Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 06
Second Law of Thermodynamics (Contd.)
Entropy Change During Spontaneous Processes

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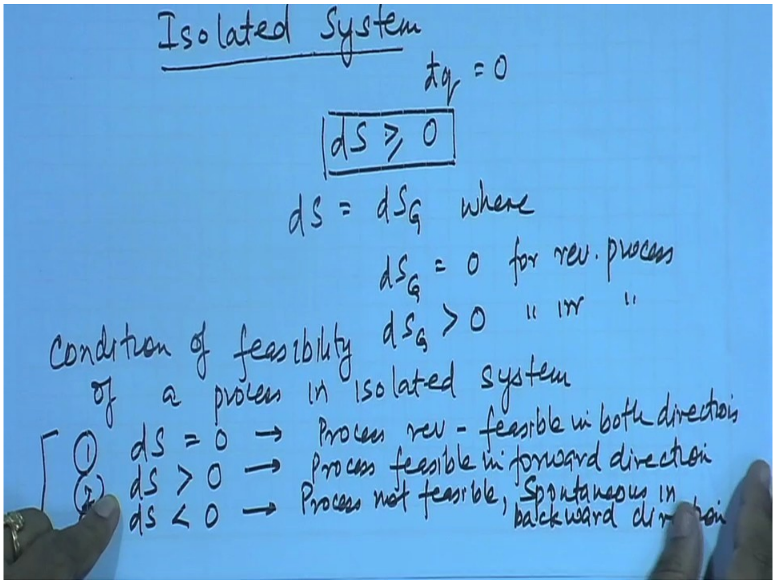

Isolated System

$đq = 0$

$\boxed{dS \geq 0}$

$dS = dS_G$ where

$dS_G = 0$ for rev. process

$dS_G > 0$ " irr "

Condition of feasibility of a process in isolated system

① $dS = 0 \rightarrow$ Process rev - feasible in both directions

② $dS > 0 \rightarrow$ Process feasible in forward direction

③ $dS < 0 \rightarrow$ Process not feasible, Spontaneous in backward direction

Well, so in the last class we had concluded with this particular slide where we had shown you the criteria of spontaneity of a process. So therefore in an isolated system how you going to find out whether a process is going to be possible you are going to calculate the entropy of the process. Now for calculation of the entropy we need to remember that the entropy is equal to the heat interaction divided by the temperature at which the interaction occurs only when the interaction occurs along a reversible path.

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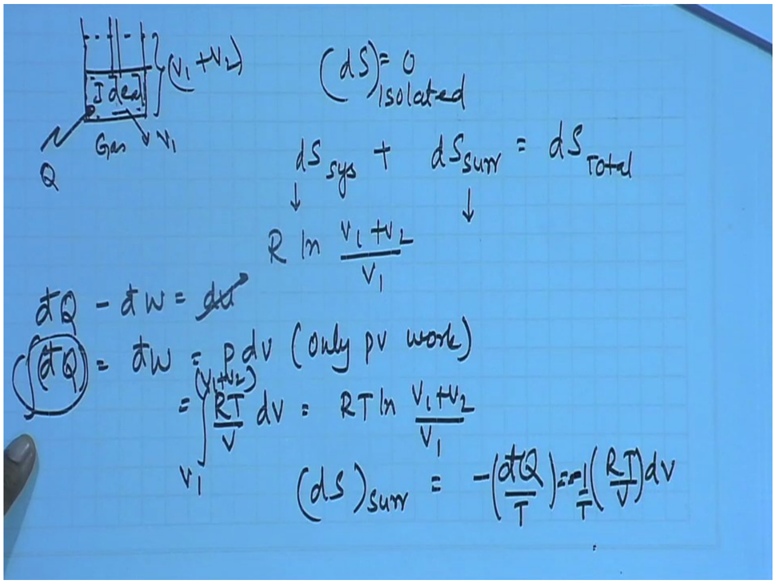

$$(dS)_{\text{Isolated}} = 0$$

$$dS_{sys} + dS_{surr} = dS_{Total}$$

$$dS_{sys} \downarrow \; R \ln \frac{V_1+V_2}{V_1}$$

$$đQ - đW = \cancel{dU}$$

$$\int \boxed{đQ} = đW = P\,dV \text{ (only pv work)}$$

$$= \int_{V_1}^{(V_1+V_2)} \frac{RT}{V}\,dV = RT \ln \frac{V_1+V_2}{V_1}$$

$$(dS)_{surr} = -\left(\frac{đQ}{T}\right) = -\frac{1}{T}\left(\frac{RT}{V}\right)dV$$

Or in other words we know that dS can be evaluated from dq by T provided the path is a reversible path it can be any Dem path but it has to be a reversible path but once the entropy change has been calculated along a reversible path even between the same 2 initial and final state if the system undergoes an irreversible path also the entropy change will be the same because it depends just on the initial and final states.

What I mean to say is that along an F-r plot suppose the system moves from state one to state 2, I would like to know or rather I would like to take a system from state 1 to state 2, I would like to know whether this particular process is possible or not or am I going to find out whether this process is possible.

What I will do? I will try to find out the entropy change which the system undergoes when it moves from state 1 to 2. Now in order to find out the entropy change between state 1 and 2 or in order to find out s2 minus s1 what do I need to do? I need to connect these 2 states by a reversible path, a reversible path may be fictitious it may not have any particular connection where the actual irreversible path which the system had followed in moving from state one to state 2 but we calculate the entropy change along this reversible path and it is important to remember that the entropy change along the irreversible path is also the same.

For example let us take up a very few common example which I had shown to you in the last to last class that these processes are feasible and the other reverse process is not feasible and I had taken up 3 examples, what were the 3 examples?

The first example was free expansion, okay. In this particular case what did I do? There was a cylinder which is broken by or rather which is divided by a partition and it is surrounded by an adiabat an insulated wall such that no heat transfer from the surrounding occurs and I had some amount of gas which was concentrated here at within the volume V1 and then this particular partition was removed and the entire gas expanded and occupied the entire, sorry this volume is V2 the gas occupied the entire volume V1 plus V2.

We know that this is an spontaneous process but the reverse is not spontaneous, so therefore if this process has to occur then definitely this must be accompanied by an increase in the entropy. Let us see whether it happens or not or in other words how to calculate the entropy change of this particular process of the gas expanding from a volume V1 to a volume V1 plus V2 when it is kept enclosed in a adiabatic container.

What is, we have to first consider the initial and final states of the system what was the initial state of the system? Initial state of the system was gas at V1 and say some particular temperature T, what was the final state of the system? It was the same gas which has occupied the volume V1 plus V2 and it was under the same temperature T and the process was adiabatic. I want to calculate the entropy change of the process what should I be doing?

I should devise a reversible path connecting the initial state and the final state now they are connected by an adiabatic process, can you tell me what should be the equivalent reversible path connecting these 2? We find that from this state to this state the temperature remains constant and there is a volume expansion.

Can we assume that the equivalent reversible path can be a reversible isothermal process? During which gas undergoes expansion from V1 to V1 plus V2, please note that this reversible isothermal process is not adiabatic but this is an equivalent reversible process connecting the same 2 initial and final states which the gas had during the actual adiabatic free expansion process. Now if we try to calculate the entropy along this reversible isothermal process.

What will be dS equals to? This is nothing but equal to dq by T, what is dq by T? This is nothing but dU plus PdV by T. Now suppose we assume an ideal gas, right? For an ideal gas will be proving later but for the time being it is sufficient for you to know that for an ideal gas U is a function of T only, right? And this is given by CvdT, so therefore since the temperature remains constant dU for this case should be equal to 0 and therefore dS should be equal to PdV by T.

Suppose it is an ideal gas then for this particular case what do we have? We have R by V dV, so therefore what dS equals to in this particular case or integral dS from say state 1 to state 2 this should be equal to R by V dV from state 1, so the volume is V1 to V1 plus V2 or in other word this is equals to R ln V1 plus V2 by V1 and as we know this is nothing but greater than 0. So now do you understand that why free expansion is a spontaneous process?

Because the entropy generated in the process is greater than 0 in order to calculate the entropy generated we had devised a reversible isothermal process connecting the initial and final states which had no connection with the actual process which took place but it was an equivalent reversible process which was connecting the same initial and the same final states we connected the entropy change via the reversible process related the entropy change to the actual irreversible process which had occurred and then found out that the process occurred because the entropy change was greater than 0.

Now I have one question for you suppose the gas would have actually undergone a reversible adiabatic process then in that case we find that entropy change is greater than 0, where is the anomaly? I have told you that in this case the gas undergoes a reversible process, if the gas undergoes a reversible process than dS should be equal to 0 but I find that for a reversible adiabatic process dS is greater than 0, how do you explain this anomaly?

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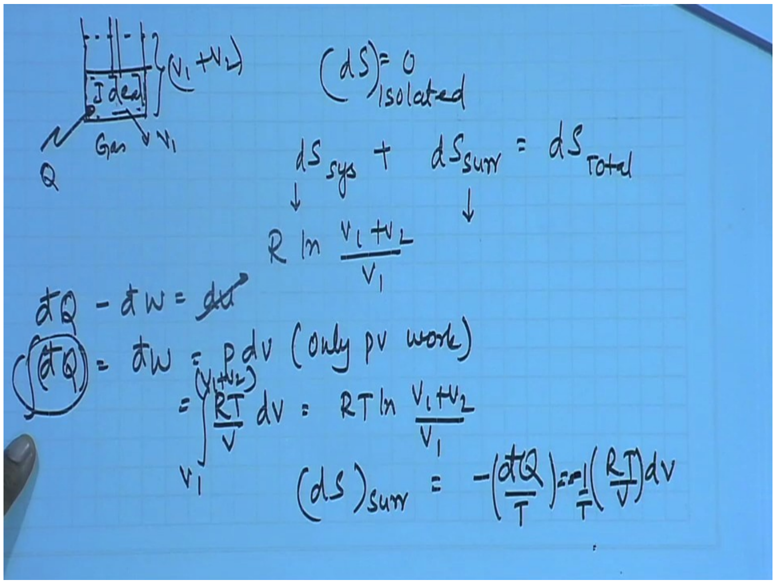

$(dS)_{\text{Isolated}} = 0$

$dS_{sys} + dS_{surr} = dS_{Total}$

$\downarrow \quad R \ln \frac{V_1+V_2}{V_1}$

$\text{đ}Q - \text{đ}W = \cancel{dU}$

$\int \text{đ}Q = \text{đ}W = P\,dv$ (only pv work)

$= \int_{V_1}^{(V_1+V_2)} \frac{RT}{V}\,dv = RT \ln \frac{V_1+V_2}{V_1}$

$(ds)_{surr} = -\left(\frac{\text{đ}Q}{T}\right) = -\frac{1}{T}\left(\frac{RT}{V}\right)dv$

In this case try to consider what happens this is the gas and this particular ideal gas it is occupying a volume V1 and it is undergoing a reversible expansion and it has finally the final volume is V1 plus V2, right? From this particular initial state to this particular final state it had undergone a reversible process, now during this reversible isothermal process in order to maintain a constant temperature what was necessary?

It was necessary that some amount of heat was introduced or rather some amount of heat was flowing into the process due to which the gas expanded and from initial volume V1 it went to initial volume V1 plus V2. So therefore since heat was flowing inside this along with the change in the entropy of the system which in this case is the ideal gas confined within this cylinder there must be some entropy change in the surrounding as well from which heat was flowing into this particular gas.

So therefore when I had said that dS equal to 0 this was for an isolated system. So therefore in order to calculate the entropy change for this particular system I need to find out the dS of this system and I need to find out the dS of the surroundings and then the total dS the sign of the total dS is going to decide whether the process is going to be reversible or not.

Now we know what is dS of this system? We have already calculate this is Rln V1 plus V2 by V1. Let us see what is dS surrounding? Why is the entropy changing in the surrounding? Because heat is flowing from the surrounding into the system, what is amount of heat which is flowing? This amount of heat is leading to this particular amount of change. So therefore from first law we know that the amount of heat which has entered minus the amount of work which has been done is equal to the change in internal energy of the gas.

In this case since the gas is at constant pressure dU equals to 0, as a result of which dq equals to dW and since there is only Pv work associated here, dW is PdV since only Pv work is associated here, so therefore this is RT by V dV and therefore in this particular case we find that the amount of heat which has flown from the surrounding is equal to RT by v dV and what is the total amount of heat which has flown from the surrounding into the system? This is equal to V1 to V1 plus V2 or in other words this is equal to RT ln V1 plus V2 by V1, agreed?

Now what is the entropy change of the surroundings then? We need to remember that this amount of heat has flown into the system, so since it has flown into the system it has a positive sign but if we consider the surrounding as a system then the surrounding is losing this amount of heat, so therefore for this particular case dS surrounding is minus dQ by T where this dQ is equal to RT by v dV, 1 by T and there is a minus sign here.

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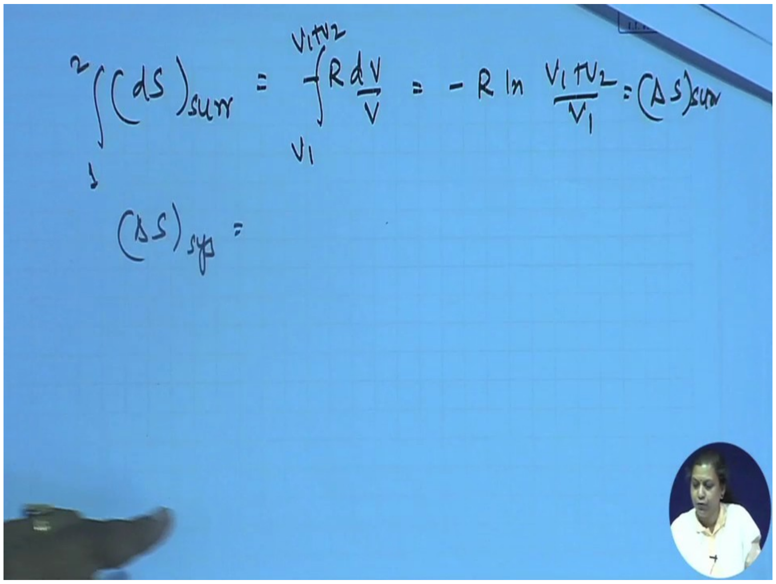

$$\int_1^2 (dS)_{surr} = -\int_{V_1}^{V_1+V_2} R\frac{dV}{V} = -R\ln\frac{V_1+V_2}{V_1} = (\Delta S)_{surr}$$

$$(\Delta S)_{sys} =$$

So therefore if we need to calculate dS surrounding then what do we need to do? The dS surrounding again let me repeat it and let me write it down, dS surrounding is nothing but equal to minus Rdv by V and from state 1 to state 2 the change is from V1 to V1 plus V2 as a result of which this is minus R ln V1 plus V2 by V1. So therefore this is dS this is nothing but Delta S surroundings and we have already calculated Delta S system earlier.

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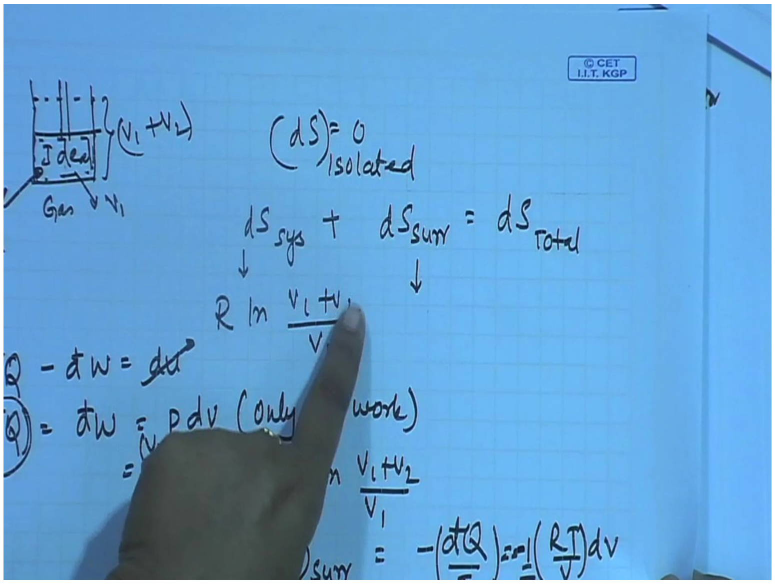

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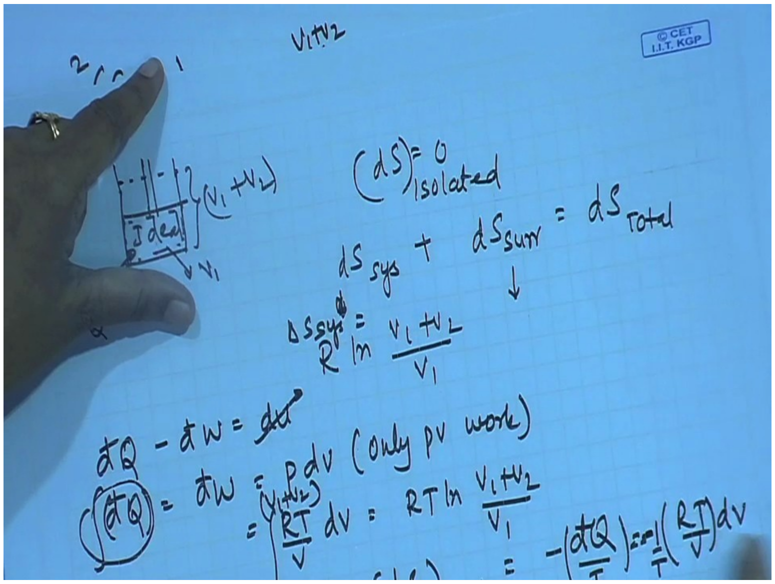

If you remember Delta S system was equal to R ln this particular thing, this actually should be delta S system.

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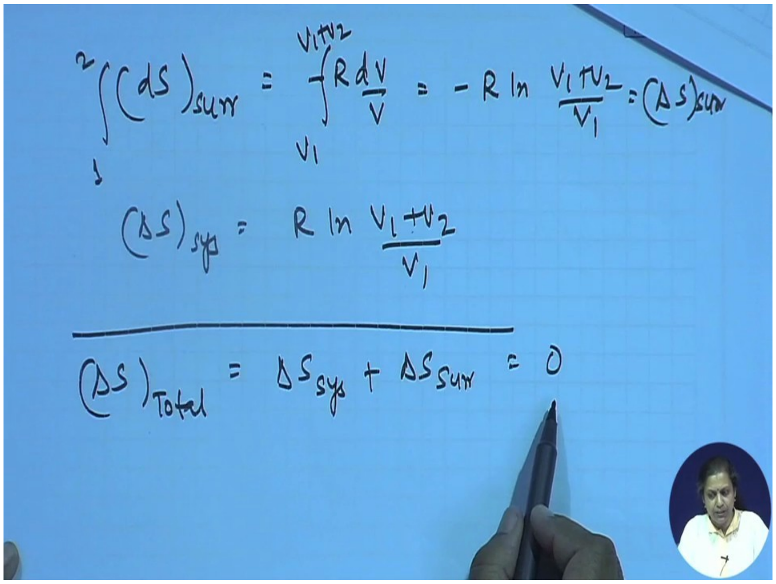

$$\int_1^2 (dS)_{surr} = -\int_{V_1}^{V_1+V_2} R\frac{dV}{V} = -R\ln\frac{V_1+V_2}{V_1} = (\Delta S)_{surr}$$

$$(\Delta S)_{sys} = R\ln\frac{V_1+V_2}{V_1}$$

$$(\Delta S)_{Total} = \Delta S_{sys} + \Delta S_{surr} = 0$$

So therefore Delta S system this is equals to R ln V1 plus V2 by V1. So therefore if we add the 2 what do we get? We get Delta S total we assume that the system plus surrounding comprises of an isolated system. So this is equal to Delta S system plus Delta S surrounding which is nothing but equal to 0 which shows that a reversible isothermal process has 0 entropy change but a free expansion it has a positive energy change.

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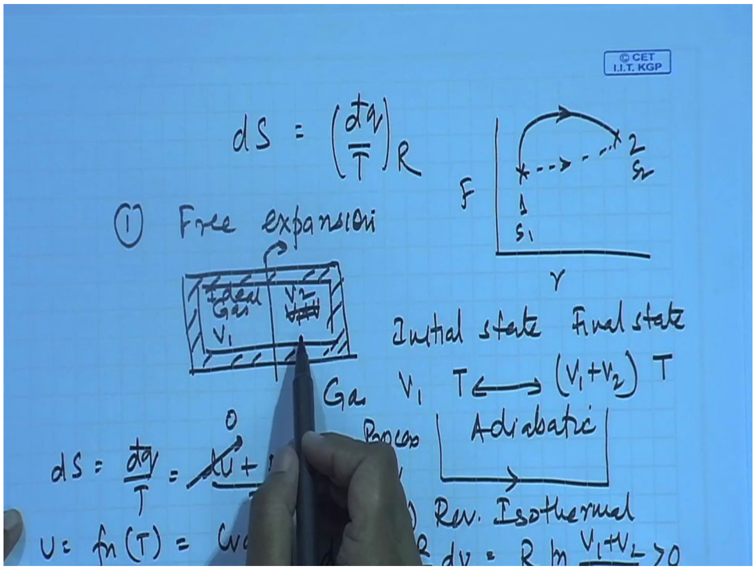

$$dS = \left(\frac{dq}{T}\right)_R$$

① Free expansion

Initial state Final state

Gas V_1 $T \longleftrightarrow (V_1+V_2)$ T

Process Adiabatic

$dS = \frac{dq}{T} = \overset{0}{\cancel{dU}} +$

$U = fn(T) = Cv$

) Rev. Isothermal

$R\,dv = R\ln\frac{V_1+V_2}{} > 0$

We need to remember that since the container was insulated in this particular case, so therefore for this particular case dS surrounding was equal to 0. So therefore dS total was equal to dS system which is this.

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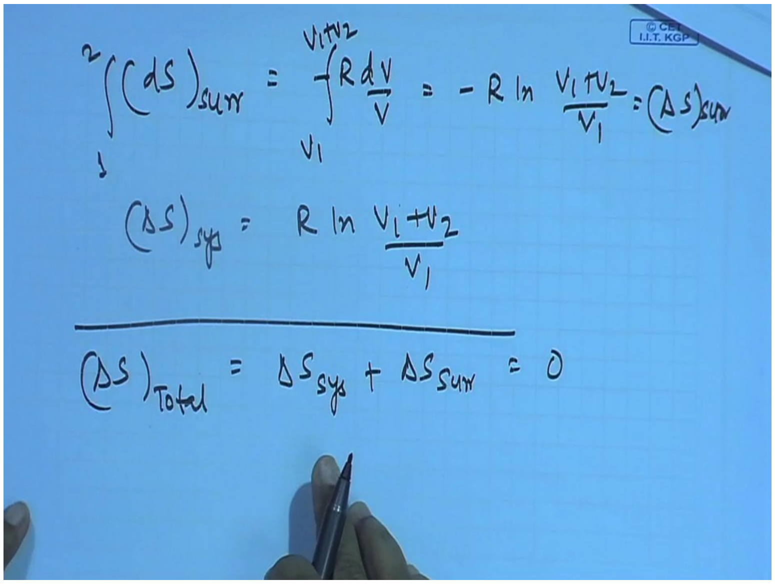

$$\int_1^2 (dS)_{surr} = -\int_{V_1}^{V_1+V_2} R\frac{dV}{V} = -R\ln\frac{V_1+V_2}{V_1} = (\Delta S)_{surr}$$

$$(\Delta S)_{sys} = R\ln\frac{V_1+V_2}{V_1}$$

$$(\Delta S)_{Total} = \Delta S_{sys} + \Delta S_{surr} = 0$$

This explains why free expansion as well as a reversible isothermal process both have the same entropy change of the system but one of them is feasible the other in one direction the reverse is not possible and the reversible isothermal process is possible in both the directions. So by this example I tried to show a number of things, first thing which I tried to show was that how to devise a reversible path and how to calculate the entropy change for any particular irreversible process.

The second thing which I showed was the entropy change I proved that the entropy change is greater than 0 for a very well known irreversible process and the entropy change is equal to 0 for a reversible process but we had to remember in this process that the entropy change had to be calculated for both the system and the surroundings because the feasibility that we had proposed in terms of entropy change was for an isolated system.

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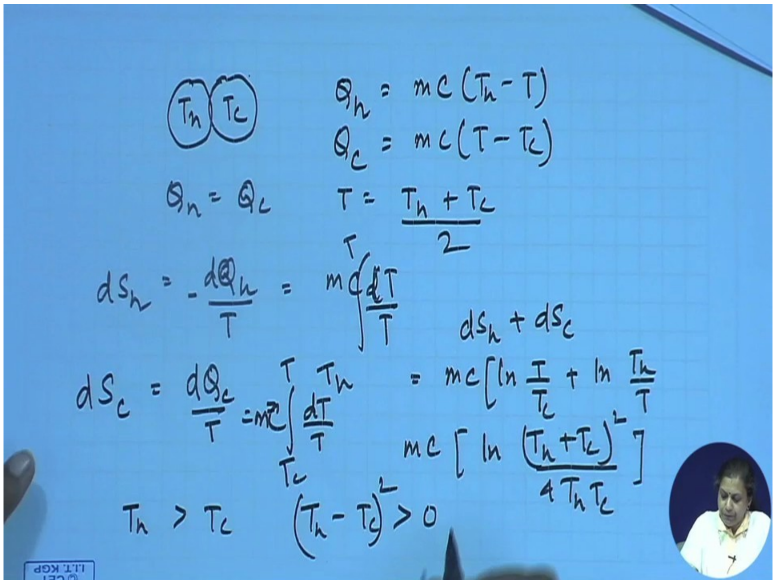

Now there is also one more very common example which I was discussing in the last class that we had two copper balls one was at 20 degrees, 30 degrees we brought them together and the temperature was 25 degrees I said that the this particular process is possible the reverse one is not possible. So let us see why this happens two identical balls one is at Th one is at Tc, right? Now when both of them are brought in contact with one another Q lost by the hot body that is mC Th minus T, Q gained by the cold body naturally this is plus and this is minus we have mC T minus Tc, we know that under thermal equilibrium conditions Qh equals to Qc as a result of which T equals to Th plus Tc by 2.

Now let us see that in this spontaneous process what is the entropy change? Now we can assume that this particular composite system comprising of the 2 bodies is an isolated system because whatever heat it is giving the same heat is being taken up by the cold body and we assume that there are no heat losses to the surroundings. So therefore this particular unit can be assumed as an isolated system. Now let us take up the entropy change of the hot body this is nothing but equal to dQh by T what is Qh? This is mCdT by T where T is varying from Th to T.

What is dS for the cold body? This should be minus this should be plus. So therefore this is dQc by T which is nothing but equal to integral of Tc to T, dT by T mC, what is the total entropy change? dSh plus dSc this will be equal to mC ln T by Tc plus ln Th by T or in other words this is going to be ln Th plus Tc whole square by 4 Tc, isn't it? So therefore from this what do we get?

From this we get that this is the total entropy change which has occurred in this particular process?

Now let us see the sign of this how can we see it? We know Th is greater than Tc, so therefore Th minus Tc has to be greater than 0. So therefore Th minus Tc whole square has to be greater than 0.

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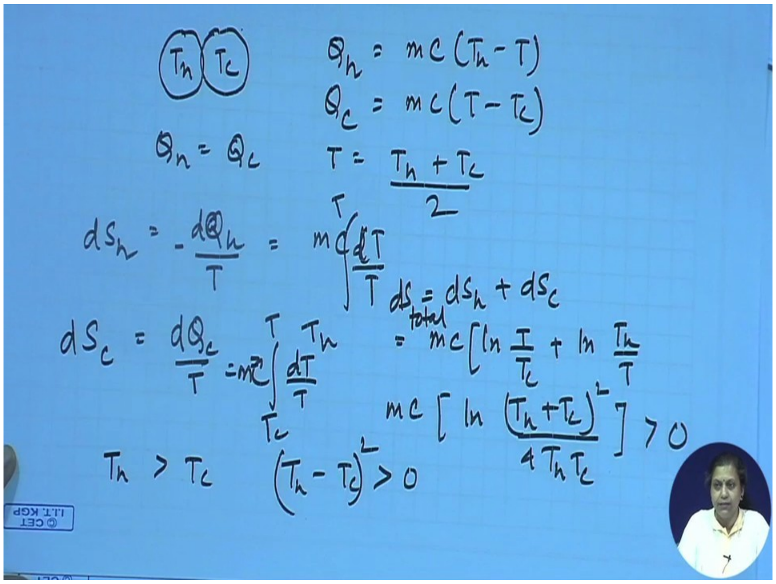

$Q_h = mc(T_h - T)$

$Q_c = mc(T - T_c)$

$Q_h = Q_c$

$T = \frac{T_h + T_c}{2}$

$dS_h = -\frac{dQ_h}{T} = mc\int^{T}\frac{dT}{T}$

$dS_c = \frac{dQ_c}{T} = mc\int_{T_c}^{T}\frac{dT}{T}$ T_h

$dS_{total} = dS_h + dS_c$

$= mc\left[\ln\frac{T}{T_c} + \ln\frac{T_h}{T}\right]$

$mc\left[\ln\frac{(T_h+T_c)^2}{4T_hT_c}\right] > 0$

$T_h > T_c$ $(T_h - T_c)^2 > 0$

Or in other words Th square plus Tc square minus 2ThTc has to be greater than 0. I add a 4 Th Tc and I add 4 Th Tc this side what do I get? I get Th plus Tc whole square is greater than 4 Th Tc or in other words what do I get? I get the denominator is greater than the numerator as a result of which the total dS total for this system is greater than 0.

What did I assume in this process? I assumed that there are no heat losses to the surroundings and the heat transfer which was occurring that occurred so very slowly that we can assume a we can assume that the heat transfer was occurring irreversibly, right?

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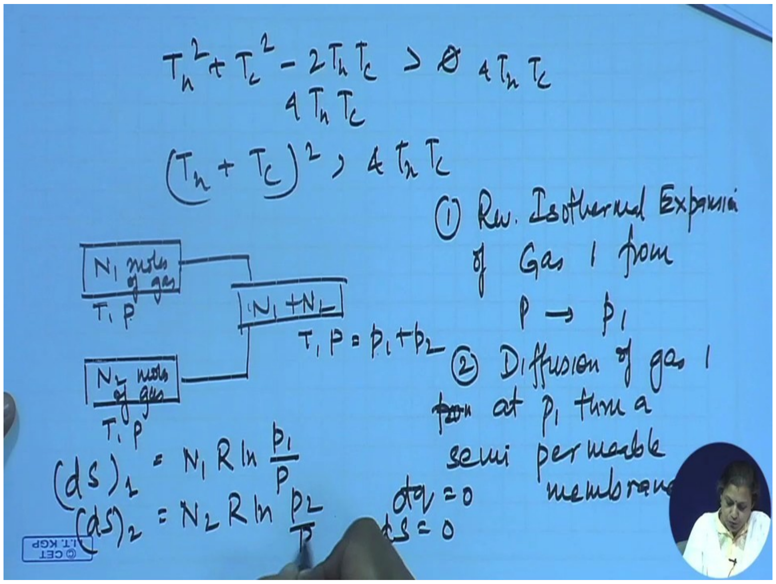

$T_h^2 + T_c^2 - 2T_hT_c > \cancel{0}\ 4T_hT_c$

$4T_hT_c$

$(T_h + T_c)^2 > 4T_hT_c$

① Rev. Isothermal Expansi of Gas 1 from $P \rightarrow p_1$

② Diffusion of gas 1 ~~from~~ at p_1 thru a semi permeable membran

$(dS)_1 = N_1 R \ln \frac{p_1}{P}$

$(dS)_2 = N_2 R \ln \frac{p_2}{P}$

$dq = 0$

$dS = 0$

So therefore from these 2 processes what I had deduced is, there was another process which I leave you as an exercise the mixing of 2 ideal gases. In this particular case also yesterday I had discussed, so this particular example is present in a large number of textbooks so I will not go into details of this suppose we have N1 moles of a gas, right?

And I have N2 moles of another gas, okay. I simply mix them up and we will find they spontaneously mix up to give me N1 plus N2 moles of the gas but if I have N1 plus N2 moles of gas then they do not spontaneously unmix to form this, so therefore this also should be a spontaneous process in order to find whether it is spontaneous or not what do we need to do? We need to find out the entropy changes which occurred during the process.

In order to find entropy change we need to devise a reversible path, what should be the reversible path in this particular case? Just see the process for the gas 1, what happens? There were N1 moles of gas at a temperature T, pressure P and then it gets mixed up here, right? For this final state also the temperature was T the pressure was P.

But remember one thing this pressure of P here was for N1 plus N2 moles of gas it was but in this case the pressure P was just for N1 moles of gas, so therefore actually what did this gas do in the process of mixing?

It expanded from the total pressure P to a partial pressure P1 in this particular case and the gas 2 it expanded from a total pressure P to the partial pressure P2, such that P was equal to P1 plus P2 this was the exact process which takes place during the mixing of the 2 gases both the gases they expand from the total pressure to the partial pressures such that the partial pressures when added up gives the total pressure.

So in this particular case also what can be the reversible path? The reversible path in this particular case is the reversible again the temperatures are all constant, so in this particular path this particular process we can assume that there are 2 reversible processes comprising the whole system of the mixing of gases the first process is reversible isothermal expansion of gas 1 from P to P1 and then we assume that there is a semi permeable membrane here through which the gas 1 after expanding it just diffuses into this particular container, right?

So therefore diffusion of gas 1 at P1 through a semi permeable membrane, right? Now since in this particular case there is no amount of heat interaction so for this particular case we can assume dq equals to 0 and dS equals to 0 and for reversible isothermal expansion we have already deduced the entropy change the same thing happens for gas 2 as well so therefore in this particular case we will find that the dS for the gas 1 this can be given by N1 R ln P1 by P and dS for the gas 2 is N2 R ln P2 by P.

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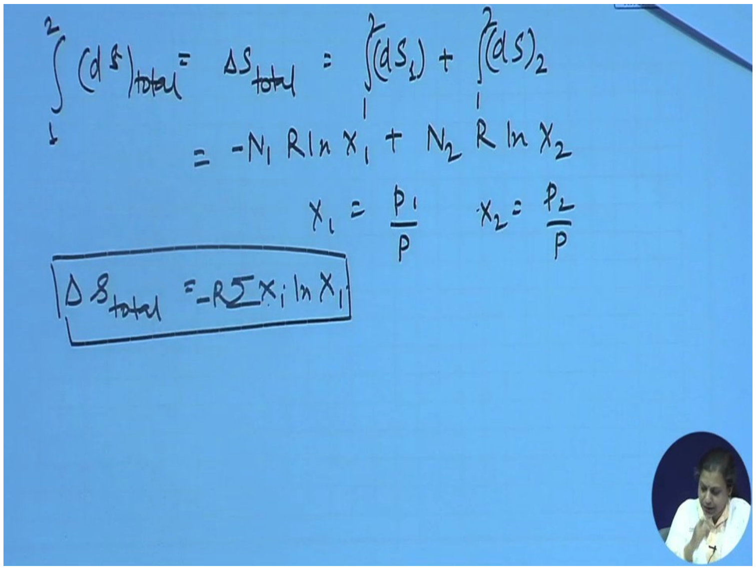

$$\int_1^2 (dS)_{total} = \Delta S_{total} = \int_1^2 (dS_1) + \int_1^2 (dS)_2$$

$$= -N_1 R \ln x_1 + N_2 R \ln x_2$$

$$x_1 = \frac{p_1}{P} \quad x_2 = \frac{p_2}{P}$$

$$\boxed{\Delta S_{total} = -R \Sigma x_i \ln x_1}$$

As a result of which we find that for this particular case the dS total of the gas integrating from state 1 to state 2 which gives you Delta S total is integral 1 to 2 dS for gas 1 plus integral 1 to 2 dS for gas 2 and we know that this is nothing but equal to N1 R ln X1 plus N2 R ln X2 where X1 is nothing but equal to P1 by P, X2 is nothing but equal to P2 by P, right? And therefore if we would like to calculate the molar enthalpy the total molar change in the molar entropy of the system then we get this is nothing but equal to Sigma Xi R Sigma Xi ln Xi.

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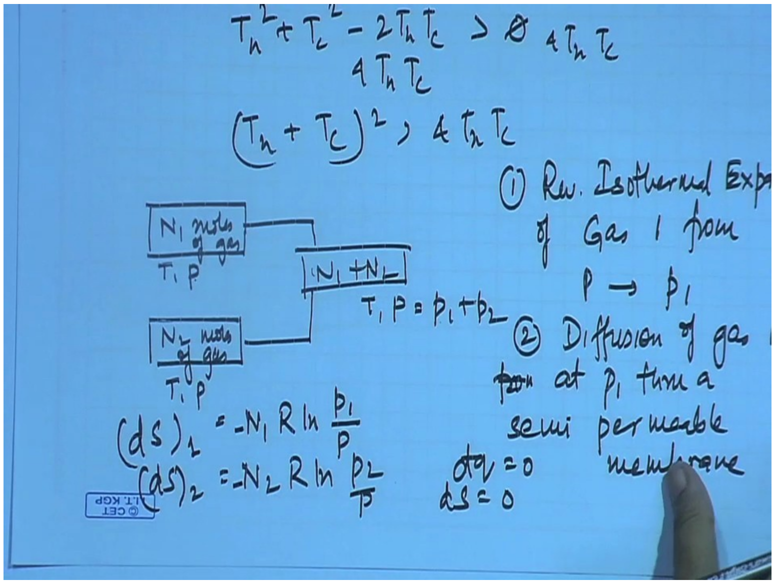

So therefore the molar entropy change of mixing of a large number of gases is nothing but R Sigma Xi ln Xi and since we know that sorry minus there is going to be a minus sign here very sorry because it is V1by V2 so I missed out a minus sign in everything so therefore this has to be a minus here.

So we find that since ln Xi is less than one so therefore this particular term for mixing of several non-identical gases that is greater than 0 and that is why mixing of gases it is a spontaneous process unlike the un-mixing of gases which is not a spontaneous process. So with this I think I have completed my discussions on entropy. There are several other aspects of entropy which you need to consider for an example how entropy is a measure of the randomness of the, it gives the measure of the extent of randomness of a particular system.

How it is related to the thermodynamic probability of the system? How entropy is related to the available energy of the system but I am not going to go into the details of all those things because they do not pertain to phase equilibrium thermodynamics you can go through it through any particular textbook and in case you have doubts on those particular topics we can take them up in the interactive courses but as far as the assessment of this course or the assignments of this course are concerned they will just be concentrated on the topics which you are covering in this particular class.

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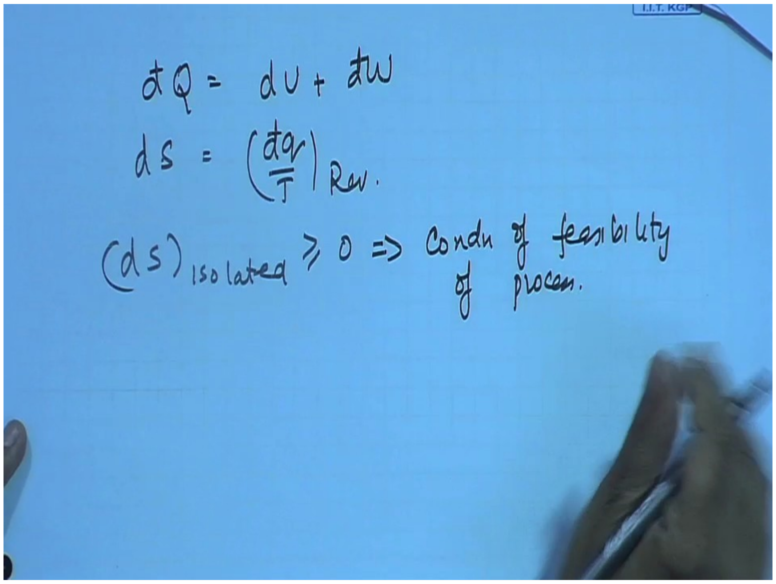

$$đQ = dU + đW$$

$$dS = \left(\frac{đQ}{T}\right)_{Rev.}$$

$(dS)_{isolated} \geq 0 \Rightarrow$ Condn of feasibility of process.

So with this we complete the first and second law and what we have found out rather where we have come up is from the first law of thermodynamics we have got dQ equals to dU plus dW and the other equation is dS equals to dQ by T for a reversible process. We have also found dS for an isolated system is greater than equal to 0 which gives the condition of feasibility of a process. So with this I end this class and we are going to discuss much more interesting results arising from the equations or arising from the combined first and second law which we have discussed so long, thank you very much.