Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 24
Further discussion on relation between Cp and Cv

Let us continue our discussion on the various thermodynamic properties and their relation. And in this lecture we will discuss on the relationship between C p and C v. So, usually we say that C p minus C v is equal to n r, but C p minus C v equal to n R is only applicable to perfect gases. And when the gases are not perfect then C p minus C v is not equal to n r, but it is modified it is different than nR.

And moreover, this C p and C v are not just the thermodynamic quantities for the gases. C p and C v can be defined or measured for a substance in any of it is phase be it is solid liquid or vapor. So, today we will develop thermodynamic relations between C p and C v which are applicable to all the systems. Let us first begin with a general definition of C p and C v. C p minus C v. Let us write down for C p minus C v.

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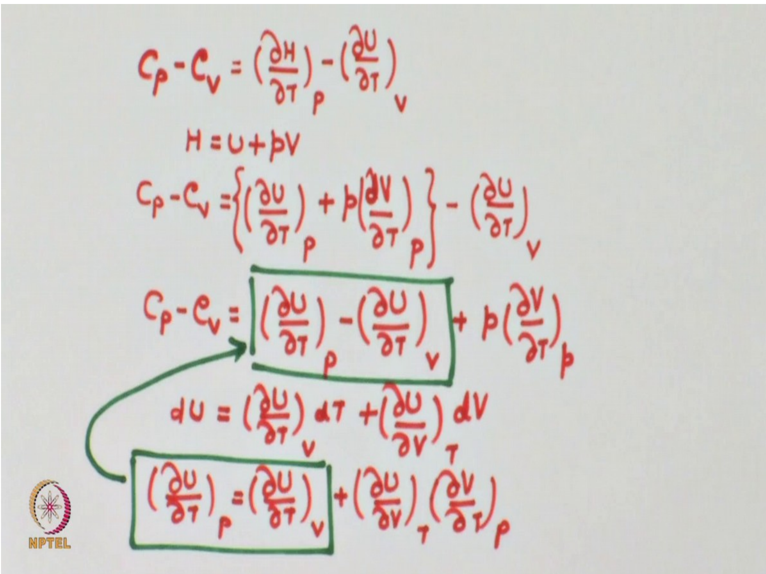

This is equal to C p is dou h dou T at constant pressure and C v is dou u dou T at constant volume. This I have substituted the exact definitions of C p and C v. Now you know that h is equal to u plus p v. So, C p minus C v gets modified to, let us take it is derivative with at constant pressure. This will be dou u dou T at constant pressure plus p dou V dou T at constant pressure. This is just the differentiation of h that is for dou h by dou T at constant, p minus dou u dou T at constant volume. What I have here is C p minus C v is equal to variation of internal energy with respect to temperature at constant pressure, minus variation of internal energy with respect to temperature at constant volume, this and this I have combined plus p into variation of volume with respect to temperature at constant pressure.

We have just discussed that d u if in the previous session, d u is equal to dou u dou T at constant volume d t, plus dou u dou V at constant temperature d v, we just discussed that. And from this I can write variation of internal energy with respect to temperature at constant pressure is equal to variation of internal energy with respect to temperature at constant volume, plus variation of internal energy with respect to volume at constant temperature into variation of volume with respect to temperature at constant pressure. I have divided throughout by dT at constant pressures the reason is I have done this. Because, I am interested in substitution for this which I can get from this I can substitute over here

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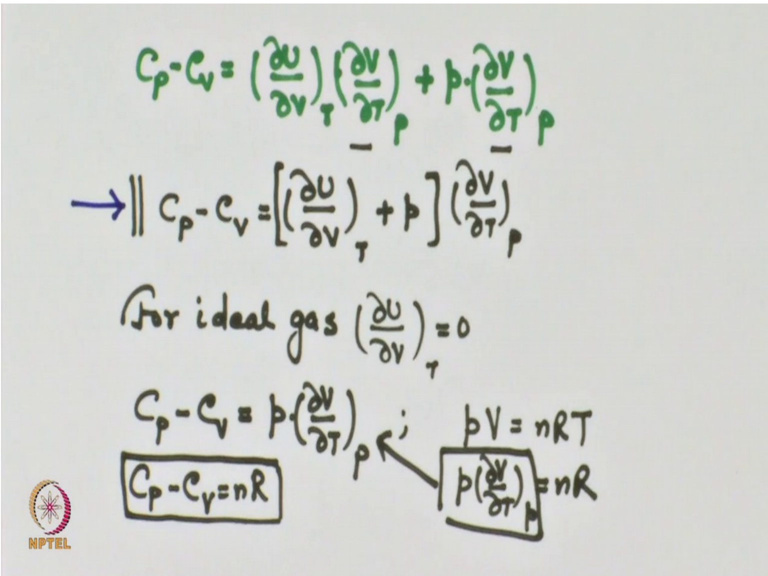

So, I will use this in the next slide, what I will get is C p minus C v and for that difference it will be dou u dou V at constant temperature, into dou V by dou T at constant pressure plus p into variation of volume by temperature at constant pressure. So, what I have is C p minus C v is equal to, I take this as common, variation of internal energy with respect to volume at constant temperature plus p, into variation of volume where the temperature at constant pressure see.

What I have done is we have not so far used any condition for ideality; that means, the equation that we have developed between C p for C p minus C v is applicable to all the systems. It is not just applicable to the ideal gases, but it is applicable to all the systems. It allows for the deviations from ideality. Now from these equations I can further derive 2 equations. Let us say for ideal gas, for ideal gas the variation of internal energy with volume at constant temperature is going to be 0.

So, if I substitute 0 over here, I have C p minus C v is equal to p into variation of volume with temperature at constant pressure. Now you remember that p V is equal to n R T this is for ideal gas. So, according to this p into variation of volume with respect to temperature at constant pressure is going to be n R, derivative of volume with respect to temperature here temperature derivative with respect to temperature is 1. So, we have n R and this I can substitute over here once you substitute over here, you get C p minus C v is equal to n R this is the equation that is applicable to ideal gas.

And this is the most widely given answer when someone is asked what is C p minus C v for ideal gases it is equal to nR. Now let us keep this equation in mind, I will rewrite this equation and will show you that how it takes up another form. So, we will come back to this equation.

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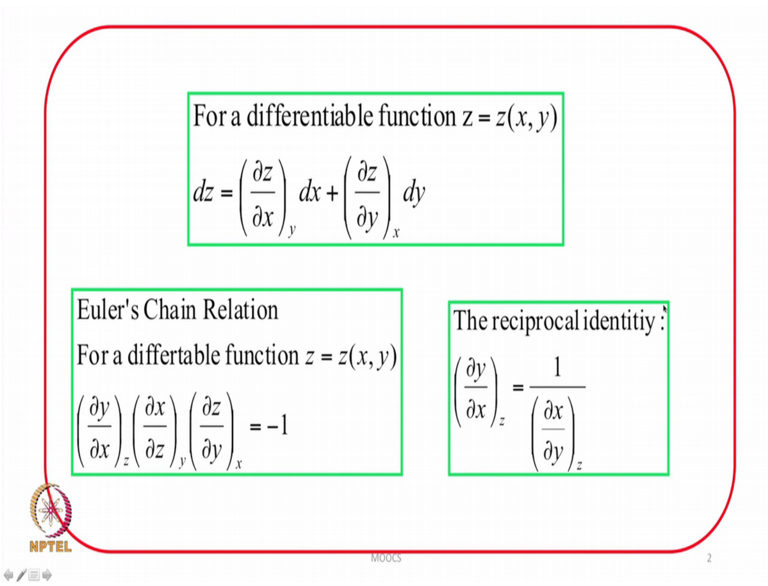

But, before that let us look at some very useful mathematical relations; this relation we have been using. So, far that if z is a function of x and y, then any variation in z that is the differentiable function z d z is equal to dou z dou x at constant.

Y d x plus dou z dou y at constant x d y, this we have been using. Another relation that we will be using now in solving the further questions is Euler chain relation. This is sometimes also called chain relation or this is also sometimes called cyclic rule. That is for any differentiable function z, which is a function of x and y dou y dou x at constant z into dou x dou z at constant y, into dou z dou y, at constant x is equal to minus 1. This is a cyclic rule because you are just you making a cycle between y x and z. So, you see note down here dou y dou x at constant z, then we will shift it to dou x dou z at constant y, you see here and then we shift it to dou z dou y at constant x.

See here this has to be equal to minus 1 keep that in mind and one more relation that is the reciprocal identity, that we will be using dou y by dou x at constant z is equal to 1 over you take a reciprocal of this dou x by dou y at constant z. So, these mathematical equalities of these mathematical equations will hold and we will make use of these relations in solving further numerical problems.

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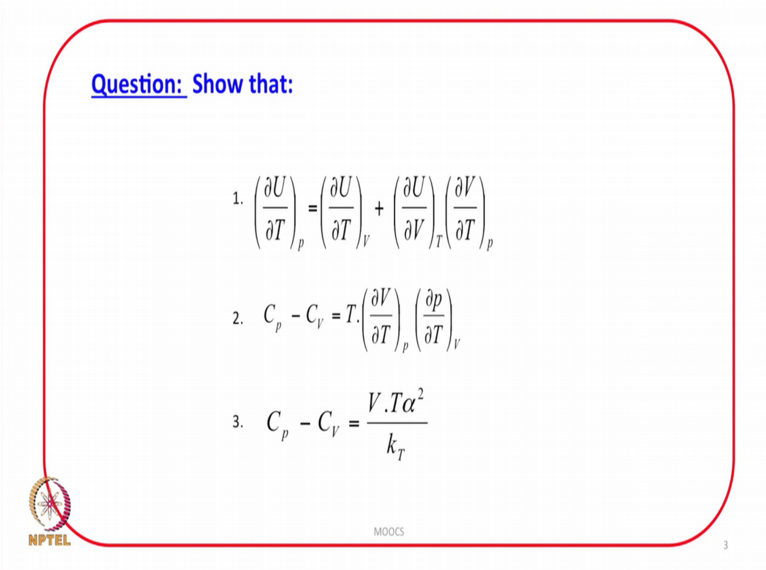

Let us now take up one by one. Question number one, show that dou u by dou T at constant pressure is dou u dou T at constant volume, plus dou u dou V at constant temperature into dou V dou T at constant pressure, we have just discussed this at length.

Therefore, we will switch over to the next question, is to show that the difference between C p and C v is equal to T times dou V dou T at constant pressure into dou p dou T at constant volume. So, the best way to attempt these type of questions are to solve these kinds of questions is that we actually start with the definition of C p, and definition of C v, and proceed now let me again come back to the same equation that we just derived. I will use this equation and proceed from here to get an answer to question number 2 that is being asked. So, let me rewrite this equation on a different slide.

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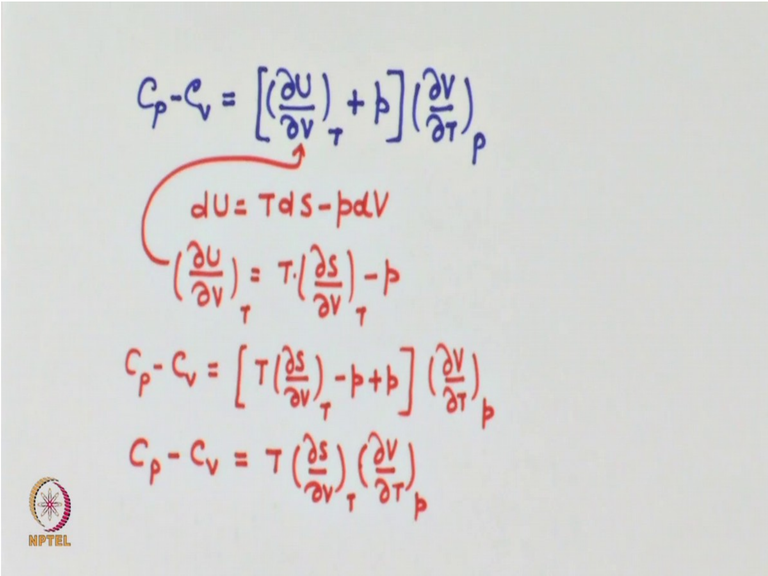

What we have is C p minus C v is equal to variation of internal energy, with volume at constant temperature, plus pressure into variation of volume with temperature at constant pressure. And if you look at the slide question number 2, the variation of volume with temperature at constant pressure is already there in the answer.

But in the answer there is no separate pressure term although derivative is there. Therefore, when we look at the slide this expression, we need to get rid of pressure. So, the strategy should be that we find out an expression which we substitute in this, and that should allow us to get rid of the pressure, which how we can proceed. Can we write an expression for the dou u by dou V at constant temperature? And that should allow us to get rid of pressure. Let us think maybe this equation d u is equal to TdS minus pdV, this is the fundamental equation you see this equation can allow us to express variation of internal energy with respect to volume at constant temperature and pressure will also appear in this.

So, if I divide throughout by V at constant t, what I will get is T variation of entropy with volume at constant T minus p. And if I substitute this over here I will get rid of p what do we get now C p minus C v is equal to T variation of entropy with volume at constant temperature, minus p plus p, and what I have is variation of volume with temperature at constant pressure.

So, what I have C p minus C v is equal to T into delta s delta V at constant temperature into delta V and delta T at constant pressure. Now if we look at the question number 2, we has arrived at a relationship which is closer to what is required, but we do not have in the final answer variation of entropy with volume at constant temperature, but what we have is here the variation of pressure with respect to temperature at constant volume. So, therefore, we need to convert or write another derivative, which is equivalent to this and should be able to connect pressure and temperature. And here we will use those one of those Maxwell relations.

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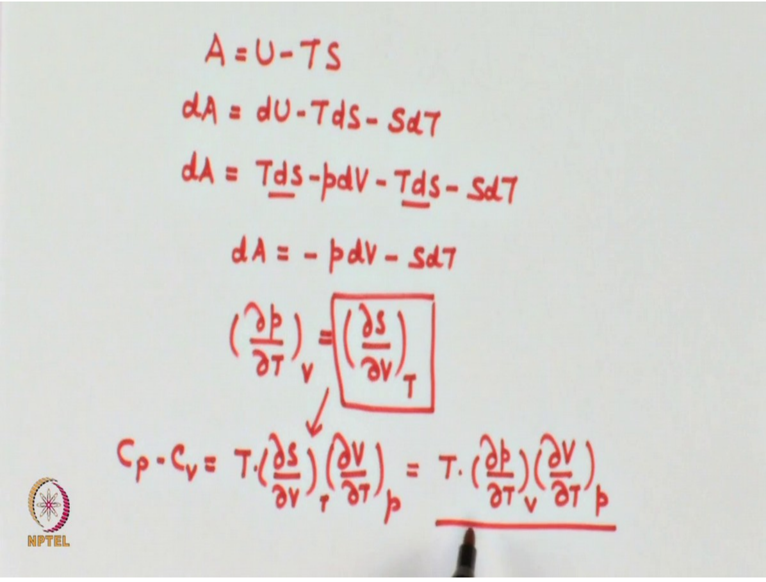

What are those Maxwell relations we have discussed earlier? That is, you remember that if you start with A, A is equal to u minus TS, and dA is equal to this may have discussed earlier many times d u minus TdS minus s dT or dA instead of d u if I write d u is equal to TdS minus pdV this is d u minus TdS minus s dT this and this get cancelled. So, what

I have is dA is equal to minus pdV minus s dT. This will allow me to write a Maxwell relation that is dou p by dou T at constant volume is equal to variation of internal energy with volume at constant temperature. And that is what I was looking for that can I connect this variation of entropy with volume at constant temperature with pressure temperature and volume.

So, what I had earlier was C p minus C v is equal to temperature, into variation of entropy with volume at constant temperature variation of volume with temperature at constant pressure. And I will substitute this is what I have is T into variation of pressure with temperature at constant volume variation of volume with temperature at constant pressure. This is what was asked look at in the slide the question number 2 C p minus C v is equal to temperature into d V by dT at constant pressure dp by dT at constant volume. So, we have here proved that this relation holds 2.

Please remember again, that the equation that we have derived is not just applicable to ideal equation. It is applicable to all the systems. What we need to know how the various thermodynamic properties depend upon volume depend upon pressure depend upon temperature. And this equation number 2 that we derived you can yourself show that for ideal gas this will convert equal to nR. If you just find out for ideal gas what is this variation of volume with temperature at constant pressure. And the variation of pressure with temperature at constant volume you will find out that C p minus C v for ideal gas turns out to be equal to the nR.

Now, the question number 3, is to show that C p minus C v is equal to V times T into alpha square over isothermal compressibility k t. So, we can use this equation the equation that we derived to get this result.

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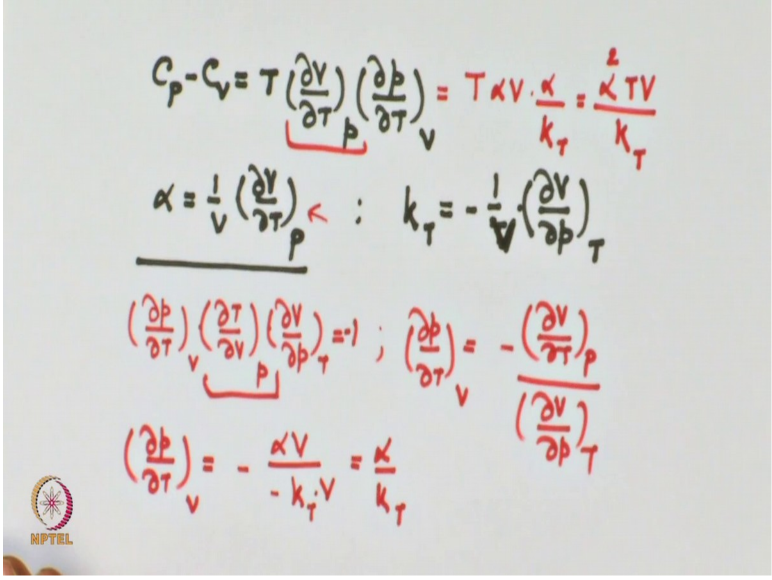

Let us see; how do we do that. The equation that we derived is C p minus C v is equal to temperature into variation of volume with temperature at constant pressure, into variation of pressure with temperature at constant volume. Variation of volume with respect to temperature at constant pressure, you remember that earlier I introduced expansion coefficient alpha which is one over V into dou V dou T at constant pressure. This is expansion coefficient.

And isothermal compressibility, k T isothermal compressibility is equal to minus 1 by T into how the volume responds to pressure at constant temperature. See this was expansion coefficient this is compressibility and isothermal I am putting that is why t, but in the in this equation, I do not have V p T. You know you see here p T V and V p T and that reminds us that we can use the cyclic rule. That means, if I use this p T V, T V, p V p T equal to 1 minus 1 this is a cyclic rule this will allow me to write for variation of pressure with respect to temperature at constant volume, is equal to what do I write minus variation of volume with respect to temperature at constant pressure divided by variation of volume with respect to pressure at constant temperature. You see this when I am taking on the other side I am using the inverse relation V T p and this I am taking directly in the denominator.

So, this allows me to write dou p by dou T at constant volume is equal to minus, this if I use this this is equal to alpha times V. And this if I use from here which is equal to minus k T times, I am sorry let me correct over here this has to be per unit volume not temperature per unit volume please correct. This variation of volume per unit volume, into what I have here is 1. So, this is equal to alpha over k T. And now if I substitute over here what I have T for this I will use alpha V for this delta V by delta T it constant ratio is alpha V into I have alpha by k T, which is equal to alpha square T V by k T this is what was asked from us.

Now, let us take a look at another question.

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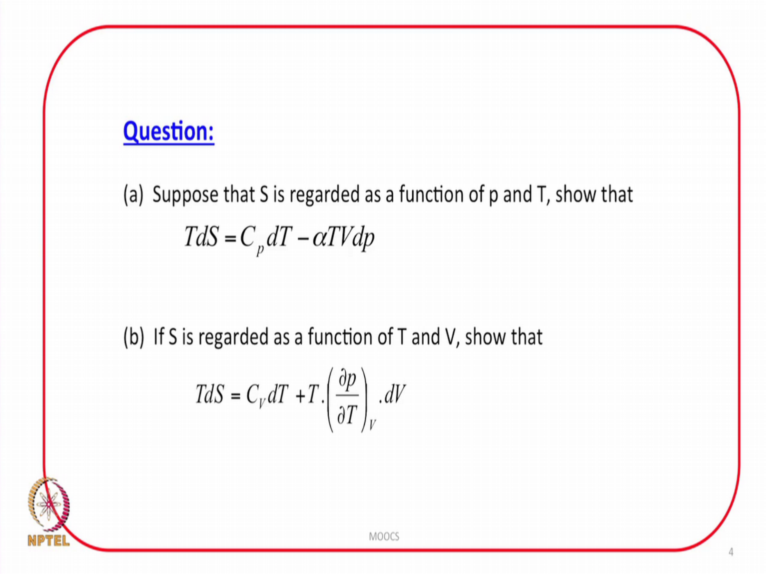

Suppose s is regarded as a function of p and T, then show that TdS is equal to C p dT minus alpha TV dp. Let us see how we use the given information to come up with the answer, we are asked to treat s depends on p and t.

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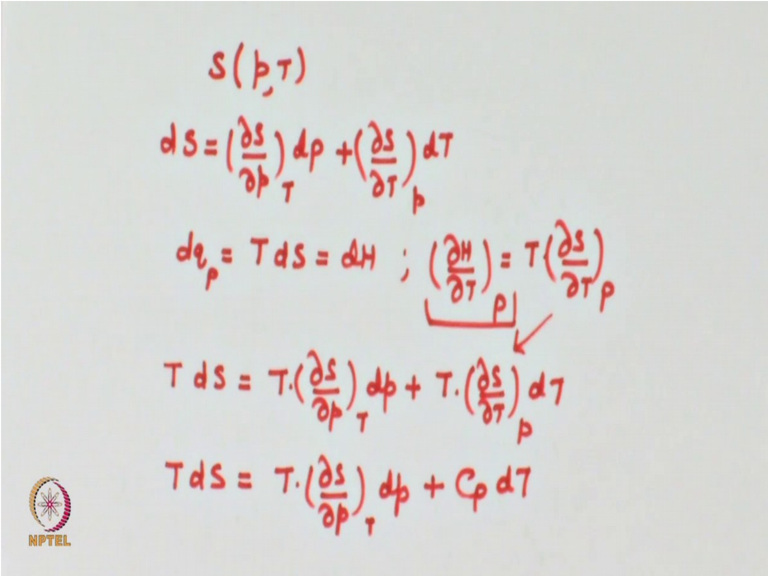

So, immediately I will write d s is equal to variation of entropy with respect to pressure at constant temperature dp, plus variation of entropy with temperature at constant pressure dt.

In the given question along with the dT term there is the C p, how do we get C p. I can get you know that dq at constant pressure is equal to dq is always is equal to TdS, and constant pressure means I will say dH. So, from this equation can I write dou h by dou T at constant pressure is equal to T, into d s by dT at constant pressure right. And this is nothing this is C p. So, I can substitute now, here let us multiply T on each side TdS is equal to T times dou s dou p at constant temperature dp, plus T times dou s dou T at constant pressure d t.

Now, I can use this information over here, and I have TdS is equal to T into dou s dou p at constant temperature dp plus C p d t. So, at least one part we have been able to get as asked in the question C p dT you there. Now we need to get the other part and in order to get the other part we can again use the Maxwell relation, and what we need now is the variation of entropy with pressure and for that.

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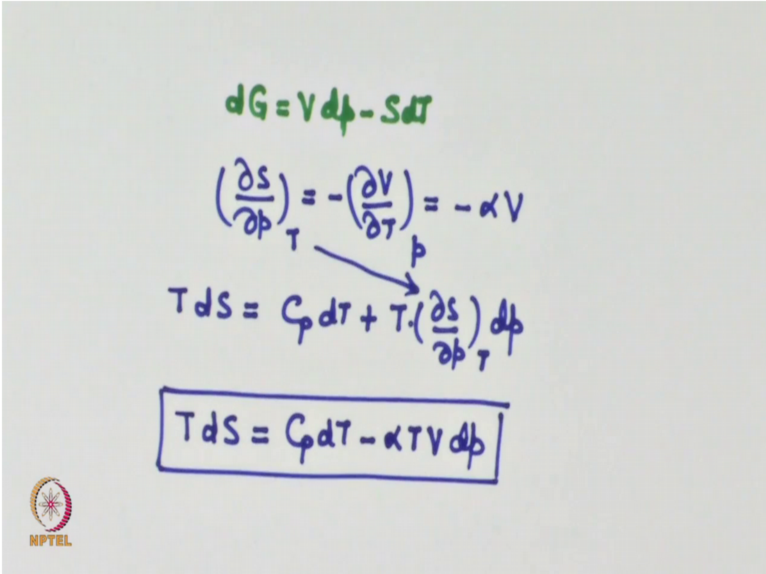

We can use again another Maxwell relation from d g is equal to V dp minus s dT, because this will allow me to express the variation of entropy with respect to pressure at constant temperature.

According to this the variation of entropy with pressure at constant temperature is minus variation of volume, with temperature at constant pressure. And will it is it not equal to minus alpha times V because I have already discussed that what is alpha is one over V dou V dou T at constant pressure this is equal to minus alpha V. So, now, if I substitute in the equation that we just derived the TdS is equal to C p dT plus T into dou s dou p T dp that was the equation that we just derived in the previous slide, and for this dou s dou p dou T at constant temperature I will put alpha v. So, I end up with TdS is equal to C p dT minus alpha T V into dp this was the required answer.

Now, you can integrate and calculate the changes in entropy, when the other properties of the system are known. So, these kinds of equations allow us to account for the deviations from ideality. Please remember again that these in deriving these equations we have not assumed any ideal behavior. And for example, this particular equation will allow you to calculate T entropy changes when the temperature changes and pressure changes. So, what information do we need on the systems then is the heat capacity expensivity the temperature and volume.

Similarly, we can get another equation in terms of C v and this you can try yourself the approach will be exactly the same. Only thing is in in place of constant pressure you will be using constant volume condition. So, what we have discussed in this particular lecture is that the various thermodynamic properties which are not just applicable to ideal systems. The differences for example, in C p and C v can be expressed in many forms and what we have to look for is that we should express this in a form which results into the thermodynamic properties, which can be experimentally determined.

And these equations allow deviations from ideality and once you use the rules for ideal gases or ideal solutions. You will see that these various equations will take the form which we have earlier derived for ideal gases or ideal solutions.

Thank you very much.