Concepts of Thermodynamics
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Lecture - 40
Thermodynamic Property Relationships; Entropy change for Solids, Liquids and Ideal Gases

In our previous lecture, we had discussed the concept of entropy not really what entropy physically means, but mathematical definition of the change in entropy in terms of heat transfer in a reversible process. So, the entropy change was defined through this, and there are several facets of this particular equation that we will now discuss. The first facet is that when we talk about the change in entropy for say a reversible process, that means, let us say there is a process may be in TS diagram you have state 1 and you have state 2.

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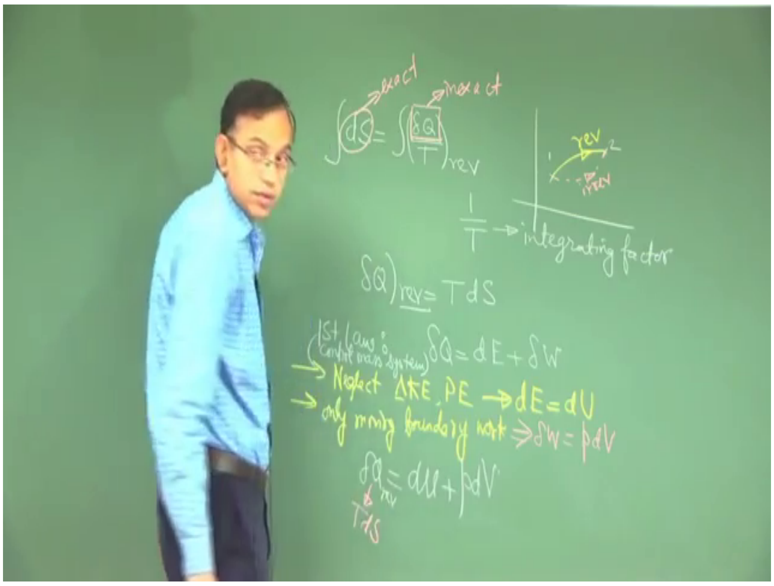

So, you can construct a reversible path may be hypothetical, but you can construct it, calculate the heat transfer during this reversible process, and calculate this integral of del Q by T over this path that will be the integral of dS which is S 2 minus S 1. Now, once you calculate S 2 minus S 1 that value can be used even for another process which is irreversible and this is the beauty of this equation.

So, very important this has to be integrated along reversible path, but once integrated the change in entropy can be used for any process no matter whether it is reversible or irreversible because entropy is a point function. So, how this is possible, this is a remarkable thing in mathematics where you have a in exact differential, and here you have exact differential. So, an inexact differential is converted into, so this is also integral ok, both sides integral ok. So, inexact differential is converted into exact differential how it is converted into exact differential by introducing something which is called as an integrating factor.

So, here 1 by T is an integrating factor that converts the inexact differential to exact differential. Now, let us see that how you can use this to calculate the change in entropy for any process. So, we can write from here del Q for reversible process equal to T dS right. This is a consequence of the second law of thermodynamics. First law as it says is del Q is equal to d E plus del W. Now, we make certain assumptions, neglect changes in kinetic energy and potential energy. If we make this assumption then dE as good as dU. This is first law for a control mass system we have to understand it. I am not writing it explicitly may be let us just write control mass system.

So, once we do this, then you have del Q. So, we are applying this for the reversible process. So, for the reversible process, delta W will be the reversible work. What is the reversible work? Is it p dV or it can be also anything else? Well, it is P dV, if it is a simple compressible substance undergoing a quasi equilibrium that is internally reversible process, and the only form of work is the moving boundary work. If there are other forms of work like say electrical work or work due to stretching of wire. So, all those types of work, they can still be reversible work, but not expressed by the formula p dV, but something else.

So, when we replace delta W with p dV we have to make sure that it is only a moving boundary work of a simple compressible substance in a quasi equilibrium process. So, this is the second assumption only using boundary work. So, only by moving boundary work we are essentially meaning that it is a simple compressible substance, because you know simple compressible substance is ruling out the electrical magnetic and other effects which could be in addition to pressure volume and temperature changes. So, only moving boundary work we are not again repeating that it is a quasi equilibrium process, because it is reversible it has to be internally reversible, that means, a reversible process must necessary be a quasi equilibrium process.

So, you have to understand it very clearly. Reversible process must be quasi equilibrium. Quasi equilibrium need not be reversible because it can be externally reversible ok, so only moving boundary work that will mean delta W equal to p dV. So, then you have del Q is equal to dU plus p dV. And we are assuming a reversible process. So, del Q reversible in place of this we will write T dS.

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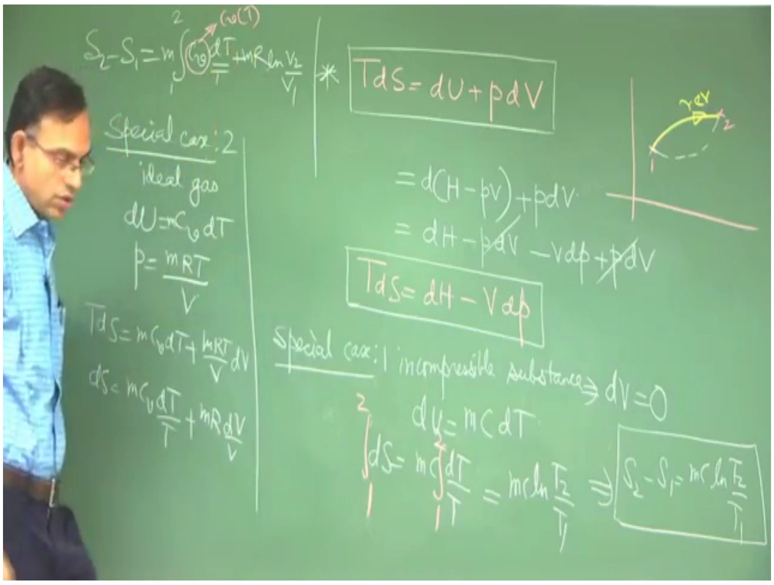

So, we come up with a expression T dS is equal to dU plus p dV. This is one of the famous thermodynamic relationships, property relationships which relates various properties. So, the question is because it relates various properties, and all this properties are point functions, we can definitely say that this equation is valid for any process, but that is a little bit lose statement.

By that what we actually mean is something like this that we have derived it for a reversible process. So, if we are interested to calculate a change in entropy say between states 1 and 2 ok, so when we are interested to calculate the change in a entropy between states 1 and 2, how can we use this, we can integrate this equation only along a reversible path because T dS equal to del Q is valid only for reversible process. So, imagine you construct a hypothetical reversible path, but the actual process may be irreversible actual process may be this ok. Normally irreversible processes we show by dotted line in the process diagram, because the intermediate states are not in equilibrium and they may not be exactly known.

So, then if you integrate this you will get an expression for S 2 minus S 1. Once you get an expression for S 2 minus S 1, then you can use it even for the irreversible path right, so that means that this equation has to be integrated over a reversible path. Once integrated, the final result can be used for any process. So, this is a two step way of looking into it. It is said that this is true for any this, this can be applied for any process that is correct, but before applying it for any process conceptually it has to be integrated over a reversible path. The result of that integration can be used for any process. I hope I have clarified it, because there is a lot of doubt and confusion of these in the mind of the students.

So, this you have so with this assumptions that is you know you have only moving boundary work and neglecting changes and changes in kinetic energy and potential energy. If you have other forms of work, you can have similar T dS relationship with you know other work terms added with it. Now, this equation can be written in terms of enthalpy also. So, U is H minus p V right, because H is equal to U plus p V. So, you can write in this way. So, you can write this as dH minus p dV plus minus V dp plus p dV.

So, this p dV and p dV gets cancelled. So, you have the other T dS relationship which is equivalent is d H minus p dV these V dV. These equations are so popular because you know just property relationships. You these are combined consequences of first law and second law. So, you can neither call it you know an expression for first law, you can neither call it an expression for second law, it is a combined effect of first law and second law, but this can be used for finding the change in entropy during any process. So, this T dS, these are called as T dS relationships.

So, we will apply this T dS relationship to two special cases; one is an incompressible substance, and another is ideal gas. So, special case incompressible substance; so, for incompressible substance, the terms dV or dp, these are not important right that there is no change in volume. So, incompressible substance will mean d V equal to 0. And what is dU, dU is mass into specific heat into change in temperature. For incompressible substance that is no distinction between C p and C v, so you can just call this m C dT.

So, you can write dS dS m C d T by T ok. So, if you integrate it between state points 1 and 2, and assuming that you know C is not a function of T which is you know a restrictive as assumption because for many substances the specific heat itself is the function of temperature. So, this is giving rise to m c ln of T 2 by T 1. So, S 2 minus S 1 is equal to m c l n T 2 by T 1. This is the formula that we can derive for incompressible substance.

The next example, so this is special case number 1. We will consider a special case number 2. Special case number 2 is ideal gas ok. So, for ideal gas you can write an d u is equal to m c v d T right. And you can write p V equal to m R T. So, p is equal to m R T by V. So, if you substitute this in the first T dS relationship, you will get T dS is equal to m C v d T plus m r T by v dV so that means, dS is equal to m C v d T by T plus m R dV by V that dT gets cancelled out.

So, if you integrate from 1 to 2, state 1 to state 2, and assuming so if you what you know these assumption of C v being temperature independent is a over restrictive assumption in most of the cases. So, we will generalize this a little bit, and write S 2 minus S 1 is equal to m integral of C v dT by T 1 to 2 plus m R ln of V 2 by V 1. This C v in general for ideal gas is a function of temperature. What is that special case when C v is not a function of temperature; it is a constant it is called as calorically perfect gas.

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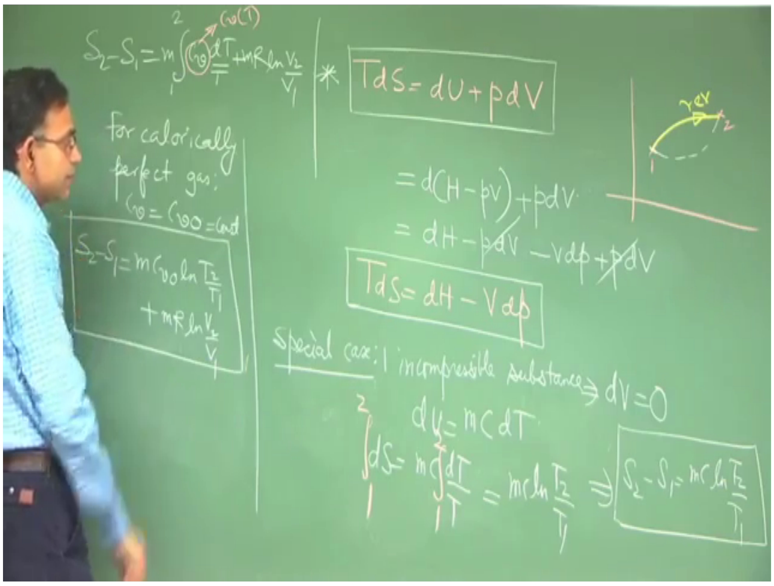

So, for calorically perfect gas C v equal to C v 0 that means, S 2 minus S 1 is equal to m C v 0 ln this is constant. So, this is from the first T dS relationship. You can alternatively use the second T dS relationship to get another expression which is in terms of C p.

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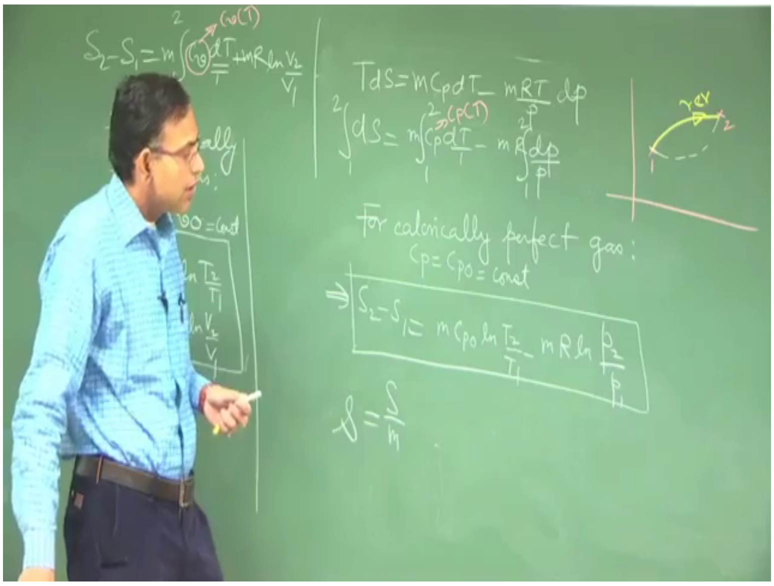

So, for that you use this expression. So, T dS for ideal gas, this will be m C p dT dH minus V is m R T by p dp. So, dS is m C p T by T minus m R dp by P. So, if you now integrate it is this, C p is function of temperature in general ok. For calorically perfect gas, C p is equal to C p 0 equal to constant. This means S 2 minus S 1 is equal to m C p 0 ln T 2 by T 1 minus m R ln P 2 by P 1 ok. So, you have nice expressions for ideal gas with constant C p, C v.

For non-ideal substances, how do you calculate change in entropy you have to refer to the property tables. And just like you have internal energy enthalpy are tabulated, you will also have entropy tabulated. And then you know specific entropy is what is tabulated that is the total entropy per unit mass. For phase changing substance just the same interpolation rule that you use for specific volume, internal energy, enthalpy, the same interpolation rule that you can use for entropy, so that is how entropy is calculated, but these are entropy changes that are calculated that you must remember not the absolute values of entropy ok.

The next item that we will consider is that we have so far considered reversible processes for calculating the change in entropy, but what happens to the change in entropy for an irreversible. So, change in entropy for an irreversible process, but you know I thought that before entering into irreversible process, we will talk about a special type of irreversible process which will give us a whole lot of insight and that is very common in most of the thermodynamics cycles that we talk about is reversible adiabatic process.

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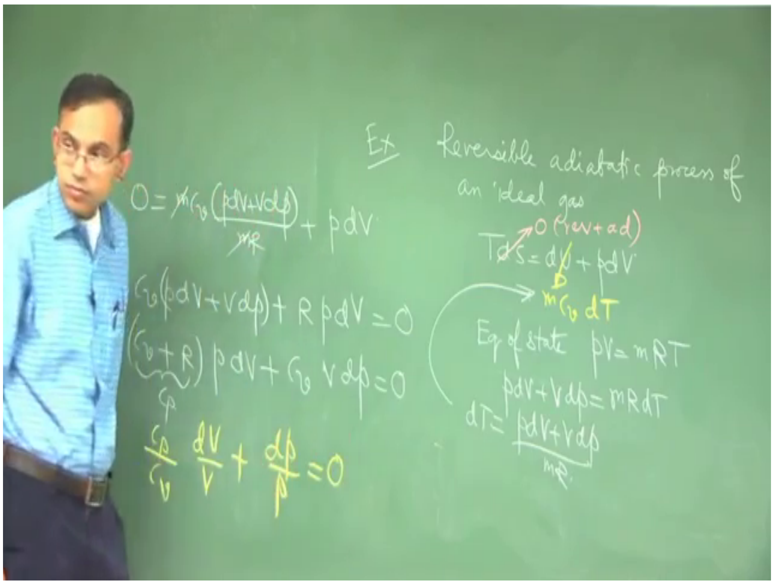

So, we will consider a specific example before entering into irreversible process that is reversible adiabatic process of an ideal gas. So, for an ideal gas, reversible plus adiabatic if you use, so reversible you can use del Q equal to T dS ok. If it is adiabatic that means del Q equals to 0. So, T dS equal to 0, and you have T dS equal to dU plus p dV. So, T dS equal to dU plus p dV reversible and adiabatic is isentropic.

So, remember you require both reversible and adiabatic to you know set these to 0. And for ideal gas dU is m C v dT ok. For ideal gas, you have another constraint which is the equation of state of an ideal gas p V equal to m R T. So, if you now differentiate both sides p dV plus V dp is equal to m R dT. Now, you can eliminate dT from these two to get a relationship between pressure and volume for reversible adiabatic process of an ideal gas.

So, you can write for example you can write dT is equal to p dV plus V dp by m r and that you can substitute here if you substitute that here you will get let me utilize this part of the board. Now, 0 is equal to m C v p dV plus V dp by m R plus p dV. So, you will have you can write this as C v into p dV plus V dp plus R p dV equal to 0. So, C v plus R p dV plus C v V dp is equal to 0. C v plus R is C p, it does not matter whether it is constant C p, C v or variable C p C v. Even if C p and C v are variable that difference is always R. So, you can write now you divide both sides by say p V, p into V. And so you can write C p by C v dV by V plus dp by P is equal to 0 ok. And C p by C v is called as gamma, the ratio of specific heats.

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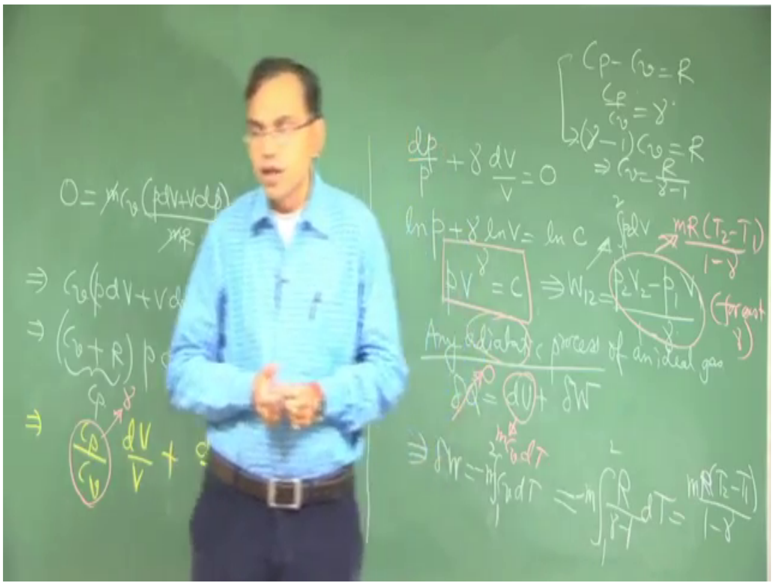

So, we can write dp by p plus gamma dV by V is equal to 0. If you now integrate it, you can write ln p plus gamma ln V is equal to say some constant ln C, which is constant of integration, so that means, p v to the power gamma equal to constant. So, it shows that for reversible adiabatic process you can fit it in the form of a general polytrophic process p V equal p V to the power equal to constant where n is a very special value here which is C p by C v.

Again it does not require C p, C v to be constant. The instantaneous the C p and C v at that particular state that ratio you can use to define a particular state using this p V to the power gamma equal to constant. So, this is the proof that for reversible and adiabatic process p V to the power gamma is equal to constant for an ideal gas. For a non ideal gas that is not true.

Now, if this is true, we have shown that the work done, this is integral p dV this we have done during the in the chapter heat and work. So, I am not repeating here. Let us see consequence a very important consequence when the substance is not undergoing a reversible process, but only adiabatic process. So, the reversible restriction is withdrawn, but the adiabatic restriction is not withdrawn. So, irreversible adiabatic process or we can say any adiabatic process may be irreversible or reversible.

So, any adiabatic process, for any adiabatic process, we cannot say dS equal to 0, but we can say del Q equal to 0; so, any adiabatic process of an ideal gas. So, del Q is equal to dU plus del W not p dV right, because any means it is not it need not be reversible, it need not be quasi equilibrium, it could be really any, only assumption is you neglect changes in kinetic energy and potential energy. So, the heat transfer is 0, because it is adiabatic dU is still m C v dT ok. So, the work done here you can calculate right. So, can you express this in terms of r and. So, just to make a parity with this expression this is p 2 v 2 is m r T 2 and p 1 v 1 is m r T 1; so, m R T 2 minus T 1 by 1 minus gamma, no this one.

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This is minus yes. So, this is m R T 2 minus T 1 by 1 minus gamma. Now, you can express C v in terms of R and gamma to make a parity of these two. So, how do you do that it is very simple C p minus C v is equal to R, and C p by C v is equal to gamma right. So, you can write C p as gamma minus 1 this left hand side is equal to R that means C v is equal to R by gamma minus 1.

So, can you write these as m R by gamma minus 1 dT right ok. So, if you write that with a minus 1 to 2, these also gives m R T 2 minus T 1 by 1 minus gamma looks very surprising even without reversible assumption we have come with an expression of work which we derived for reversible process right. Here we have not assumed p V to the power gamma equal to constant. And in fact p V to the power gamma equal to constant is not true for any adiabatic processes this is true only for reversible adiabatic process of an ideal gas, but without that we come to an expression which is same as this. Well, there are two hidden things about it.

The first hidden thing is when we are writing p V to the power gamma equal to constant, this does not imply constant gamma. This could be even variable gamma. When we are writing these we are integrating this for a constant gamma right. If gamma is variable, then you know the integral p dV that variable gamma has to be included. So, this is for constant gamma. And this is also for constant gamma. So, if gamma is constant that is C p the ratio of C p by C v which is constant if either C p and C v you mean both are constant then the ratio is also constant.

Then the eventual expression for work done for reversible adiabatic and only adiabatic they are the same, but the process expression for reversible adiabatic, this cannot be applied for any adiabatic process. And this is so generic that this can be applied to a reversible adiabatic process no matter whether C p and C v are variable or constant, but only restriction it has to be ideal gas. And here again the only restriction is adiabatic, ideal gas, constant gamma no restriction of reversible.

So, this is a very interesting thing. In the school level, we do this derivation in the higher level we come up with the derivation where we use the T dS relationship and where do this merge where they are I mean equivalent were they are not that has to be clearly understood. We stop here in this lecture, we will continue with ore discussion on change in entropy in the next lecture.

Thank you.