Engineering Thermodynamics Professor Jayant K Singh Department of Chemical Engineering Indian Institute of Technology Kanpur Lecture 34 Change in entropy of solids, liquids, and ideal gases

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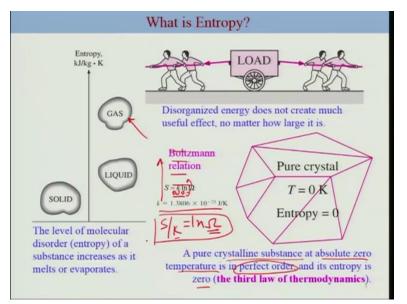
	Learning objectives
•	Apply the second law of thermodynamics to processes.
•	Define a new property called <i>entropy</i> to quantify the second-law effects.
•	Establish the increase of entropy principle.
•	Examine a special class of idealized processes, called <i>isentropic processes</i> , and develop the property relations for these processes.
•	Calculate the entropy changes that take place during processes for pure substances, incompressible substances, and ideal gases.
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•	Derive the reversible steady-flow work relations.
•	Develop the isentropic efficiencies for various steady-flow devices.
•	Introduce and apply the entropy balance to various systems.

Welcome back, in the last two lectures on in the particular topic of entropy we discussed that entropy is a property is a state function and in this particular lecture we will be talking about bit of more details of the entropy and as well as calculate the entropy changes for the case of incompressible substance gas. And develop some property relation for some processes which we will call as entropic processes.

So what is entropy, entropy is nothing but major of disorderness, we already discussed that if you have an isolated system, the entropy change of the isolated system should continuously increase or remain constant or the entropy change will be zero or there will be no change in the entropy if it is a reversible process otherwise for any isolated system if it undergoes a process the entropy should keep increasing ok.

So entropy is related to the disorderness is the way the molecules arrange themselves the probability of having more possibilities in a given system, so let us just look at first how the entropy change with the state.

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So as I have already mentioned the level of molecule disorderness which we describe in terms of entropy of a substance increases as we increase the temperature, so with solid to liquid to gas this is indication that the kinetic energy of the molecules of this different states or phases increases with as you provide more temperature. That means the kinetic energy of this is quite high as compared to the liquid which essentially means this is more disordered compared to the case of the solid ok.

Now having high kinetic energy of the molecules is not a indicative of usefulness of energy ok, this is quite well you can understand if you have a container having gas with a high kinetic energy and you put for example paddle or shaft, higher category of molecules do not cause rotation of the staff, so essentially even though energy is high is not building any significant uses of the energy ok.

So that's what we say that this organised energy which would be the high temperature case, does not create much useful effect no matter how large it is and certainly the molecules start reducing its translation energy with the reduction in the temperature so if you reduce the temperature and bring it to the solid the molecule translation or the kinetic energy is umm much less and here the case of the solid molecules vibrates ok.

And particularly when you have a pure crystalline solid and the temperature is zero so overall the vibration minimizes for the pure crystal and in such case when you have a perfect order that

means the particles or the molecules are sitting on the lie thesis ok and it is the entropy is considered to be zero because there is no disorderness, everything is ordered in that sense ok.

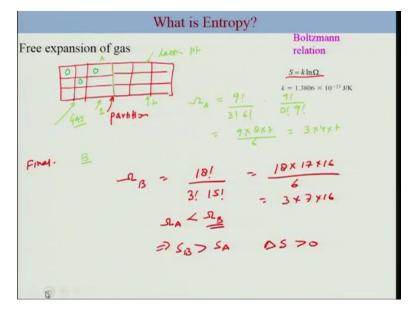
So this becomes the reference, so anything you consider T equal to zero kelvin as a reference I calculate the entropy of a any substance which is higher than temperature than zero kelvin would be absolute entropy ok. And this is what turns out to be the third law of thermodynamics where we say that the pure crystalline substance at absolute zero temperature is in a perfect order ok and is entropy is zero ok.

Now as I said that entropy essentially can be related to the disorderness in some says how the specific possibilities of the configurations or number of the configurations of the molecules in a given state. So having higher temperature indicates higher possibilities or number of the configurations because molecules can move around, so they can access possible energy levels, as we know of that you have different energy levels, these are different energy levels in a molecules can sit on a ground level at a very low temperature and you will provide kind of energy it will excite to the higher energy level.

Thus possibilities of different energy level increases at higher temperature which would be the case of gas and essentially which means that you can have more possible configurations and this is entirely now is related to some relation which we call it Boltzmann relation which relates s by k is ln of omega where omega becomes the number of possible configuration where S is entropy and K is Boltzmann constant which the value is given here ok.

So we can try to relate this just to understand a bit that for a given process if it to occur the entropy should increase or at least remain constant for the case of the reversible, it should increase for non-reversible or any particular process.

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So let us consider the case of unrestrained expansion of free expansion as a gas and try to see if we can make use f this expression. So if you consider a box ok, where this is let us say a partition ok, and this is a kind of room box where the gas is there and in order to make use of this expression what we are going to do is we are going to divide this let us say into some kind of a lattice or this arrangement where the particles can sit in it.

So let us say we have three particle and they can fill this place and they can of course fill many possible all this places which is the boxes and these are the possible arrangements and similarly you have other room also in the similar sense and this is your partition again as I said this is your partition.

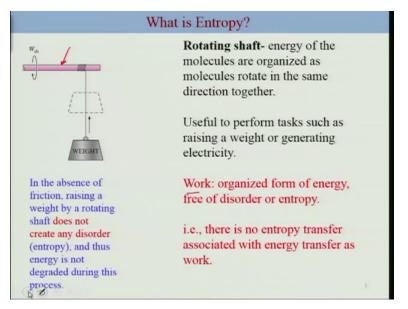
So this is before the expansion the gas was here ok, so what is the possible arrangements of the gas molecules, let us say we have three, so the possible arrangements if we define as omega A, this becomes the line initial possibilities let us say box one and this is two, so this is 9 factorial divide by 3 factorial and then the rest is 6 factorial, 6 is of course the empty regions and the other case of course they are 9 lattice this regions we can say this is nothing but lattice point ok and this essentially has no particle in this particular second box and hence this essentially be 9 into 8 into 7 divided by 6, so that becomes your number, so this is your 3 into 4 into 7 ok.

Now you take out this partition, you allow this gas to expand, what you see is a condition of let us say B, B is a final state ok, so B is a final state, in this final state what is a possible number of configuration where molecules can arrange themselves and this would be omega B. Now you have 18 lattice points and 3 is number of particles, it has more possibilities which can clearly see ok and thus you have following number ok.

So this is your 3 into 7 into 16, clearly omega A is less than omega B which essentially means that the number of possible configuration for the case of B after expansion is much larger. Essentially this indicates as Sb is much greater than Sa ok and this is what tells you that your delta S is greater than zero for this simple exercise.

So what we did was, we connected this S entropy change to the molecular disorder which essentially (got) we represented in terms of the number of possible arrangements in a given box ok. This is a way to understand the microscopically their entropy change in a for a given process. Let us little bit look at more into details of different types of processes and how does it cause changes in the entropy.

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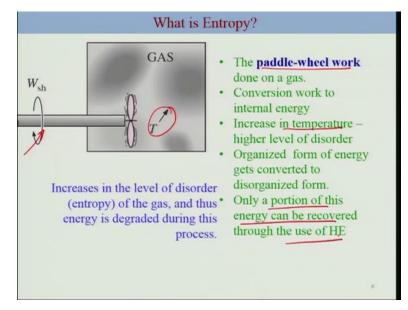


As we already discussed that the entropy change is either due to the heat transfer or due to the irreversibility, irreversibility would be due to frictions or unrestrained expansion or any finite temperature based heat transfer or or temperature gradient heat transfer ok.

So let us consider this rotation shaft, now the molecule of this rotating shaft is quite organised consider this solid air is rotating in a specific way and by considering this to be a frictionless, this

particular organised way of energy can be used to perform task such as raising weight ok and thus or this is a kind of a energy which is a organised form of energy and it is free of a disorder entropy.

And thus we say that the work is basically an organised form of energy and this is a for this particular form of energy there is no entropy transfer associated with energy transfer as work ok. So there is no entropy change and there is no degradation of energy in this kind of operation, in this kind of process.



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But now if we consider anything related to the heat, you will see a significant degradation of the quality of the energy ok. Ok so let us consider this as an example, this is a case where a paddle wheel which is worked on this gas by doing a work on this gas, the temperature increases considering the internal energy increases because the conversion of the work to the internal energy occurs in this case increase in the temperature we know that increases the disorder ok. So higher the level of disorder at higher temperature that we already test upon in the previous slide.

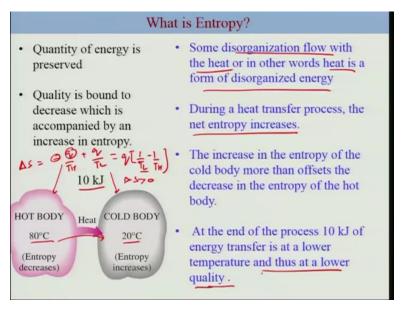
Now hence the organised form of energy which was this got converted to disorganised form. So by conversion of the internal energy and raising in temperature which essentially means that if you want to convert back this disorder to the ordered form, only a small portion of this energy can be converted and you have to make use of the heat engine ok.

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	What is Entropy?
•	Quantity of energy is preserved
•	Quality is bound to decrease which is accompanied by an increase in entropy.

So as we discussed already that the quantity of energy is preserved but quality of the energy (will) is bound to decrease as during the process ok and this decrease in the quality is accompanied by the increase in the entropy, so if entropy is been generated which essentially means the quality decreases or in other word if entropy increases is essentially means the quality of the energy decreases.

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Ok, so let us consider this case which is associated with the heat transfer ok and this is specifically a heat transfer from a hot body to cold body, let us say you have 10 kilo juice which is transfer from the 80 degree Celsius body to 80 degree to 20 degree ok. Now you can do analysis of your entropy of this combined system, your delta S considering this is a reversible process then we can write this as minus Q by TH plus Q by TL and so the Q is of course say 10 kilo juice minus is because this corresponds to loss in energy and plus of course is gain in energy. Now TL is low so overall this can be written as Q1 by TL minus 1 by TH and since TL is less than TH your delta S is greater than zero.

So thus the combine system the entropy is of course increasing, so we can say there is some disorganisation flow with the heat ok. So there is a flow of heat or the heat transfer and thus entropy is increasing of the system to there is a disorganisation along with this heat flow occurs or in other word heat is a form of disorganised energy. During a heat transfer process the net entropy increases this we can now clearly see ok.

The increase in the entropy of the cold body is more than the decrease in the entropy of the hot body, so essentially the cold this increase in here off side the decrease in here, thus it increases the overall entropy. Now there is another important aspect that though the 10 kilo juice got transferred from hot body to the cold body and we know that the quality of the energy decreases with the decrease in the temperature that was based on our efficiency analysis of a convert cycle or in general for any devices, so we clearly said that lower the temperature your efficiency is lower and higher the temperature the efficiency is higher. So at the end of the process this 10 kilo juice of the energy transfer is at the low temperature and thus at low quality.

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The Tds relation Saint, ver - Swint ver = -pdy = dy ~ Tds = du tpdv kj Gibbs Eq TdA = du tpdu Kj h = UtpV dh= du + pdu tVdp => [Tdo = dh - udp Deconf Tdo rel. $ds = \frac{dv}{T} + P \frac{dv}{T} - (D)$ dn = dh - udy - (D)

Ok, so let us now derive this Tds expression first connect this entropy change to the other properties, so we can start with a basically the reversible process, particularly the internal reversible process and we can start with your first law of the thermodynamics so let me write here Dq internal let us say reversible ok, minus del W again internal reversible so this is a heat in and this is of course out is equal to change in Du so this is for off closed system ok. For internal reversible or reversible you have this Tds as expression and this is your Pdv. Thus you can write Tds minus Pdv is nothing but Du ok.

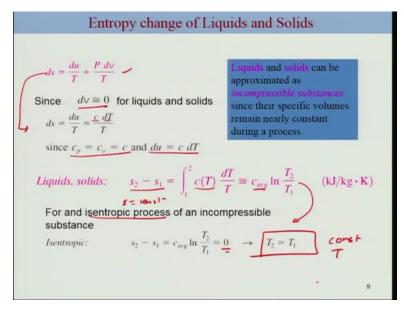
Now this expression though we have derived for internal reversible case but note that the Du on the right hands side is a state function ok and these are all state functions, these are properties, so it depends on the only the state of the system, so thus the change in the delta U this expression is valid for irreversible or as well as reversible process ok. Though Ds Tds will not going to be Del Q for the case of irreversible but this expression tells you there is change in the internal energy can be written in this form ok. Now I can write this in this form Tds is Du plus Pdv I can also write in per unit kg ok, so this would be your kilo juice per kg, this would you be your kilo juice ok.

Now this becomes your first Gibbs expression, so this is nothing but gives the equation ok, now you can extend this exercise for the case of enthalpy considering that enthalpy is nothing but U

plus Pv ok. So you can come up with Dh is nothing but Du plus Pdv plus Vdp and this is nothing but you Tds ok. Thus your Tds is Dh minus Vdp ok.

So this is an another expression or another Gibbs expressions I can Tds expression or relation ok, you can summarize this in terms of Ds in differential form as Du by Dt from here plus Pdv by T and for the case of enthalpy ok, you can write in this form ok. So this expression are going to be used for our analysis for ideal gas in other cases ok. So these are the two specific expression which are quite useful for our other analysis.

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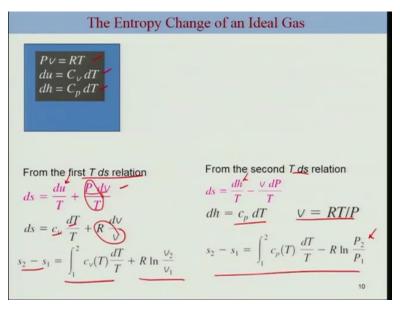


So let us look at this, we will start with this first equation ok and Du by T plus Pdvby T and we can write this here now our interest is to find out the entropy change of liquids and solids ok for the case of liquid and solid which will be considering incompressible of fluid your change in the delta V is going to be zero ok and thus we can write this expression in this form simply Du by T and since we know that for liquid and solid this can be written as simple the C and Dt considering the C is constant of whether is for the solid and liquid ok.

So this is a common constant specific heat and then you have this Du is equal to Cdt, so you can replace here ok and the you can integrate, so that becomes your change in the entropy and this is integration from one to two now we have already discussed earlier that specific heat for liquid and solid depends on only temperature, you can express this in terms of average specific heat and then the expression will come out to be simply the log of temperature ratio T2 by T1 ok.

Now if you consider an isentropic process which means that S is constant ok for this liquid and solid which is incompressible fluid which essentially means from here we can consider this to be zero which indicates clearly that this is a (co) for isentropic process would be a constant temperature process it should be also isothermal process ok, this is a clear deviation based on our assumption of this ok.

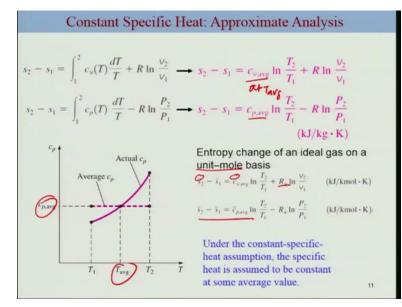
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Now we can extend this analysis for the ideal gas, we know for ideal gas your Pv is equal to Rt and the relation of the change in internal energy can be written as in terms of your specific heat at constant volume, change in enthalpy in terms of Cp and we start with this first relation which is this and we also written here as the second relation for in terms of enthalpy ok. So we can write down the expression of Du here so Du would be in terms of Cvdt and we can also rewrite in terms of so that we get only the temperature expression, so we can also place this in terms of volume so that we can integrate easily and now it is written here so Du is written as Cvdt and P by T is express in terms of R by V ok.

So thus your expression of for the case of ideal gas is clearly written in this form, the change in entropy is this term plus the this term which relates the change in the volume ok, Similarly you can do the exercise for the using the second expression which relates enthalpy and the pressure to the change in the entropy and this is your Cpdt for the change in enthalpy and again make use of ideal gas and you get this expression of entropy change in terms of Cp T dt by T and then you

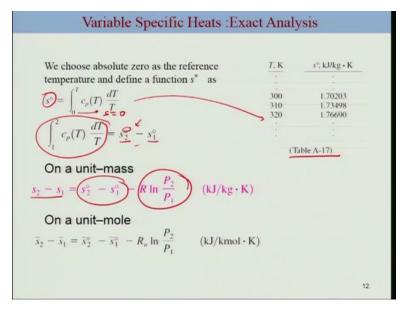
have this pressure ratio in log form. So these are the two contributions now. So depending on the statement you can make use of this expression accordingly ok.



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So let us look at specific case, cases where the we can consider specific heat as constant ok and for the exact analysis where you have exact information of the entropy, so let us look at here for the constant heat approximation Cv will be taken at a average temperature so this become Cv average, so this is Cv average at T average ok and similarly for the same for the Cp average, so essentially it means that you are taking the Cp at a specific T average ok. Now you can write this in terms of unit mole bases ok, so there R will be Ru and we have used this bars indicating unit mole and this is the same for the case of the second Ts relation based change in entropy.

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We talked about approximate analysis we will consider now the exact analysis for the case of entropy where the entropy is calculated based on absolute zero as a reference where the temperature T equal to zero is considered as a reference where the entropy value of that is going to be zero, so S here is simply zero T TCp T dt ok which essentially means here for the refers case S is zero ok, So this becomes your absolute entropy in a calculation and this is given in table A 17 ok.

So now if you want to take a difference between S2 S1 this indicates based on this absolute zero as reference, this becomes a simply this relation ok. So this is only connects the temperature difference nothing more, so but of course we know that S is a depends on temperature and pressure both ok, so because you have this relation S here, so this is one part ok and this is another part here.

We will consider the pressure part so here this is one part and this is another part, so if you are considering this based on this analysis then you can rewrite this expression of change in the in entropy for unit mass in terms of this eh in terms of your absolute zero as a reference temperature that will be the change in the entropy plus the other part which is a contribution due to the change in the pressure. Ok and this similarly further unit mole you can write in this form, so that is based on the exact analysis of a specific heat where we calculated the the entropy absolute entropy based on the reference zero to kelvin ok.

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Isentropic Processes of Ideal Gases Constant Specific Heats (Approximate Analysis) R In Setting this eg, equal to zero, we aet ln VALID FOR [®]isentropic proce constant specific heats R The isentropic relations of ideal and thus (R/c gases are valid for the isentropic processes of ideal gases only. Tut-1 = constant = constant $Pv^k = constant$

So now we will consider a specific case which is isentropic process for ideal gas and we will connect this to polytrophic process, so we can start again with this expression ok, one of the expression it consider this to be zero for constant specific heat when you consider this to be zero, so you can rewrite this expression in this form ok, where Cv here is of course is Cv average.

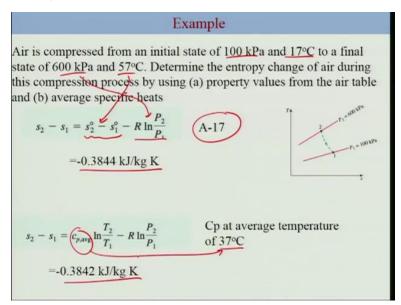
Now you can rewrite this expression, take it here and it goes to power and this can be rewritten as considering that R is Cp minus Cv and K is the ratio of the Cp and thus your R by Cv which is this is nothing but your K minus 1, so you can rewrite this expression in terms of this ok. So this can be written as in this, so this because logs can be taken out and this can be written as into K minus 1.

So this is one expression based on a constant specific heat analysis and here we have considered isentropic process because that means the entropy is constant. You can change the variable because this is ideal gas you can you make use of Pv is equal to Rt and cover with the different kind of expression which is what is written here, so this is expression based on ratio the P or you can connect the pressure ratio with volume ratio ok, so these are three different individual expressions ok and thus you can summarise this that for isentropic process of ideal gas this

expression holds this all constant and this is true for ideal gas, isentropic process and constant specific heat and if you recall this is nothing but your expressions which we have written earlier for polytrophic process where gama or K, sometimes write also gama is nothing but Cp by Cv and Pv is equal to annot is constant was the case of polytrophic process where N was considered as simply gama or K ok.

Now this is the expression which we calculated for adiabatic cause static equilibrium or in this case adiabatic reversal case. It also tells you that isentropic process is nothing but adiabatic reversible process for ideal gas.

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So with that we will do just an example and finish up this lecture, so this is an example of air compressed from initial state of 100 kilo Pascal and 70 degree Celsius to a final state of 600 kilo Pascal and 57 degree Celsius. What we need to find out is entropy change of air during this compression process by using the property table or by considering the average specific heat.

If you want to use the property table, we have this expression which connects the change in entropy to the change in entropy first calculated from the absolute zero as a reference and then the contribution due to the ratio or change in the pressure and from A 17 you can directly take these values considering the values or given as far as the temperatures are concerned, so temperature is needed for this part and of course the pressure be used for this part ok, so with that the value comes out to be this ok and for the second case, you have this expression and Cp

average would be calculated at a average temperature 17 plus 57 divided by 2 which comes up with 37 degree Celsius and with this the value comes out to be this which are very close enough.

So this is something which we can use this was the illustration of making use of the table and average specific heat for calculating change in entropy.

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Next lecture
Apply the second law of thermodynamics to processes.
 Define a new property called <i>entropy</i> to quantify the second-law effects.
Establish the increase of entropy principle.
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 Calculate the entropy changes that take place during processes for pure substances, incompressible substances, and ideal gases.
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Derive the reversible steady-flow work relations.
Develop the isentropic efficiencies for various steady-flow devices.
Introduce and apply the entropy balance to various systems.

Ok, so with that this would be the end of this particular lecture, so in the next lecture we will discuss the reversible steady flow work relation and other steady flow devices and the corresponding isentropic efficiency of those devices. Ok, so see you in the next lecture.