Chemical Principles II
Professor Dr. Arnab Mukherjee
Department of Chemistry
Indian Institute of Science Education and Research, Pune
Module 05
Lecture 31
Definition of Entropy

Now we let us say we will talk about definition of entropy.

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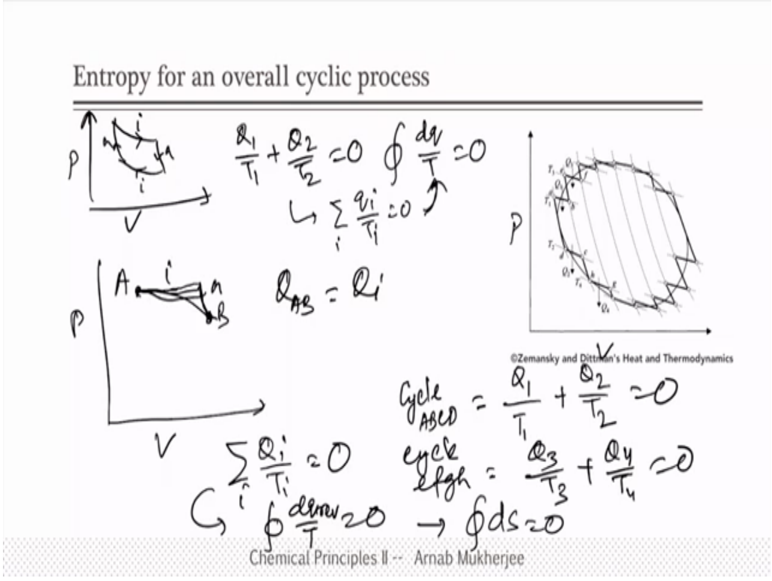

Entropy for an overall cyclic process

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So remember we discussed about the definition of entropy from Carnot cycle what we showed for the Carnot cycle is that an ideal Carnot cycle that for the Carnot engine which is an alternating isothermal and adiabatic processes the Q1 by T1 plus Q2 by T2 is equal to 0 and we know that it is a reversible Carnot engine right but what if it is an arbitrary process and with and therefore we our argument was that for a cyclic process the total change in q by T is going to be zero meaning we came it from this particular step that sum over i q i by T i is equal to 0 and then we went there when there are multiple I know many more many small changes.

Now from this to this when you want to go and we want to talk about any arbitrary cycle we need to discuss that how for an arbitrary cycle also this can be true so for example let us say we let us say we talk about any arbitrary processes going from this point to this point let us say A to B, now idea is that this arbitrary cycle can be mapped into an isothermal and an adiabatic step a reversible isothermal and adiabatic step and since adiabatic in adiabatic processes the change in Q is zero therefore all the change that is going to happen in is in the isothermal step.

So therefore the change or heat change from A to B will be the heat change that happens only in the isothermal part and we know that an isothermal case there is a fixed temperature, so you can divide by the temperature and we can get the entropy change for that particular part A B and like that if we can construct for the whole big system then we can map any arbitrary cycle that is shown here in terms of an adiabatic an isothermal process for example we show here this is a generalized some cycle cyclic process that is going on and that has been broken into several isothermal adiabatic steps.

Now look at here that this is the A and B this is an isothermal step A B EF and yeah, so here we are showing A B and E F, so A B is an isothermal step and these lines are adiabatic lines the dotted lines that you can see there are all adiabatic lines. So now you see A B C D construct a cyclic process of alternating isothermal and adiabatic steps, so in this the change in heat is Q 1 through A B at temperature T 1 and then you have a change in heat Q 2 at temperature T 2.

Now we know that for a closed reversible cycle of alternating adiabatic and isothermal this will be 0, so now this A BC D so this is for A B C D cycle, cycle A B C D that will be equal to 0 now add that with e f g h cycle Q 3 by T 3 plus Q 4 by T 4 equal to 0. So now once you do that for you can construct many cycles and therefore you can construct for the whole overall cycle such that you can write for any arbitrary process Q i by T i is equal to 0.

So what we are doing is that we are doing we are converting a generalized cyclic processes into several Carnot cycles of an reversible Carnot cycle such that the Q i and T i, Q i bi T i comes to be zero, so it says that for any cyclic processes this particular quantity now you know that sum becomes integral so this particular quantity for any cyclic processes turns out to be zero.

So we talked about that for only Carnot cycle now we are talking about that for any generalized cycle and this as we as we know is defined again it has to be reversible because remember the generalized cycle may not be reversible but what we have done is that we have constructed a reversible multiple reversible equivalent cycles each of which is giving rise to a zero value of intro.

Now so that means for a reversible cyclic processes d q by T is zero which is defined to be d s so d s is equal to 0 and for a cyclic process a quantity becomes zero indicating that that is the state function, so got a new set functions which Clausius termed as entropy and that is the definition of entropy.

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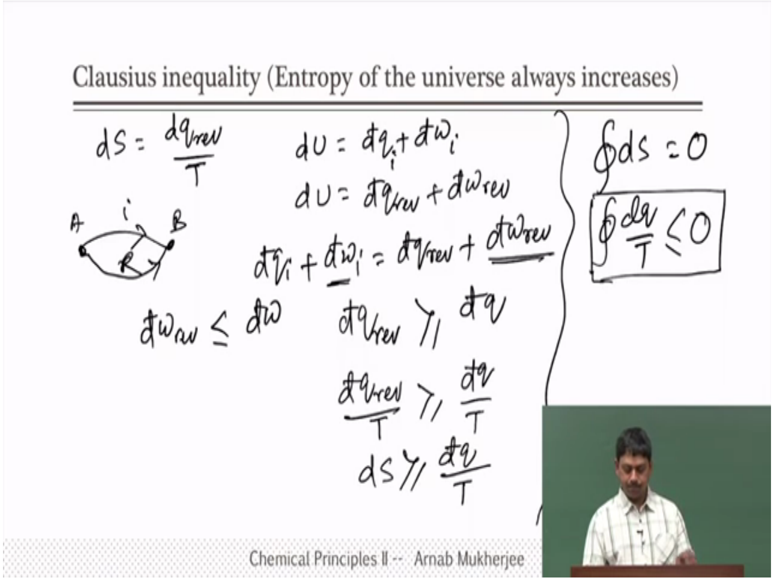

Clausius inequality (Entropy of the universe always increases)

$$dS = \frac{đq_{rev}}{T}$$

$$dU = đq_i + đw_i$$

$$dU = đq_{rev} + đw_{rev}$$

$$đq_i + \underline{đw_i} = đq_{rev} + \underline{đw_{rev}}$$

$$đw_{rev} \leq đw \qquad đq_{rev} \geq đq$$

$$\frac{đq_{rev}}{T} \geq \frac{đq}{T}$$

$$dS \geq \frac{đq}{T}$$

$$\oint dS = 0$$

$$\boxed{\oint \frac{đq}{T} \leq 0}$$

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Now we are talking about entropy and irreversibility, so that is a so basically what you have learnt is that d s is d q reversible by T this is very important it is not d q by T it is d q reversible by T. So let us talk about a cyclic process going from A to B in an irreversible manner and coming back from B to A in a reversible manner, ok. So now for the first law of thermodynamics you know d U call to d q plus d w whether it is irreversible or reversible it does not matter right.

So let us say that we are taking the irreversible path ok we are going to from A to B and we can also take the reversible path this r means reversible, so both will be equal right so d q is reversible plus d w is reversible is d q reversible plus d w reversible ok. Now we have remember in the while talking about the first law of thermodynamics we showed that d w reversible so a reversible work done on the system is always minimum i means irreversible talked about that already right.

Now if this one is less than this one which means so this d w reversible is less so this has to be more so d q reversible has to be greater or equal to irreversible is it clear which means that d q reversible by T has to be larger than d q by T which means d s has to be greater equal to d q by T, now when I saying irreversibility is always greater so what I am trying to what I am saying is that in general any process be it reversible or irreversible, so I am just when I am talking about equal to sign then I am not assuming any reversibility or irreversibility ok.

So this up to this part was fine here I am talking about in general d w so less is when it is irreversible equal to when it is reversible similarly here greater equal to d q means it is equal to when it is d q is reversible greater when it is not. Now d s is greater than d q by T they have got that right, now there is a natural conclusion is that we know that s s for a cyclic process is 0 now d q by T is less equal to d s so therefore d q by T which is less equal to d s must be less equal to 0 this part is this part clear because for a cyclic process d s is 0 and d q by T has to be less than d s so it has to be less than 0 ok and that is what is called Clausius inequality it says that d q by T is less equal to zero, so that is the Clausius inequality and implications of that we are going to talk about in a moment and I say what I have written.

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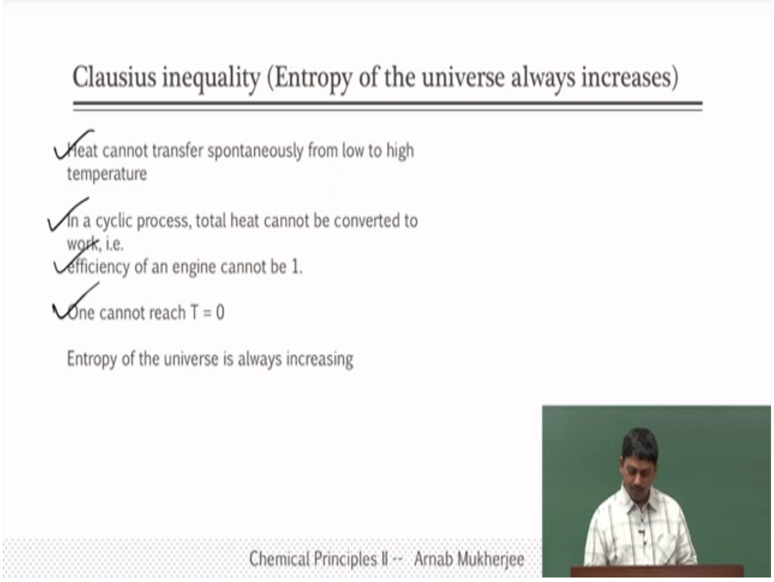

Clausius inequality (Entropy of the universe always increases)

✓ Heat cannot transfer spontaneously from low to high temperature

✓ In a cyclic process, total heat cannot be converted to work, i.e.

✓ efficiency of an engine cannot be 1.

✓ One cannot reach T = 0

Entropy of the universe is always increasing

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We know that from Clausius statement that heat cannot transfer spontaneously from low temperature to high temperature right we know that and in a cyclic process total heat cannot be converted to work that also so this is the Clausius statement this is the Kelvin statement these two are statements of the second law of thermodynamics and there is a corollary to that is that the efficiency of the engine cannot be one corollary to that is that the temperature cannot go to zero but we still did not connect so this one we have connected to be equal to this on,e to equal to this one, to equal to this one, we still did not connect this last one how? Which is entropy of the universe is always increasing.

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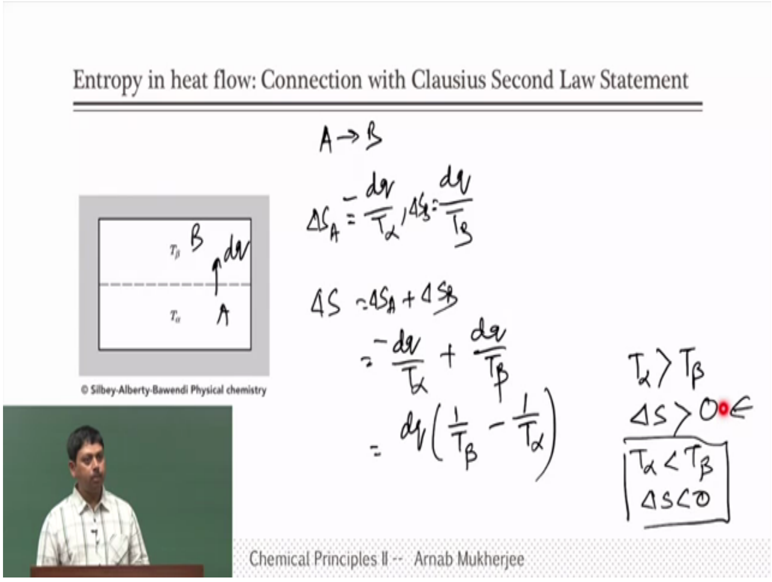

Entropy in heat flow: Connection with Clausius Second Law Statement

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$A \rightarrow B$

$\Delta S_A = \frac{-dq}{T_\alpha}, \Delta S_B = \frac{dq}{T_\beta}$

$$\begin{aligned} \Delta S &= \Delta S_A + \Delta S_B \\ &= \frac{-dq}{T_\alpha} + \frac{dq}{T_\beta} \\ &= dq\left(\frac{1}{T_\beta} - \frac{1}{T_\alpha}\right) \end{aligned}$$

$T_\alpha > T_\beta$

$\Delta S > 0$

$\boxed{\begin{matrix} T_\alpha < T_\beta \\ \Delta S < 0 \end{matrix}}$

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So in order to connect that we let us say talk about a system an isolated system in which there is first there is a boundary in which there is no heat transfer is possible initially let us say one system is a T alpha another (sys) another system is at kept at T beta, T beta and T alpha and a small amount of heat changes happening from alpha to beta, let us say this system is A and this system is B, so there is let us say a transfer of heat goes from A to B so what will happen to the entropy of the system and they say it is very small amount of heat d q so therefore it is taken to be a reversible process.

Now heat goes from A to B, so the change in entropy of the system A is minus d q by T alpha and the change in B is plus d q by T beta so this is the change in the entropy for S A and this is the change in the entropy for S B so what is the total change and then there is no surrounding so it is an isolated system so total change is S A plus del S A plus del S B which is minus d q by T alpha plus d q by T beta and I can take d q common 1 by T beta minus 1 by T alpha.

Now you see an interesting thing happens is that if T alpha greater than T beta then Delta s is if T alpha greater which is 1 by T alpha is smaller then it is positive right if T alpha less than T beta then this will be negative, I have said that the heat goes from alpha to beta now if T alpha is higher temperature and T beta is lower temperature then entropy will be positive which means the heat that cannot transfer from low temperature to high temperature because in that case the entropy change will become negative.

So which means we are connecting now the Clausius statement to a statement where we are talking about change in entropy, so a spontaneous change in n change in entropy for a spontaneous process if it is cannot be negative however change in entropy for a spontaneous process can be positive.

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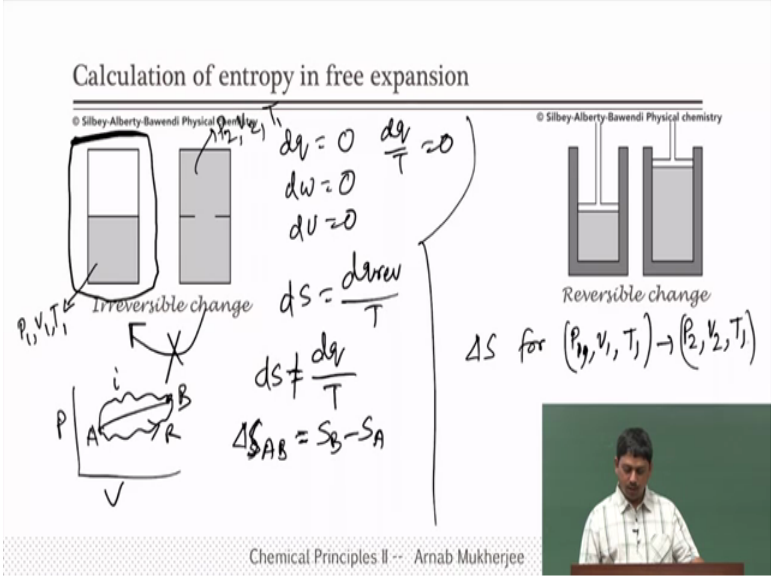

Calculation of entropy in free expansion

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Irreversible change

Reversible change

$dq = 0 \quad \frac{dq}{T} = 0$

$dw = 0$

$dU = 0$

$dS = \frac{dq_{rev}}{T}$

$dS \neq \frac{dq}{T}$

$\Delta S_{AB} = S_B - S_A$

ΔS for $(P_1, V_1, T_1) \rightarrow (P_2, V_2, T_1)$

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So we showed one irreversible process of heat transfer so basically we know that heat transfers from low high to low temperature spontaneously because entropy increases ok so that we have seen. Now let us talk about a free expansion process let us initially the system is some gas is kept in a part of the cylinder confined to a part of the cylinder and we make a hole and then it expands to the full cylinder and the outside is actually insulated this is insulated so heat cannot go in or out.

So now since this is an adiabatic expansion right, so in this adiabatic expansion process we know what is the d q 0, so d q equal to zero and in a free expansion process what is d w 0 because there is no external pressure we have talked about that which means our d u equal to also 0 of course for ideal gas we are talking about right remember we said that for free expansion for a real gas it is not we talked about joules coefficient and all that we are talking about ideal gas situation right now and see all of them are 0 however intuitively we know that once it expands it cannot come back spontaneously.

So can it go from here to here spontaneously? Never which means that this is an irreversible process from left to right is an irreversible process however d q equal to zero so how do we know that it is a you know it is a favourable entropically favourable process because our d q equal to 0 is it an entropically favourable process? Yes it looks like but our calculation says that it is equal to 0 how do you understand this?

So let me tell you, so we say we are we kind of understand that there is an entropy increase but looking at the q we get confused because you have to understand that d s is d q reversible by T it is not d q by T ok d s is not equal to d q by T so that is why I try to emphasize this one it is not equal to just d q by T it is equal to d q reversible by T, d q by T is 0 but d q reversible by T is not 0 how do we know that?

So let us say we are going from this point to this point we can take an irreversible path just like what we did last time and we can take a reversible path entropy is a state function so entropy difference between A and B is just S B minus S A it does not depend on the path it is in path independent because it is a state function, so we can always choose a reversible path to calculate the entropy value right because there may be many irreversible path but there will be a fixed or we can choose a reversible path whichever a reversible path we choose it will be fine it will give you the same value between B and A because it is a straight function.

So this expansion process we can do it reversible how do you do reversible? You cannot do free expansion because that is not a reversible one, you can take this reversible change where again you can very slowly move the piston so you have to go from half the volume to the full volume right you can choose let us say this situation is P 1 V 1 and T 1 and obviously your pressure has changed your volume has also changed and let us say the temperature did not change because you can always will it change? No.

Student is answering:

So in real gas it changes.

So in real gas it changes but in ideal gas the temperature does not change but pressure and volume both have changed, so I can keep the temperature to be T1. So now all that we have to do is that we have to calculate the entropy change for a system going from P 1 V 1 T 1 to P 2 V 2 and T 1 kind of an isothermal process right, an isothermal, isothermal expansion process if we calculate that then we will be able to get the entropy change and how to calculate entropy change for an isothermal expansion process?

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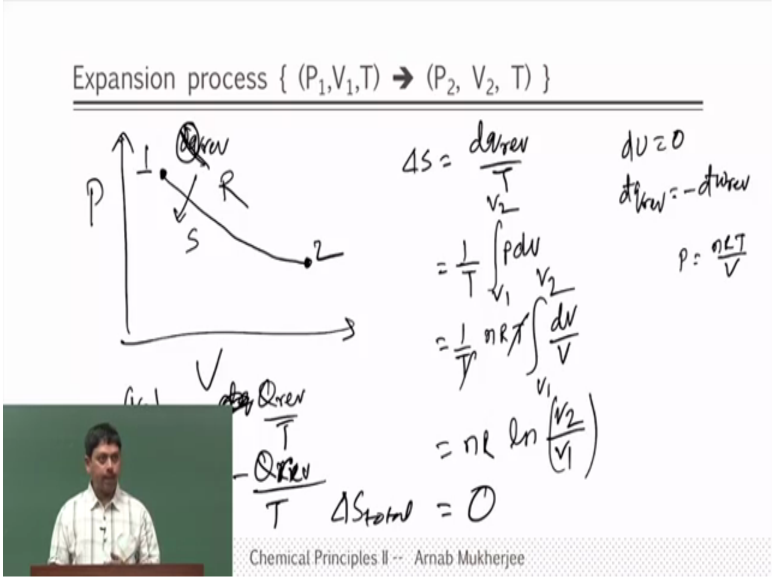

Expansion process { $(P_1, V_1, T) \rightarrow (P_2, V_2, T)$ }

$\Delta S = \frac{dq_{rev}}{T}$

$= \frac{1}{T}\int_{V_1}^{V_2} p\,dV$

$= \frac{1}{\cancel{T}}\, nR\cancel{T}\int_{V_1}^{V_2} \frac{dV}{V}$

$= nR \ln\left(\frac{V_2}{V_1}\right)$

$dU = 0$

$dq_{rev} = -dw_{rev}$

$P = \frac{nRT}{V}$

$\frac{Q_{rev}}{T}$

$-\frac{Q_{rev}}{T}$ $\Delta S_{total} = 0$

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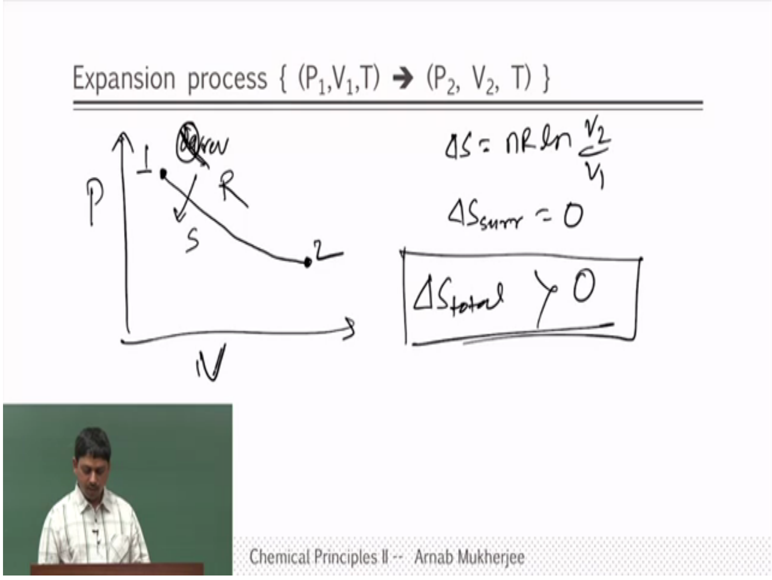

Expansion process { $(P_1, V_1, T) \rightarrow (P_2, V_2, T)$ }

$\Delta S = nR \ln \frac{V_2}{V_1}$

$\Delta S_{surr} = 0$

$\boxed{\Delta S_{total} > 0}$

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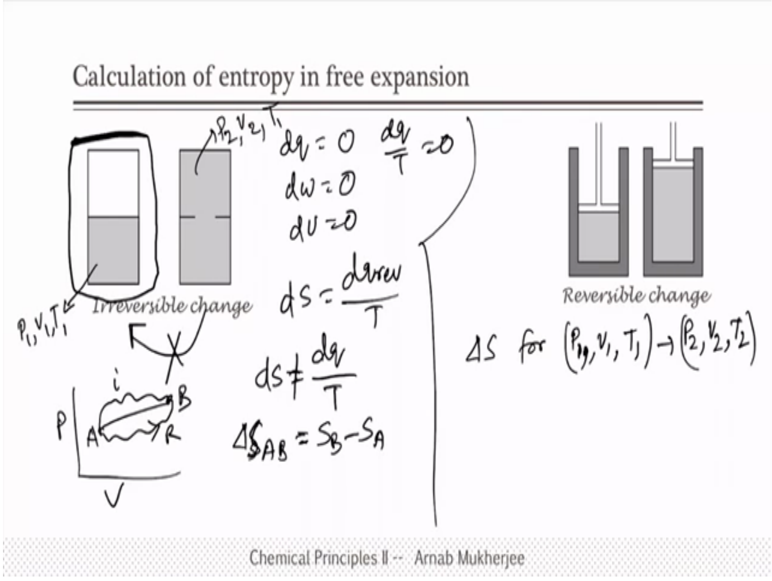

Calculation of entropy in free expansion

$dq=0$ $\frac{dq}{T}=0$

$dw=0$

$dU=0$

$dS=\frac{dq_{rev}}{T}$

$dS\neq\frac{dq}{T}$

$\Delta S_{AB}=S_B-S_A$

ΔS for $(P_1,V_1,T_1)\to(P_2,V_2,T_2)$

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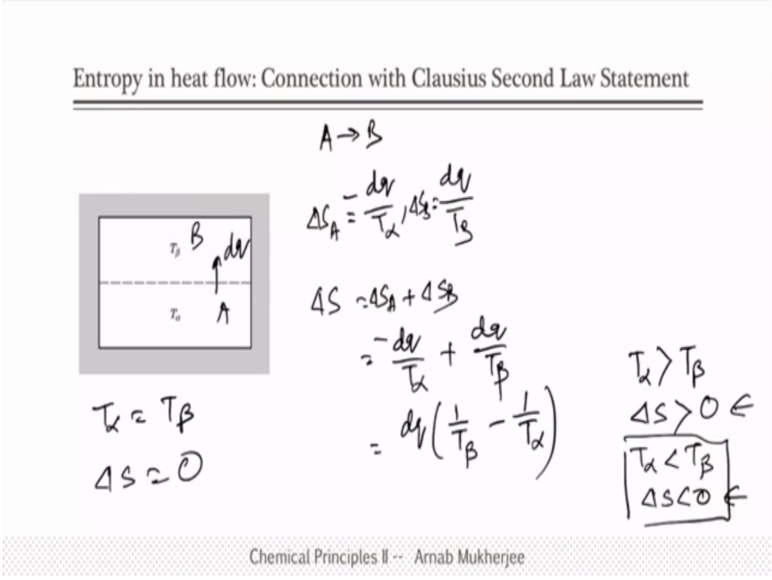

Entropy in heat flow: Connection with Clausius Second Law Statement

$A\to B$

$\Delta S_A=\frac{-dq}{T_\alpha}, \Delta S_B=\frac{dq}{T_\beta}$

$\Delta S=\Delta S_A+\Delta S_B$

$=-\frac{dq}{T_\alpha}+\frac{dq}{T_\beta}$

$=dq\left(\frac{1}{T_\beta}-\frac{1}{T_\alpha}\right)$

$T_\alpha=T_\beta$

$\Delta S=0$

$T_\alpha>T_\beta$

$\Delta S>0$

$T_\alpha<T_\beta$

$\Delta S<0$

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Let us draw a diagram P V, so this an expansions of volume increases and pressure decreases. So let us say it is like this just like an isothermal expansion, so if it is a reversible path then we can calculate delta s by d q reversible by T and since it is an isothermal step then your d u equal to 0 so therefore d q reversible is minus d w reversible which means it is 1 by T and minus d w is plus pdv right, so pdv v 1 to v 2 and we know P is nothing but pv equal to nRT so nRT by v TT cancels n r ln v tuple v 1, so this is the change in the entropy for an expansion process going from v 1 to v 2.

So even if it is a free expansion this much entropy change will actually occur ok, since it cannot go to (())(20:05) now if you calculate the total change in the heat. So let us say let us talk about two situations in which there is a reversible expansion so let us say this is a reservoir and this is our system and there is a reversible amount of heat change happened d q reversible.

Let us say first step of the Carnot cycle then the change in the systems entropy is going to be plus nR ln v 2 by v 1 why because it is equal to Q reversible by T but change in the surroundings surrounding is losing same amount of Q reversible right I write Q reversible, so change in the surrounding is exactly equal ok, so the total change of entropy for this isothermal reversible process from 1 to 2 is 0.

So for a reversible processes entropy change for system and surrounding together is going to be 0 ok, so now first so now you understand that in case of a reversible expansion process the overall change in entropy is 0 now we now let us understand what is what is happening for an irreversible process let us say 1 to 2 happens in an in reversible manner we have just seen that for the free expansion case the change in entropy of the system is going to be nR Ln v 2 by v 1 but it is an adiabatic expansion which means no heat is taken in or out, so change in the surroundings entropy is going to be zero so the total change is greater than zero.

So see that for that free expansion case the overall change in the entropy is positive overall change means system plus surrounding is positive and that is an irreversible process so we can say that for irreversible processes the change in entropy is going to be positive, if it would be reversible process then it will be equal to zero. Now let us say when there is an exchange going on and things come to an equilibrium for example you talked about a temperature differences.

So let us go back to the temperature differences, so here let us say what will happen when the temperature becomes equal? So you can clearly see when the temperature becomes equal so initially there will be a heat transfer and at some point it will come to a thermal equilibrium at thermal equilibrium your T alpha will be equal to T beta and delta s will be equal to zero from this which means that when the system will reach thermal equilibrium so it will increase the entropy spontaneous you know for a spontaneous process but when it reach equilibrium it will no longer increase it is entropy, so the entropy will be the maximum after that no more entropy change will be possible when the system comes to the equilibrium.

So at equilibrium the entropy of the system plus surrounding is highest so if the system is not in equilibrium entropy will increase it will increase, increase, increase till it reaches equilibrium once it reaches equilibrium entropy will not no longer change and therefore no spontaneous change also will happen or other way around not spontaneous change is happening therefore no more entropy changes are happening does it answer your question?

Student is answering:

Yes.

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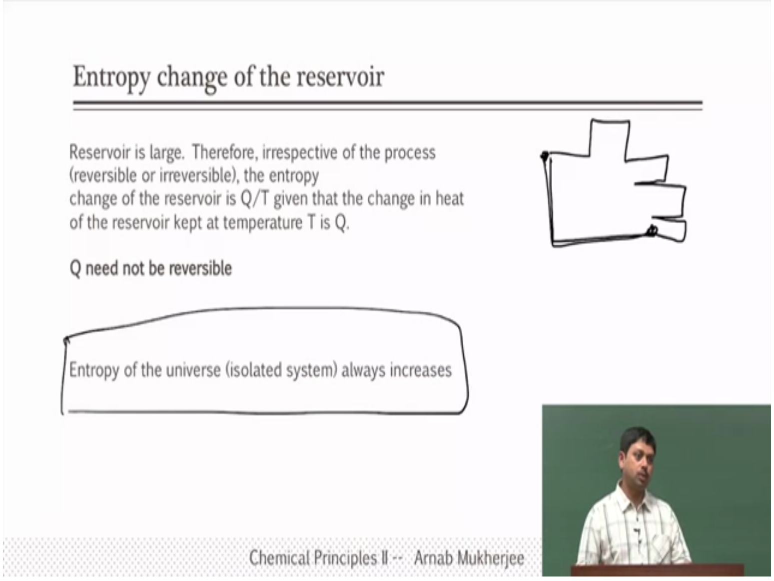

Entropy change of the reservoir

Reservoir is large. Therefore, irrespective of the process (reversible or irreversible), the entropy change of the reservoir is Q/T given that the change in heat of the reservoir kept at temperature T is Q.

Q need not be reversible

Entropy of the universe (isolated system) always increases

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Ok, so now we have seen that for irreversible processes entropy change of the system plus surrounding increases and to understand is even better we can we can say that we have already said that the this particular point that the reservoir is large therefore irrespective of the process whether it is reversible or reversible entropy change the entropy change of the reservoir is Q by T, see we said that entropy change for the system is Q reversible by T because the process has to be reversible for the system but surrounding is so big that even a chunk amount of heat changes goes out of the reservoir in it is infinitesimal for the reservoir.

So therefore you can regard that as an infinitesimal change and therefore the Q by T will be the entropy of the reservoir whereas for calculating the internal the system you have to always consider a reversible path even if the process happens irreversibly because the entropy is a state function even if the process happens reversibly you should always construct a state function it should always construct a reversible path and that path can be anything for example if I want to come from here to here I can choose this path does not matter I can choose any path it will still give you the same value of entropy because it is a state function.

So the calculation of entropy remember for the system always you will have to calculate with respect to a reversible path and when you do that as you have seen when you do that you will see that for an irreversible steps entropy of the overall thing will increase. So what it turns out then that since every process in real life is irreversible therefore a spontaneous process therefore entropy of the universe is always increasing.

So either sometimes you will decrease the entropy of the system by doing work on the system but at the expense of increasing more the entropy of the surrounding for example I know let us say a cat comes and spills coffee you said that entropy of the you know room has increased because it will be scattered everywhere or something and then you very nicely clean everything, arrange everything and things like that and you say that ok entropy of the system has decreased because you have arranged everything right but you have arranged everything at but at the same time the work that you have done that produced heat to the environment and when you sum them together you will see an overall increase of the entropy of the universe because we are part of the universe.

So whatever we do whatever you do is a spontaneous process what is a spontaneous process spontaneous process is such process in which no external influence comes in, now as far as our universe is concerned no external influence is coming in with because there is no nothing external to that so therefore everything is happening internal to the system which is a spontaneous one because there is no external influence which means since spontaneous one always increases.

The entropy which means that at every step of the way whatever you do entropy of the universe is increasing unless we reach an equilibrium point where no visible changes will take place and entropy will become maximum and that is the entropy curve when you showed with a big you know Big Bang picture that is still increasing and it will keep on increasing till our universe come to an equilibrium which is not right now.

Yeah so now we connected most of the statements of the second law of thermodynamics however you did not prove any of them because they are as we said postulates or hypotheses there is an indirect of course you always have to start with one hypothesis to in order to prove any of that remember that one is an observation you know that we see an Apple falls down from a tree there is an observation and you know you put a hypothesis by based on Newton is equations and it works in other cases then you know you modify you know you bring in quantum mechanics you put some hypothesis and you say that ok it can explain you know the spectra it can explain the transition and then he say ok the hypothesis must have been correct you see an observation that heat transfers from high to low always and never the other way round spontaneously which means that automatically we put a law and then see that never gets violated and that is how you kind of state.

So you always start with the hypothesis and then you see that that hypothesis holds true in all other things or not because you have to start from somewhere and similarly we will see that when you go to statistical thermodynamics we start with the hypothesis and that hypothesis will be able to explain all these macroscopic changes that we see through in terms of the microscopic motions we can we will be able to understand why heat transfers only from high temperature to low temperature spontaneously and all other things that we all why the interview of the universe always increases from microscopic point of view itself.

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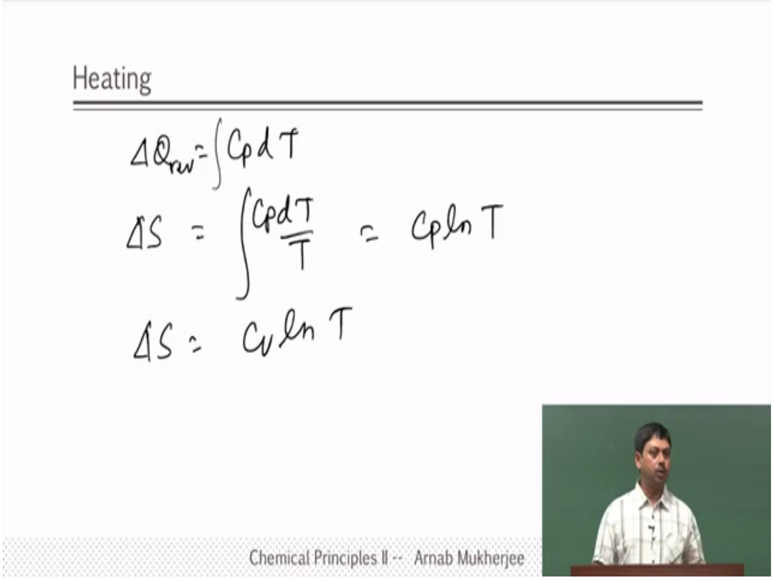

Heating

$$\Delta Q_{rev} = \int C_p \, dT$$

$$\Delta S = \int \frac{C_p \, dT}{T} = C_p \ln T$$

$$\Delta S = C_v \ln T$$

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So how does we talk about (cha) you know change in entropy for heating for example so heating can be heat is what delta Q is delta Q reversible is either C P d T or C V d T right, so entropy change at a constant pressure will be C P d T by T integration of that and if C P is taken to be constant it will be C P ln t ok and for a constant volume process therefore it will be CV Ln T that is a change in entropy due to heating.

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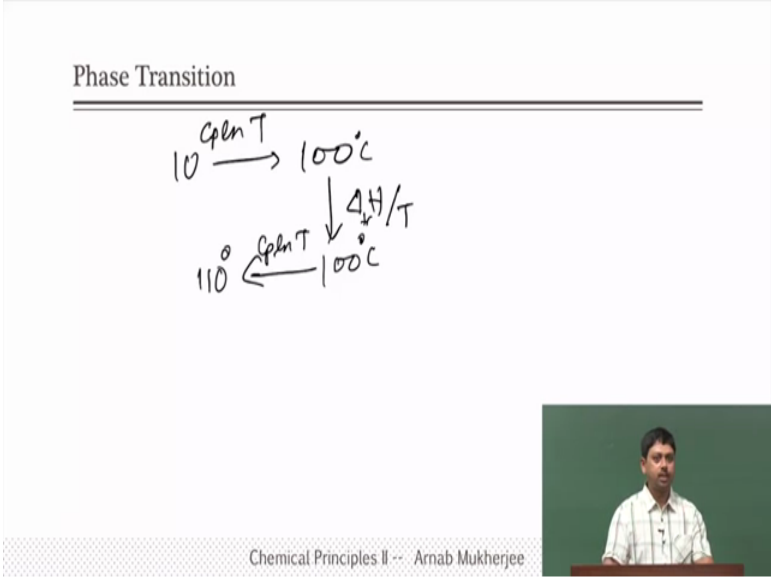

Phase Transition

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Phase transition now let us say there can be problems associated when you say that ok what is the change in entropy for converting water from let us say 10 degree centigrade to a vapor of 110 degree centigrade, so which means that you are heating the system you are heating the water from 10 degree 200 degree first water only and that at 100 degree you are using a delta H enthalpy we talked about heat of formation and heat of transition, so here you are using heat of transition from 100 degree centigrade water to vapor at 100 degree and then again you are hitting the system so here we are using CP ln T, here you are using so now delta H you know is nothing but the Q heat at a constant pressure right.

So which means that entropy change is Delta H by T, I will say tr transition and then again we are using CP ln T from going from 101 to 110 degree centigrade is it understandable this way. So in three steps overall we sum it up and we can get an entropy is you know is additive quantities extensive variable so entropy of system A and entropy of the system B when you put them together it will be a plus B just like volume.

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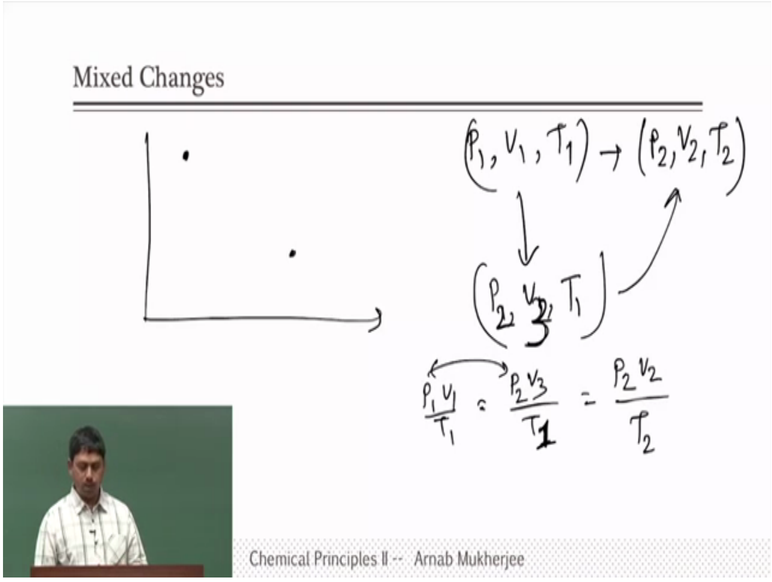

Mixed Changes

$$(P_1, V_1, T_1) \rightarrow (P_2, V_2, T_2)$$

$$(P_2, V_3, T_1)$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_3}{T_1} = \frac{P_2 V_2}{T_2}$$

Chemical Principles II -- Arnab Mukherjee

Mixed changes if you have let us say we talked about change in pressure volume thing but let us say you have change in both temperature and pressure, so let us say you are having both temperature so let us say you are going from P 1 V 1 T 1 to P 2 V 2 and T 2 in one step you it is not possible to go so what you should do is that? First construct an isothermal process P 1 V 1 or P 1 V 2 T 1 this process we can easily calculate the entropy because it is an expansion process or you can go to yeah P 2 V 2 T 1.

So it is an isothermal process for which you we know how to calculate the entropy right we can it is just Kb I know nR ln V 2 i V 1 and then from here to here it is a constant pressure heating process but ok let me just see this so this is P1 V1 to come to P 2 V 2 of course there will be you know we can say P 3 V 3 because all of them will not be equal of course because if two are they equal then third has to be equal so I said P 2 V 3 T 1 you understood why I did that because I am changing the pressure P 1 to P 2 and keeping the temperature constant so volume must be different and from here my temperature is different, my pressure is constant so volume must be different because if two of them are equal then third is dependent on the other two ok.

So it so it is like P 1 V 1 by T 1 is equal to P 2 V 3 by T 2 is equal to P 2 V 2 by ok sorry T 1 so you see here P 1 changes therefore V 1 must change and you see here P 2 is the same so V 3 changes so therefore temperature must change you cannot have two of them same because the third one will depend on that anyway so point is that in that case we can always construct multiple path in order to calculate those mix changes that way what will happen is that it will still be getting the same result although we are doing it in two steps.