[E_i + k_B T \times \left(\frac{-E_i}{k_B T} - \ln Q\right)\right]$$

$$P_i = \frac{e^{-E_i/k_B T}}{Q}$$

Now we are going to consider the another important free energy called Gibbs free energy so again we start from equation 7 where it was dU plus PdV minus TdS less equal to 0, we start with that and we are going to take both T and P constant and what we are going to get is so dU plus PdV is dH minus TdS less equal to 0 or we are going to define some quantity called H minus TS and we are going to see what H minus TS is giving us d H minus TS is dH minus TdS minus SdT.

So we have to take we took T as a 0, so we going to get dH minus TdS so we can write this particular quantity and remember that in order for a you know dU plus PdV to be dH we needed to take P constant already otherwise you could not have written that and once we write that then basically we are taking both T and P constant plus equal to 0 and this H minus TS is defined as G so dG T P less equal to 0 we are getting for (acco) as a condition of spontaneity, so as a condition of spontaneity del G at a constant temperature and pressure is less than 0 is the condition for spontaneity and this is very famous because you might have even studied in your 12 standard that for a spontaneous process free energy has to be negative and that free energy is basically they talk about Gibbs free energy.

So this is the definition of Gibbs free energy which is enthalpy minus TS, Gibbs free energy is extremely important because important for chemical reactions because temperature and pressures are typically kept constant during a chemical reaction, pressures are our normal atmosphere pressure and temperatures are normal atmosphere temperature which you call as room temperature any process that you know happens where we can see a spontaneous change for example if I put a water in sodium hydroxide tablets which we have seen some time back then spontaneously that gets dissolved and heat gets generated, so that the process of dissolve dissolving this one is a free energetically favourable process which means free energy of the system will go negative.

Similarly if you put sugar in water and sugar will actually dissolve in water which means the free energy of that system sugar water system has to go to negative change in free energy rather Delta G, so whatever was there earlier you know sugar plus water and when you mix them together the free energy of the combined system has to be lower. So any process for example we talked about binding so you know it is very important in medicinal chemistry where people take drugs and most of the time those drug are nothing but molecules that go and bind to proteins and that binding process overall has to be free energetically favourable process because if the free energy of the bound complex is negative then only it will bind otherwise will not bind.

So often people calculate or find out new drugs by finding out whether a particular drug molecule will give us a favourable binding to that particular protein or not of course you have to identify which protein is important for the particular disease protein or DNA and you have to also find out that the molecule that you are choosing whether it will have lower no negative free energy or binding if that happens then of course we know that the binding will take place favourably and of course there is something called competitive binding also is there if something is already bound then if you want to replace that then you have to have something which is stronger than the binding phrase you has to be even lower than the previous molecule in order to replace the previous molecule is the new one.

So therefore the free energy gives free energy plays a very important role again remember we are talking about only the system if you think about the overall system plus surrounding then it is again the entropy because here also what happens is that effectively is that you are you are something you are losing as entropy and then whatever in enthalpy you are getting then that contributes to the surroundings entropy change and things like that essentially it is the same thing whenever two things bind together favourably then the decrease in the free energy will eventually gives rise to positive change in the entropy of the surrounding system.

So system plus surrounding it is the same always but always you do not look at system plus surrounding we only look at the system itself for example in protein binding to the drug we are talking about only protein and the protein and drag only and not something else not beyond the system of protein drug and water. Often let us say see one of the subject that I work on is drug the inter collision.

So where that there are like flat drugs which go and you know bind between a pair of base pairs of DNA and that has to be again free energetically favourable process otherwise that process will never happen and that binding will subsequently stop the DNA replication and therefore it is helpful for anti-cancer activity because in cancer the DNA replication is always goes on and cancer has several different stages so people try to block at many different stages.

So here anti-cancer drugs which are intercalator that are used in the last stage you know it directly goes to the DNA and stop the DNA replication and it can stop because it binds similarly for HIV viruses and all. So there are drug molecules that will replace the particular you know in the binding pocket that particular molecule that binds and therefore it inhibit that is that process.

So free energy Delta G is very important and you will see that from free energy Delta G you can get a lot of other quantities of like for example change in entropy and enthalpy and many other quantities you can get just from the free energy itself and we are going to discuss that a little bit now. Which part you are talking about?

Student is answering:

This is derivation A equal to dU minus dS it is previous.

Ok, very good question, this one right?

Student is answering:

Yeah.

See the thing is that U is an average energy but A is not an average ok, so now the thing is that yes a temperature if we look at in a microscopic sense it is an average quantity but we are already taking into the account of the averages already meaning whenever they are talking about e to the power E by K B T we are talking about the thermodynamic average macroscopic value of the T ,we are not really looking at the velocity wise if we do that of course we can still do that but the equation will be little bit more complicated.

So whenever you write an exponential distribution e to the power E i by KBT you are already taking into account to that ok system is in thermal equilibrium, every molecule has different velocities but overall if you measure the temperature it will give you the T value, so from

Maxwell Boltzmann distribution you know that you get only one T value right. So that you will get you know, so you are using that equation here yes you are approximating that here but you can meaning it helps you to simplify the problem.

Similarly for S, S is again a macroscopic quantity here one when you writing it that you are writing as a macroscopic quantity, you are not writing K B P i ok you are using P ln P i, so of course you are even using that as a microscopic quantity. So T you are not doing that to make things simpler and to use it in Boltzmann equation because otherwise what will happen is that in Boltzmann equation how will you distribute the energy will become very difficult.

So yeah you are actually essentially taking into a account of the average aspect of that already you are saying that is a reason that you are applying that for equilibrium system alone without the equilibrium system, see microscopically you can have all the information available but unless it is in equilibrium you cannot write that T value as one particular value because every particle otherwise will have different velocities.

So that is very important that these quantities are only applicable for equilibrium and not for you ask for me that (())(34:19) whether the statistical mechanics can be applied for every A is but it cannot be because Boltzmann distribution is not valid in non-equilibrium situation.

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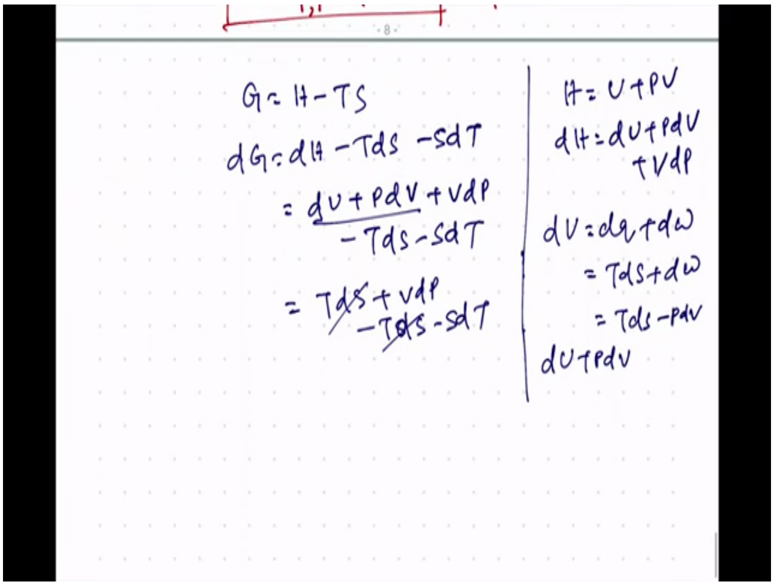


$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$= \underline{dU + PdV} + VdP - TdS - SdT$$

$$= \cancel{TdS} + VdP - \cancel{TdS} - SdT$$

$$H = U + PV$$

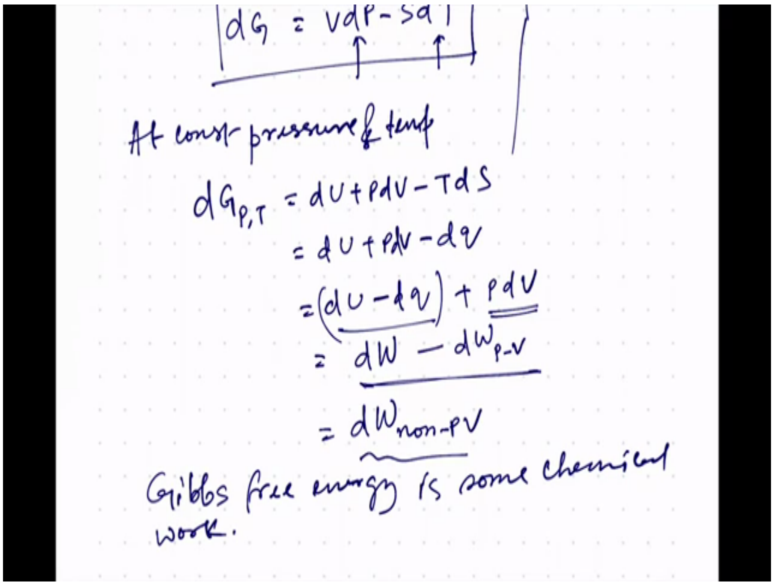
$$dH = dU + PdV + VdP$$

$$dU = dq + dw$$

$$= TdS + dw$$

$$= TdS - PdV$$

$$dU + PdV$$

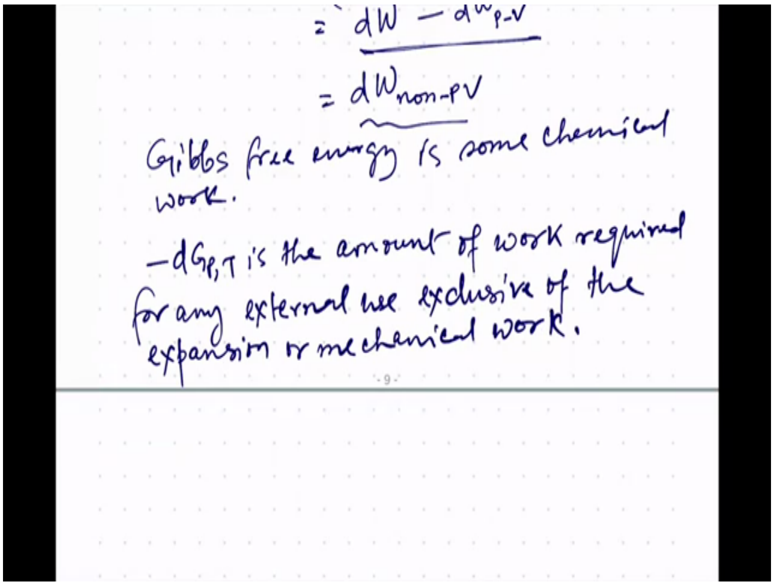


$\boxed{dG = VdP - SdT}$

At const pressure & temp

$$dG_{P,T} = dU + PdV - TdS$$
$$= dU + PdV - dq$$
$$= (dU - dq) + PdV$$
$$= dW - dW_{P\text{-}V}$$
$$= dW_{non\text{-}PV}$$

Gibbs free energy is some chemical work.



$$= dW - dW_{P\text{-}V}$$
$$= dW_{non\text{-}PV}$$

Gibbs free energy is some chemical work.

$-dG_{P,T}$ is the amount of work required for any external use exclusive of the expansion or mechanical work.

G is H minus TS, so dG is d H minus TdS minus SdT and we know that dH is dU plus PdV plus VdP because H is U plus PV, so dH is dU plus PdV plus VdP minus TdS minus SdT. Now we know that from first law dU equal to dq plus dw or TdS plus dw or TdS minus PdV, so dU plus PdV is equal to TdS so this equal to TdS, so TdS plus VdP minus TdS minus SdT, so TdS TdS cancels giving you VdP minus SdT.

So dG is dG has these two natural variable P and T as you can see similarly ok we will do that once more later on now at a constant pressure dG and temperature of course the dG P T is dU plus PdV minus TdS because because that is what we can write as constant temperature and pressure otherwise VdP term will come as SdT term will come if they are not constant. So that is the and dU plus PdV you can write that as dU plus PdV minus TdS is dq you know, so you can write as dq and dU minus dq plus PdV and dU minus dq is some kind of W which is non P V meaning is some you know it is a W that is it is W and PdV is dw which is a P V work, so that means you are getting dw which is non P V.

So Delta G that means change in the free energy is non P V work, so dU minus dq is just W some kind of work all sorts of work whereas PdV is work done by volume expansion so P V work wherever there is a work done by volume. Now when you subtract these two quantities we are getting work which is only the non P V work. So therefore gives free energy, free energy is some chemical work which are non P V type.

For example if I bring a charge from far distance to close, so you know the kind of work that you do that will be a non P V type of work and that will change the free energy of the system, so that is how we can think about the free energy. So that means this dG P T is the amount of work required for any external use you know exclusive of the expansion or mechanical work. So dG P T is the amount of work required for any external use exclusive of the expansion or mechanical work.

So we are talking about non mechanical work as the free energy.

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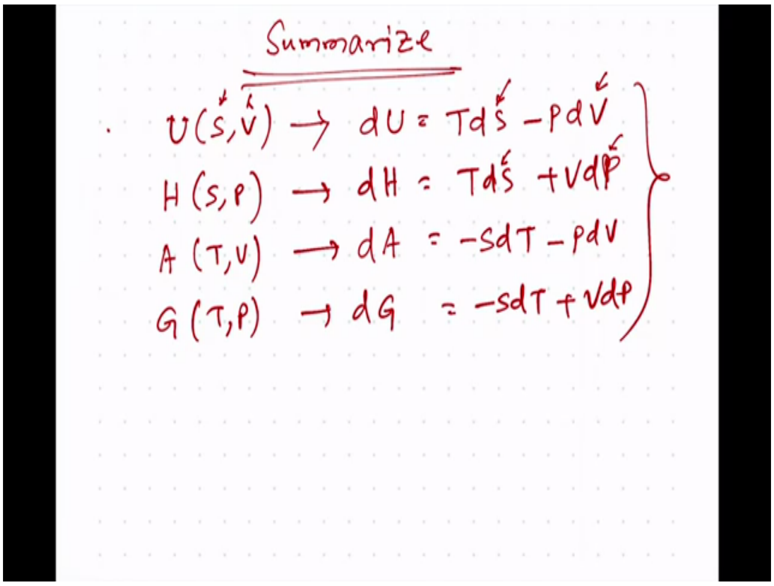

Summarize

$$\left.\begin{aligned} U(\overset{\downarrow}{S},\overset{\swarrow}{V}) &\rightarrow dU = Td\overset{\swarrow}{S} - Pd\overset{\swarrow}{V} \\ H(S,P) &\rightarrow dH = Td\overset{\swarrow}{S} + Vd\overset{\swarrow}{P} \\ A(T,V) &\rightarrow dA = -SdT - PdV \\ G(T,P) &\rightarrow dG = -SdT + VdP \end{aligned}\right\}$$

Now is summary we now we are going to summarize all the thermodynamic potentials that we learn today. So we saw that from the fundamental equation that U is a function of S and V n is also there but we are not using it and from there we wrote dU equal to TdS minus PdV that just came from fundamental equation then we have defined H as U plus P V and we saw that d H is TdS plus VdP, so here the in case of U the natural variables are S and V denoted by dS and dV, in case of H and the national variables are S and P denoted by dS and dP and then we got T V, V and T for Helmholtz free energy and we will got dA equal to minus SdT minus PdV again T and V are the natural variables of A and G we got as natural variable as T and P where without dG equal to minus SdT plus VdP.

So these are four different thermodynamic potentials and they have four different four different variables and you will see that they are just they are just different forms of each other.