Introduction to Chemical Thermodynamics and Kinetics

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Lecture - 12

Second law – part 2

So, let us discuss something more about the Carnot cycle and we are right. Now, going to discuss the spontaneity and equilibrium or the direction of spontaneity and equilibrium based on our previous discussion on Carnot cycle.

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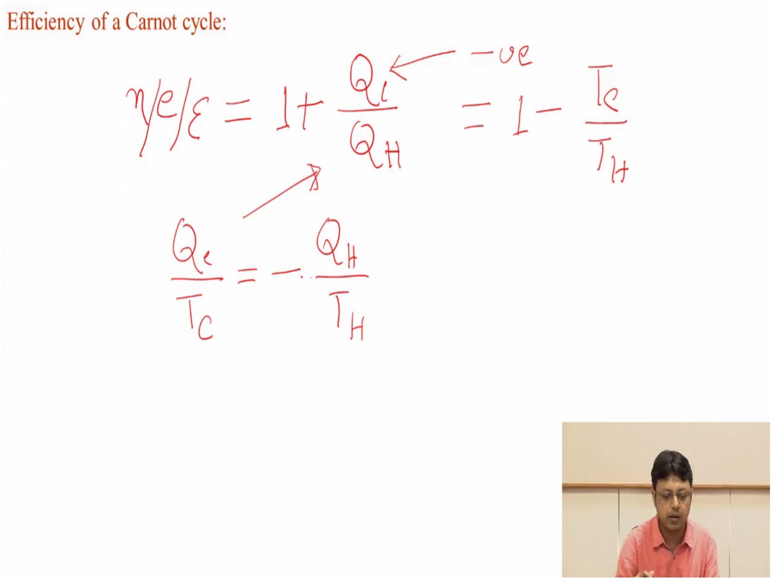

Efficiency of a Carnot cycle:

$$\eta/e/\varepsilon = 1 + \frac{Q_c}{Q_H} = 1 - \frac{T_c}{T_H}$$

−ve

$$\frac{Q_c}{T_c} = -\frac{Q_H}{T_H}$$

Now, remember that for a Carnot cycle the efficiency which is written as eta or E some textbook write it as epsilon and we wrote it as 1 minus Q C which is the heat deposited in the cold reservoir divided by Q H which is the heat withdrawn from the hot reservoir, but some textbook use the convention that they write plus with the understanding that Q C is negative here. However, whichever way you write it the expression with respect to the temperature of the hot and cold part should be always equal to T C and T H. So, the expression will be 1 minus T C by T H. If you use this convention that Q C inherently as a negative sign then you will figure out a relationship like Q C by T C is equal to minus we discussed it yesterday instead of plus actually will have a minus sign here and then you can easily get to this relationship this is just a matter of convention.

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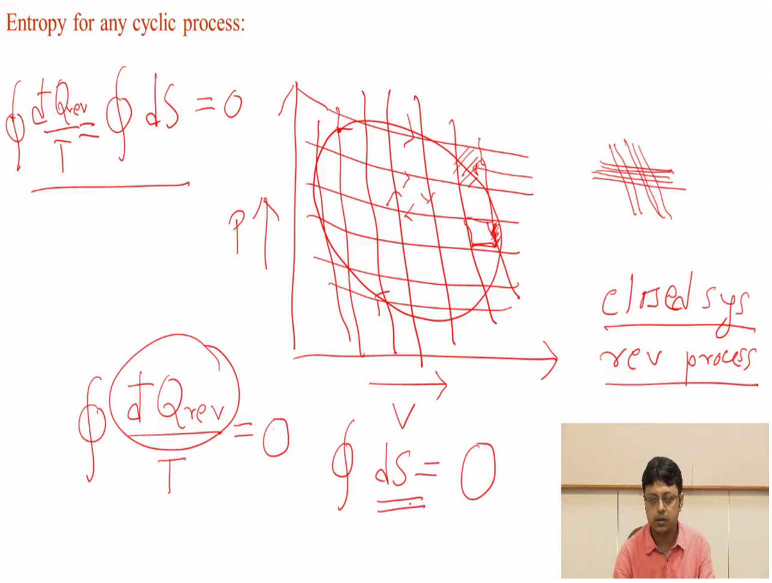

Entropy for any cyclic process:

$$\oint \frac{đQ_{rev}}{T} = \oint dS = 0$$

$$\oint \frac{đQ_{rev}}{T} = 0$$

$$\oint dS = 0$$

Now, we will discuss what happens for any cyclic process, we said that for at least for a Carnot cycle the entropy change was 0 and by entropy we define this quantity which is d cross Q reversible by T. Now from that we concluded that ace is a state function or dS is an exact differential, but this we showed only for Carnot cycle. Now, what happens for any general cycle or any general cyclic process? Now, you can think that we can write any arbitrary cyclic process in the pressure volume diagram like say this is a cyclic process, where we start from some initial state and come back to some initial state, of course, I mean the initial state can be chosen at any point.

Now, let us consider a series of parallel adiabats and also a series of say parallel isotherms. So, you can see from this diagram that this entire area which is basically equivalent to the work done can be divided or subdivided into small Carnot cycle. Now, you can have an error which is incorporated for say, for example, this Carnot cycle where we will have some area outside the closed loop which was our original arbitrary cycle. However, you can imagine that if you make this difference or between these adiabats and the isotherms, infinitesimally smaller then you can actually minimize this error and in the very large limit or large number of adiabats and isotherm you can show that the increase in the area for this cycle is actually compensated. For example, by the decrease in area for some other circle which is for example, here, I am considering only this area, however, some areas exploded.

So, by logic we can always say that for any cyclic process if we take the quantity which is d Q reversible or the reversible heat change at constant temperature that will be always equal to 0 or dS is always equal to 0 or ace is a state function. Now, this remember eased for what is the condition for a closed system, for an open system that does not hold because for open system the mass is continuously exchanged, so, it is a closed system that can exchange only energy in the form of heat with the surrounding and also it can perform or work or surrounding can also perform our work on the system and also the second thing we consider that it is a reversible process. If the reversibility is not maintained, then we cannot write this equation, because remember this is the heat withdrawn in the reversible process.

Now, this is very important that dS is identical to the heat withdrawn for the reversible process. So, the automatic question that comes up what will be the dS for an irreversible process because we often encounter a reversible process in nature. So, let us first try to give an molecular interpretation of entropy.

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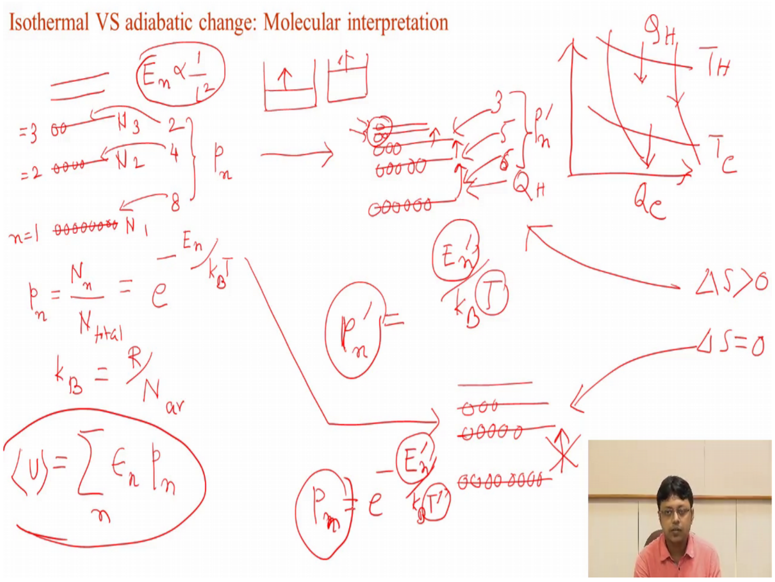

Isothermal VS adiabatic change: Molecular interpretation

Now, if you remember that when we are discussing the Carnot cycle we had to add isotherms and there are 2 adiabats which are connecting the isotherms. Now, when we do an isothermal change we know that the energy of the system does not change because the energy or the internal energy of the system depends only on the temperature of the system. So, just by changing volume does not change the internal energy of the system.

Whereas, during the adiabatic process the energy of the system changes we know that there is a drop in temperature because this isotherm was a temperature which was in equilibrium temperature between the system and the surrounding keeping the temperature equal to the hot reservoir which was T H and similarly this isotherm is for an isotherm at T C, but T H greater than T C. So, in order to connect this to isotherm the temperature of the system must have dropped when we make this adiabatic expansion.

Now, in both cases if you think in this way the volume of the system is changing. Question is why in one case the temperature is dropping in the other case the temperature is not dropping? Of course, for isothermal case the temperature should not drop because it is isothermal, but then why the internal energy is not changing. Now, we will give a very simple molecular interpretation, thinking that of the system as a particle in a box you know that for a particle in a box the energy of the box energy of the system actually goes over 1 over goes as basically n square and as a function of length it goes as 1 over length square.

So, let us assume that we have many energy levels like n equal to 1, n equal to 2, n equal to 3 and so on and then there are n 1 number of particles in a level 1, n 2 number of particles in level 2, n 3 number of particles in n equal to 3 and so on. Now, let us just for the particles we mean suppose say the molecules of the ideal gas. Suppose, I am just writing some numbers very arbitrarily I wrote the 8 here, 4 here and say, 2 here. Now, suppose this is a distribution. Now, what sets this distribution is temperature now, how this distribution is set. If you remember, we discussed it that the probability of having the molecule in a particular n which where n is their quantum number where actually the probability is nothing, but the fraction of the number of molecules we are using small n here.

So, we can actually change the notation little bit instead of small n, you can just write this as capital N for the number of molecules and we write it here as capital N by N total where N total is the total number of molecules that fraction of the probability will be nothing, but equal to the Boltzmann factor which is nothing, but the exponential of the energy of that particular level divided by k B T, where k B is the Boltzmann constant given by R, molar gas constant divided by the Avogadro number.

Now, this is a distribution, it is a specific distribution, where I have 8 molecules in the n equal to 1 state, 4 molecules in n equal to 2 state and 2 molecules in n equal to 3 state or so on. So, this is a particular distribution or the probability is actually fixed in this case which I am writing as p n. So, if we know the p n we can easily predict, what is the probability of having a molecule in some specific energy state? Now, suppose we are expanding the gas or the ideal gas by expansion we mean the length of the box will change, because remember how we expanded our system, that if we have a piston like this piston will now move so that the gas now expands to this state, which means actually in effect by changing volume we mean the linear distance of changing piston which means according to our particle in a box model one direction of the box is changing which are one particular direction which can be any you can choose any arbitrary direction for that, but the bottom line here is that the energy of the system now should drop down.

So, all these levels for energy levels will now come closer together. Since, it varies as inverse of l square. Now, suppose we had initially 8 molecules here, we had 4 molecules here, we had 2 molecules here; if you do not supply heat from outside then we cannot make a transition from this level to that level and this level to that level. Why, it is necessary? Suppose, we are keeping the temperature constant; if we keep the temperature constant, now we have a problem because the energy levels has changed and since the temperature is constant the distribution should also now change. We call it as say a p n prime, the new distribution.

Now, since the energy levels have changed, T has not changed which is for the isothermal case then the distribution must also change and by changing distribution means we will have more number of molecules in this case in the excited state than the previous case. Now, since it involves a promotion of the molecules from the ground state to the excited state which means that heat must be supplied to the system to cause this transition. And, that is why this Q H, when it was supplied to the system for any isothermal process heat exchange has to be there because the system is reversibly expanding and the energy levels are going down and then there will be probability of having the molecule in the excited state will increase.

So, that will maintain that temperature system you could have said it in other way that in order to maintain the temperature of the system same the distribution also must change. So, will have a new distribution for probably will have say here we have 6 molecules we have 5 molecules here and 3 molecules here. So, you have some distribution like 5 and sorry this was basically 6 molecules are here you have 5 molecules and you have 3 molecules here. So, this is a new distribution which we are calling as p n prime.

However, for the adiabatic situation what happens that distribution does not change why because we did not supply any energy to the system. So, the energy levels were changed because the energy levels came closer together just like the isothermal expansion, but the distribution cannot change because we have no heat flow to cause this transition. So, we will have the same distribution which means the p n should be the same as my old p n which is e to the power minus E n by k B T, but, now, remember that E n has changed to E n prime because it is a new energy level.

So, in order to keep the distribution same the temperature of the system must also drop down so that E n prime by T prime is equal to E n by T. So, that is why in an adiabatic process the temperature drops down whereas, in the ideal isothermal case the temperature of course, does not drop down there, but if you look at in the molecular way what you just saw is that for an isothermal case the temperature is kept fixed, but a distribution is changing. Now, for you can ask this question that how the internal energy or the total energy of the system is changing that we discussed briefly the other day that you have to calculate the average energy which is nothing, but these you have to take the energy part level and multiplied by the probability of having the molecule there and then you hope so have to integrate or take a sum over all these energy level and then only you can calculate some quantity which is equivalent to average of that energy. So, that if you calculate then you will realize that how this total energy or the average energy is constant for the isothermal case, but it is not constant for an adiabatic case.

Now, interesting point here is that for an isothermal case, we discussed the entropy change is there is some help for the entropy change. The entropy in this case is increasing because remember that by definition entropy is dQ reversible by T. Now, in this case, Q reversible is Q H which is the heat flown into the system which is a positive quantity which means dS is greater than 0 or for the finite process delta S is greater than 0. For the other process where actually we are dumping the heat to the cold reservoir, the entropy change is negative.

Now, let us just focus on the positive case where the system expanded and the entropy increased. Now, what is the meaning of the entropy increase? For the adiabatic case, you remember that entropy is change is 0 because heat change is 0 and there is no change in entropy, but what is happening at the molecular level think about it for the adiabatic case where we had delta s is equal to 0, we have actually the same distribution. However, for the isothermal case where we had in this case expansion where we had delta S is greater than 0, we have a very interesting situation where we are changing the distribution itself and in this case the entropy increasing means the more and more excited states are getting accessed.

So, what we will just learn is, increasing entropy means the system actually gets adjusted to a state where more and more number of accessible energy levels are occupied. Whereas, if we keep it fixed that the distribution are suppose at find we had many energy levels, but only 3 of them are occupied and here we can actually had situation where in the same token that all the higher and highered line energy levels that also occupying because if you keep the temperature constant and if you allow the transitions to happen you are more likely to occupy the higher order highered line energy levels also.

So, in that way you can assume that the distribution totally changes for the isothermal expansion and you are actually populating more and more energy levels which actually increases the systems degrees of freedom internal degrees of freedom which means actually the entropy is positive and in the adiabatic case we did not change the distribution, so, whatever was the from a probabilistic point of view the distribution of the internal energy levels are accessible energy level to the molecules that remains constant. So, the entropy change was 0.

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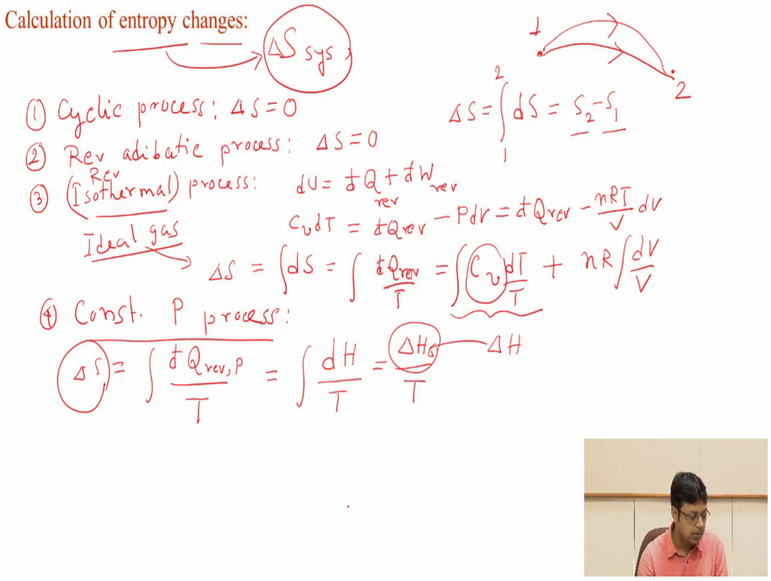

Calculation of entropy changes: $\xrightarrow{} \boxed{\Delta S_{sys}}$

$$\Delta S = \int_1^2 dS = \underline{S_2} - \underline{S_1}$$

① Cyclic process: $\Delta S = 0$

② Rev adibatic process: $\Delta S = 0$

③ (Rev Isothermal) process:

Ideal gas

$$dU = đQ_{rev} + đW_{rev}$$

$$C_v dT = đQ_{rev} - PdV = đQ_{rev} - \frac{nRT}{V} dV$$

$$\Delta S = \int dS = \int \frac{đQ_{rev}}{T} = \underbrace{\int C_v \frac{dT}{T}} + nR \int \frac{dV}{V}$$

④ Const. P process:

$$\boxed{\Delta S} = \int \frac{đQ_{rev,P}}{T} = \int \frac{dH}{T} = \frac{\boxed{\Delta H}}{T} \text{ — } \Delta H$$

Now, let us move on and first discuss that, what are the entropy changes for some processes which we experience day to day. By entropy change we mean from some state suppose one to some state to which is 2 we are making a transformation and we are just asking this question what is the dS associated with this system or since it is a finite change whereas, asking this question what is the delta S of this system. So, delta S will be nothing, but the integral over dS for going from state 1 to state 2, which is S 2 minus S 1 and since you can see that S 2 and S 1 are nothing but, the values of entropy of the system in state 2 and when the system is in state 2 and the when the system is in minus when the system is in state 1.

Now, here by delta S of the calculation of entropy we are always calculating remember the S of the system the delta S of the system because it is associated with some change. What happens for the delta S for the surrounding, that we will also discuss in a while. Now let us first try to understand that this is a path. Now, we can have another path from going from the same initial state to the same final state. However, the entropy should not change because it only depends on what was the initial state and what was the final state.

Now let us calculate it for certain processes; first one is a any cyclic process. We already discussed it, for any cyclic process the delta S should be 0 and we argued that any closed cycle can be divided into infinitesimally small Carnot cycle. So, large number of Carnot cycles and since each Carnot cycle, for each Carnot cycle we have the entropy change to be equal to 0 we can also add up all the entropy changes for the entire arbitrary cycle and we can always argue that the entropy change for any cyclic process, any arbitrary cyclic process is 0. Similarly, we also discuss for any adiabatic process or better to call as reversible adiabatic process because by definition the entropy change is equivalent to reversible heat change divided by T, there also we have delta S equal to 0.

Now, for any isothermal process what will be the entropy change we already discussed it, when we were discussing the first and the third state of Carnot cycle we can actually directly show that from first law du is nothing, but d cross Q plus d cross W and instead of isothermal it is just first I call it for an reversible any reversible process. So, for reversible process we can write some d Q reversible and d cross Q reversible and you will know that it will be nothing, but C v dT d cross Q reversible we are just keeping as it is, because we will connect it to the definition of entropy and d cross W is nothing, but P opposing d v with a negative sign, but for a reversible process P opposing is nothing, but the pressure of the system. Because, in any reversible process the pressure is always adjusted or changed infinitesimally small way so that system always adjusts in some pressure to be equal to the opposite pressures.

So, we can write it as minus PdV which we could further write it as using the ideal gas equation might d cross reversible minus n RT by V into dV. Now, we can organize it and you can easily see that these dS or the delta S will be integral of a dS which is integral over d cross Q reversible by T which is nothing, but C v dT divided by T because we are dividing the equation by T, the temperature throughout and we have here inner integral of dV by V, that we saw the other day. And, remember that usually we for calculation will assume in most of the cases that the C v or the heat capacity at constant following does not change over the change which we are making when we are changing the temperature of the system.

Now, let us consider what happens for a constant pressure process? For a constant pressure process, so, before that if it is an isothermal process, remember that this term will be also 0, because for any isothermal process we know that the heat change or the dT will be 0 and we remember that we did not write the second term del u del VT because we just showed an example for an ideal gas for which del u del VT is 0. Now, for any constant pressure process you can think that the entropy change will be nothing, but d Q reversible by T, but this d Q reversible is at constant pressure also.

Now, we know from the definition of enthalpy that heat change at constant pressure is nothing, but enthalpy of the system. So, this is nothing, but integral of dH divided by T constant pressure. So, if we just write the integral sign like this. So, we can write it as delta H by T. So, what it says is that the change in entropy can be associated with the enthalpy change of that process and we will use it to calculate; for example, when what is the entropy change which is associated with say for example, boiling of water then for that we use the delta H for boiling for water and then just simply divide it by T, where the T is the boiling temperatures which is 100 degree centigrade for water and then you can easily calculate how much is the delta S involved of the entropy change involved in that process which is boiling of water.

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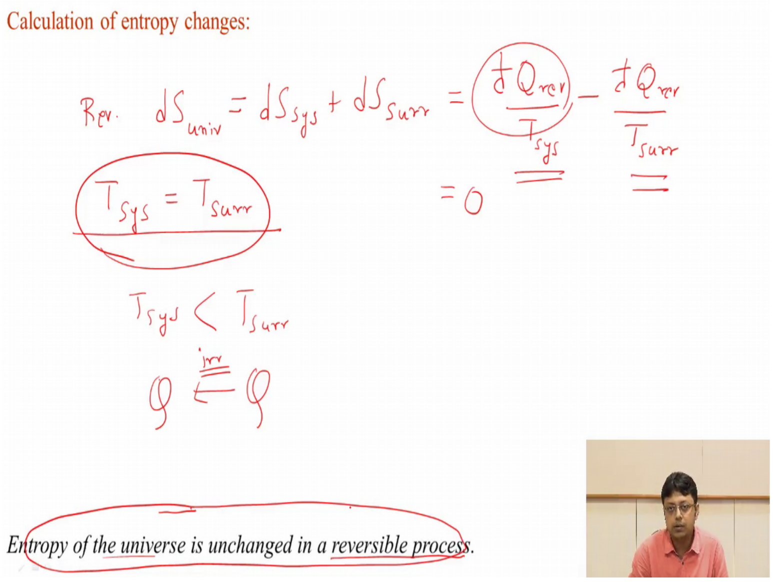
Calculation of entropy changes:

Rev. $dS_{univ} = dS_{sys} + dS_{surr} = \frac{đQ_{rev}}{T_{sys}} - \frac{đQ_{rev}}{T_{surr}}$

$T_{sys} = T_{surr}$ $= 0$

$T_{sys} < T_{surr}$

$q \xleftarrow{irr} q$

Entropy of the universe is unchanged in a reversible process.

Now let us move on and then calculate some entropy changes of other system, but before that let us try to define that what is the entropy change of the universe? Now, there is a statement which is at the bottom entropy change of the universe it says that it is unchanged for any reversible process.

Now, let us try to understand that for any reversible process what we have is that dS of the universe is nothing, but dS of the system plus dS of the surroundings. Now, for the dS of the system we have d cross Q reversible by T, minus we also have d cross Q reversible by T, but here the first T is for the Tt of the system and the second T is the T of the surrounding. Now, why are used a minus sign the reason is when the system is changing its entropy, suppose the heat is being flown from the surrounding to the system. So, d Q with respect to the system is increasing because the system is gaining d Q amount of heat and the same amount of heat the surrounding is losing so, I use the minus sign.

So, in general, since to maintain the reversibility T of the system has to be equal to T of the surrounding then we can easily show that T S of the universe is 0. Now, why this has to be maintained because remember if it is a reversible process. If the temperatures are different, suppose, the system temperature is less than the surrounding temperature, so, then there will be an irreversible heat flow from the surrounding to the system and then this process will be irreversible; however, to maintain the reversibility meaning heat can flow back and forth between the system and the surrounding the temperature must be same or in other words it must be an isothermal process.

So, in order to maintain the reversibility the temperatures must be equal which means the entropy change of the universe should be unchanged for any reversible process. Now, of course, the question remains to answer what happens for an adiabatic process. Before we go to that, what it means is that for any reversible process in order to maintain the reversibility we are also imposing the condition that it has to be an thought from isothermal. But, now we can think of a reversible adiabatic process, but then you will understand that we do not have any such situation because for adiabatic process of course, there will be the entropy change is 0, because there is no heat flow.

So, the question is what happens for an in general adiabatic process where the system is say isolated.

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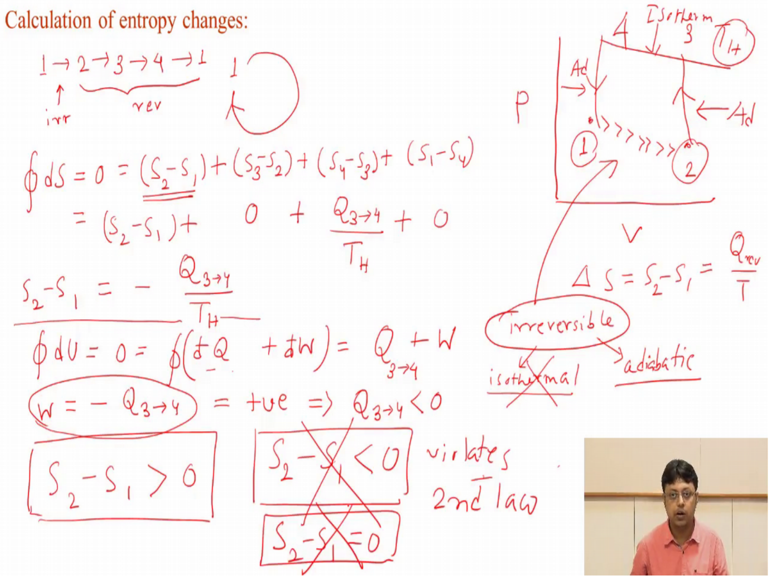

Calculation of entropy changes:

$$\underset{\uparrow\,\text{irr}}{1} \rightarrow \underbrace{2 \rightarrow 3 \rightarrow 4 \rightarrow 1}_{\text{rev}}$$

$$\oint dS = 0 = \underline{\underline{(S_2 - S_1)}} + (S_3 - S_2) + (S_4 - S_3) + (S_1 - S_4)$$

$$= (S_2 - S_1) + 0 + \frac{Q_{3\to4}}{T_H} + 0$$

$$S_2 - S_1 = -\frac{Q_{3\to4}}{T_H}$$

$$\oint dU = 0 = \oint(đQ + đW) = Q_{3\to4} + W$$

$$W = -Q_{3\to4} = +ve \Rightarrow Q_{3\to4} < 0$$

$$\boxed{S_2 - S_1 > 0} \quad \cancel{\boxed{S_2 - S_1 < 0}} \text{ violates 2nd law}$$

$$\cancel{\boxed{S_2 - S_1 = 0}}$$

$$\Delta S = S_2 - S_1 = \frac{Q_{rev}}{T}$$

Now, before we go to that let us first discuss that we are still discussing the entropy changes. How will you calculate the entropy change for any irreversible process? Suppose, I have 2 steps; step 1 and step 2 and this is an irreversible path. Now, why I am drawing it as an instead of a dotted arrow as an a broken arrow? The reason is usually this path not usually this path will be outside my pressure volume surface, if you remember that if we are always on the surface of the P V diagram. P V T diagram there was a surface and we called it as P V

T surface and also remember that this P V T surface if we stay anywhere on the P V T surface, then the equilibrium must be maintained every day. Equilibrium maintained means because every time or every point on the surface you can think of that P V equal to n R T that equation holds. So, the system is always adjusting with the surrounding and the change happens in a reversible point. So, then it would not be in an irreversible process.

So, no irreversible process entirely lies on the P V T surface it may cross the surface, but it cannot lay the entire path cannot lay on the P V T surface. All the lines which are lying on the P V T surface must be a reversible process that is why you drew it as an arrow. Now, in order to calculate entropy, remember the change in entropy of the delta S is defined as S 2 minus S 1. So, we will just consider a reversible path because otherwise we cannot calculate by definition the entropy was Q reversible by T. So, we have to consider a reversible heat change. So, we have to consider a reversible path.

All we have to do is to start from the same initial state and go to the same final state keeping the reversible path the same. Now, before we discuss that let us consider or let us try to understand what this path all about is. So, this path is an irreversible path. Now the second question is it an isothermal irreversible or is it an adiabatic irreversible path. If it is isothermal, then which means the system is always adjusting it is temperature with the surrounding then it means that reversibility is maintained which you just discussed. In order, for any system if we the reversibility is maintained then which means that system is thermally equilibrating with the surrounding. So, in the other way, that if it is isothermal the path should be reversible. So, irreversible path cannot be isothermal, but it can be definitely an adiabatic process.

So, in general, we are talking about an adiabatic change for a closed system. Now, in order to calculate the entropy change associated to with this irreversible adiabatic process let us consider a cycle where first it is just like a Carnot cycle, where we first change the temperature of the system by an adiabatic change, where we going to state 3 and then suppose, the system temperature was raised to say T H and then, again we have an isothermal compression going from state 3 to state 4 and then again we are coming back to the original state. So, these 2 are my adiabats and this is my isotherm. Interestingly, this is also an adiabat, so, this is not a Carnot cycle. So, do not get confused these are they are not 2 isotherms and 2 adiabats. What we have drawn here is that we had some state at some temperature which is denoted as 2 and then we did an adiabatic change to go to increase the temperature to T H and then we did an isothermal compression and then again an adiabatic expansion so that the temperature is again raised to the temperature which corresponds to state 1. Now, state 1 and state 2 must have different temperature because it is an adiabatic process, the broken arrow or which is basically the irreversible path.

Now, since we have, what we have done? Here, we have actually considered a cyclic process where we are going this way 1 to 2 and this step was the irreversible step and each one of this step is a reversible step. So, the way we are drawing here is that should suggest us that at the end of the day we have actually started from state 1 and we came back to state 1. So, it is also a cyclic process and we know that for any cyclic process since entropy is a state function the total change in entropy must be equal to 0 and that we can just denote it as for the first step it is basically going from state 1 to 2. So, write it as S 2 minus S 1, second step it will going from 1 to 3 sorry 2 to 3.

So, we will write it as S 3 minus S 2. Third step it is going from state 3 to 4 we write it as in S 4 minus S 3 and similarly, the fourth step is going from 4 to 1. So, write S 1 minus S 4. Now, remember we are we have to calculate this S 2 minus S 1. So, I will just keep it as it is for the second step it is an adiabatic steps. So, I will write it at 0, because for adiabatic isothermal sorry reversible adiabatic process the entropy change is zero. However, keep in mind that we are considering a irreversible adiabatic process for which entropy change should not be 0, we will see that. It can be 0, it can be non 0, but we do not know, but we cannot decide it right now, because we do not know. All we know that for any adiabatic reversible process the entropy change is 0.

So, for S 3 minus S 2 this step it is 0. Similarly, for this step S 4 minus S 3 we had some heat flow from which is associated going from 3 to 4. It can be heat flow inside the system; it can be heat flow outside the system. In this case it is a compression, so, you can understand that this heat flow is from the system to the surrounding and must have a negative sign we are coming to that and the temperature, since it is an isothermal process the temperature was kept constant and of course, it was done reversible. The entire path is reversible and again in the step 4 it was an adiabatic reversible process. So, the entropy change is 0.

So, what we get is S 2 minus S 1 is nothing, but negative of Q 3 minus 3 to 4 step divided by T H. Now the question is, what is this? So, if we understand if we ask this question similarly, that what is the associated internal energy change that is also 0, because it is a cyclic process and energy or internal energy is a state function. So, we could write that this is nothing, but d Q reversible by T because it is a work done for the entire process and we can just write it as d cross Q reversible and plus some d cross W. Now, why I am writing reversible because the work done was associated only with the isothermal expansion, but it is not necessary to write it as a reversible, it is obvious that it is reversible and for that we know that the work done is only associated with going from 3 to 4, so, the expression for the work done will be nothing, but minus of 3 to 4.

Now, if the work done in this case is positive because it is a compression work which means that Q 3 4 has to be negative. Now, if we take this work done to be negative which means Q 3 4 is positive, which means we are actually withdrawing it from the surrounding and then we are also performing some work, but then in the cyclic process you can see here, that the work done here is exactly equivalent to the heat withdrawn which does not follow the first law of thermodynamics. But, it defilers the second law of thermodynamics in the sense that we are saying that we withdraw some heat from the surrounding and completely converted the state into work which violate the second law.

So, the work done cannot be negative here. So, it is a compression work, it is a positive work and that is why the heat associated with the change going from state 3 to state 4 has to be negative which means, the S 2 minus S 1 has to be greater than 0, because we just said that the S 2 minus S 1 is nothing, but minus Q 3 to 4 divided by T H and since Q is negative we are conjecturing that S 2 minus S 1 is greater than 0 we saw. But, the possibility that S 2 minus S 1 less than 0 is also ruled out because we just said that if this is true then it violates the statement of second law, that complete conversion of heat into work is not possible. So, you are also removing this possibility.

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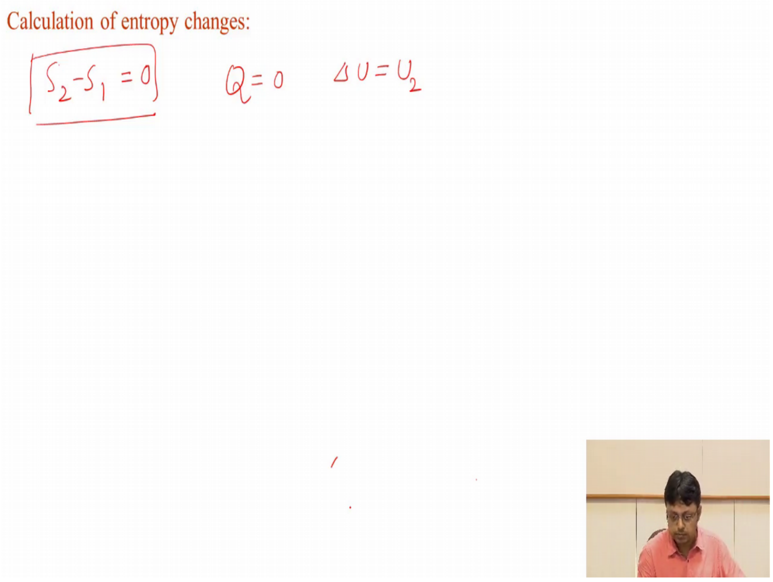

Calculation of entropy changes:

$\boxed{S_2 - S_1 = 0}$ $\quad Q = 0 \quad \Delta U = U_2$

Now that we have a third possibility and that is S 2 minus S 1 is equal to 0. We have not yet ruled it out. Now think about it if this happens then what will happen the associated heat change will be 0 and since, we had a cyclic process the associated delta U which is nothing, but U which is nothing, but the cyclic integral. Now if S 2 minus S 1 is 0, which is the third possibility then we have another problem, then actually the entropy change 0 means by all the heat changes are 0 and internal energy change is also 0, but then W are the work done has to be 0, from the first law.

But, which means actually in this case the system is not only restored in its initial step because for the system we did a cyclic process the surrounding is also restored with initial step, which cannot be possible for any irreversible process. Since, it is irreversible the conditions of the surroundings must be changed because it has a directionality. If it comes back to the original broad step then it must be a reversible state. So, this possibility is also ruled out. So, the only possibility we have for this reversible process is that S 2 minus S 1 is greater than 0. So, what we just saw is that the entropy change going from state 1 to 2 for any irreversible process is greater than 0.

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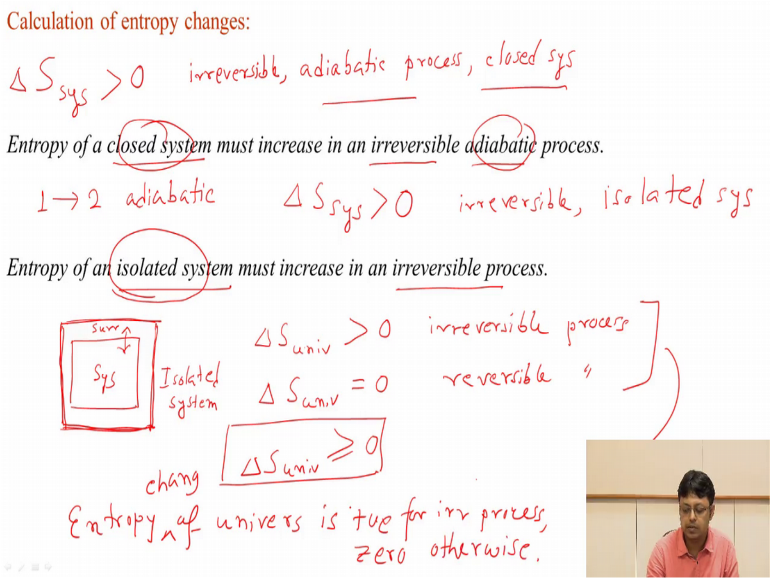

Calculation of entropy changes:

$\Delta S_{sys} > 0$ irreversible, adiabatic process, closed sys

Entropy of a closed system must increase in an irreversible adiabatic process.

$1 \rightarrow 2$ adiabatic $\Delta S_{sys} > 0$ irreversible, isolated sys

Entropy of an isolated system must increase in an irreversible process.

$\Delta S_{univ} > 0$ irreversible process

$\Delta S_{univ} = 0$ reversible "

$\boxed{\Delta S_{univ} \geq 0}$

Entropy change of univers is +ve for irr process, zero otherwise.

Now, we can summarize what happened to the entropy of the universe. Remember that, we showed that the entropy of the universe for any reversible change was 0 and just now, we showed that delta S of the system is greater than 0 for an irreversible adiabatic process, because remember that process has to be adiabatic, we argued that. It cannot be isothermal and the system was also a closed system. So, these were the conditions that we put. So, we can draw a statement here, entropy of a closed system must increase because it is greater than 1 greater than 0 in an irreversible adiabatic process for a closed system.

Now, you can think that this path 1 to 2 is adiabatic, so, no heat exchanged from the system to the surrounding and we already took the system to be a closed system which means we can think that these system also to be an isolated system. So, we can just write that for any irreversible process, for any isolated system because if it is closed and plus if it is adiabatic system, adiabatic process then the system behaves like an isolated system. So, then we can make an statement that entropy of an isolated system must increase in an irreversible process because by isolated we had combined the idea of a closed system plus the adiabatic process. So, for any irreversible process then associated with an isolated system the entropy must increase.

Now what happened for the universe? Now, think about it we had a system that was basically interacting with the surrounding, but the system is interacting with the surrounding that in its vicinity surrounding, but the system and the surrounding together can be considered as an isolated system, because this surrounding may be some part of the surrounding is also interacting with some other part, but we are considering the part which is associated with the system is just isolated from the rest of the world. In fact, there is no rest of the world, because this is just system plus surrounding which is the entire world of the entire universe itself.

So, the universe all by itself is of course, an isolated system. We make this statement when we discussed the definition of an isolated system. Now, which means the delta is of universe will always be greater than 0, for an irreversible process. Because, for any irreversible process the system plus surrounding is already an isolated system and we saw that for a reversible process delta S universe was 0. So, we can combine these 2 to write that delta S of the universe should be greater than equal to 0 for any process. If it is greater than 0 it is an irreversible process, if it is equal to 0 it is a reversible process. So, we can make a statement that the delta S of the universe or the entropy of universe is positive or entropy change of universe is positive for irreversible process or it is 0, otherwise meaning for any reversible process it is 0.

Thank you.