Thermodynamics (Classical) for Biological Systems

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Module No. # 02
Additional Thermodynamic Functions
Lecture No. # 07
Thermodynamic Relations for a Closed System with 1 mole of a pure Substance

Today, let us began by looking at the changes in enthalpy and entropy of one mole of a pure substance in a closed system, in terms of changes in temperature and pressure. As you are comfortable by now, temperature and pressure are easily measurable.

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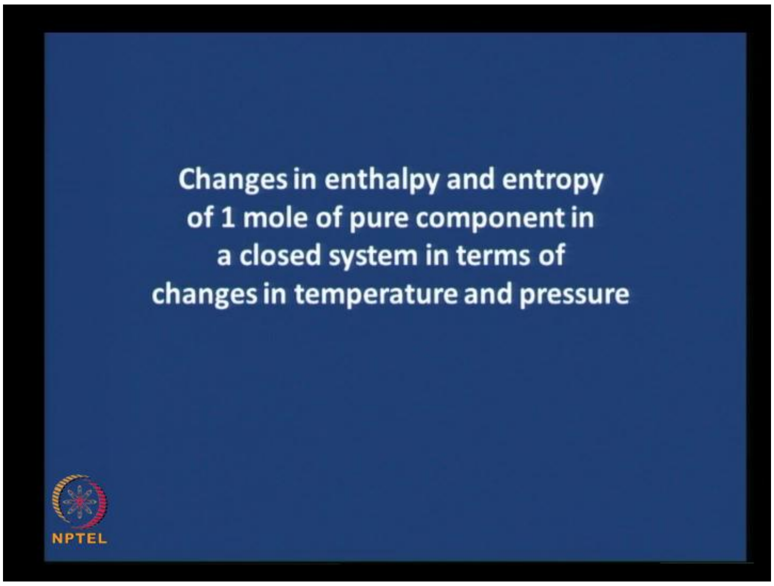

Changes in enthalpy and entropy of 1 mole of pure component in a closed system in terms of changes in temperature and pressure

And we are looking we are going to look at changes in enthalpy, and entropy as a function of the changes in temperature, and pressure.

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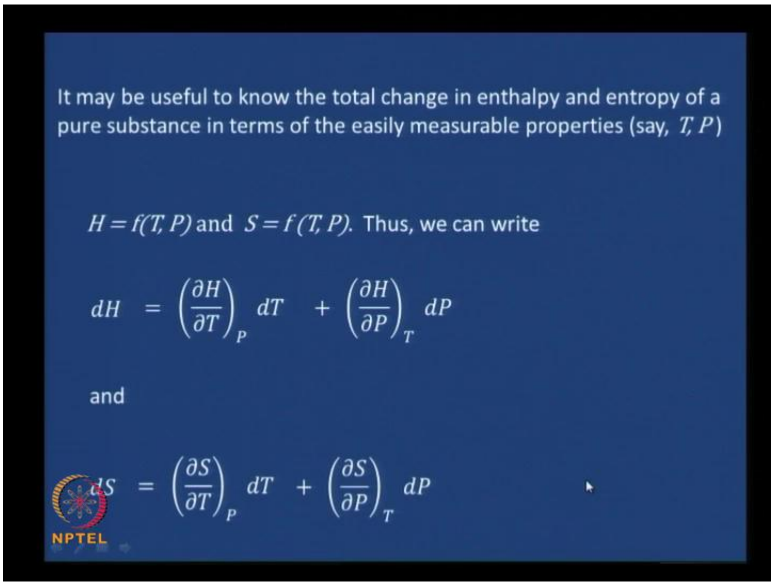

It may be useful to know the total change in enthalpy and entropy of a pure substance in terms of the easily measurable properties (say, T, P)

$H = f(T, P)$ and $S = f(T, P)$. Thus, we can write

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

and

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

To do that, let us write enthalpy as a function of temperature and pressure; and also entropy as a function of temperature, and pressure. Again, by now, you should be comfortable with this: the total differential d H in enthalpy is equal to dou H dou T at constant P. Remember we have taken this as a function of temperature, and pressure. So, dou H dou T at constant P times d T plus dou H dou P at constant T times d P. And we can write a similar expression for entropy also. The differential of entropy, total differential d S equals dou S dou T at constant P d T plus dou S dou P at constant T d P. By now you might begin getting ideas as to how to handle these partial differentials.

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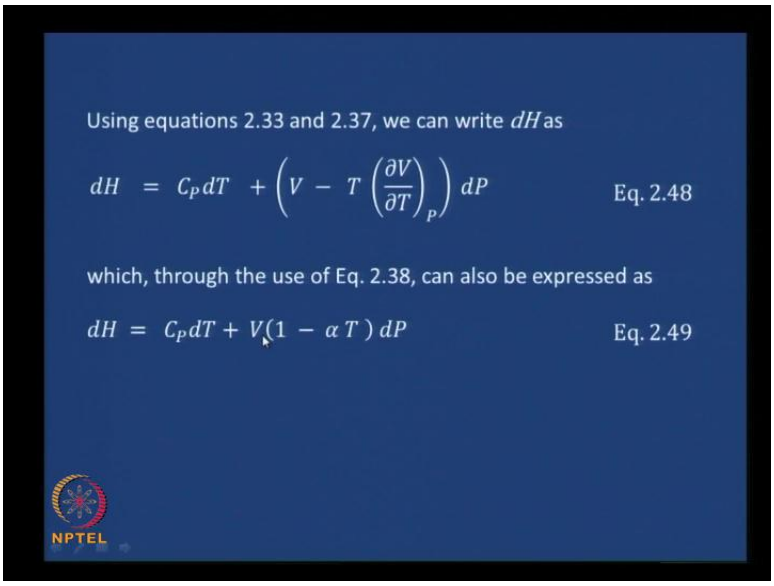

Using equations 2.33 and 2.37, we can write dH as

$$dH = C_P dT + \left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right) dP \qquad \text{Eq. 2.48}$$

which, through the use of Eq. 2.38, can also be expressed as

$$dH = C_P dT + V(1 - \alpha T)\, dP \qquad \text{Eq. 2.49}$$

Using the earlier equations – I give you the numbers here; you can go back and check what these equations are. As we present it should come back to you. We can write d H as C P d T recall that we are replacing dou H dou T at constant P dou H dou T at constant P is nothing but specific heat at constant pressure. And also note the term for this dou H dou P at constant t. So, d H is C P d T plus as we had seen earlier dou H dou P at constant T can be written as V minus T dou V dou T at constant P; this is what comes from equation 2.37 that you can go back, and verify.

Let us call this equation 2.48. If you use equation 2.38, you can again go back and check, but, it is going to be quite evident here, this V minus T dou V dou T at constant P. This is nothing but a part of the definition of alpha, the expansivity – expansivity was 1 by V dou V dou T at constant P; and therefore, you could replace this with V minus alpha V T. And if you take V common out, you will get V into one minus alpha T times d P; and of course, the C P d T remains here which equals a total differential. Let us call this equation 2.49.

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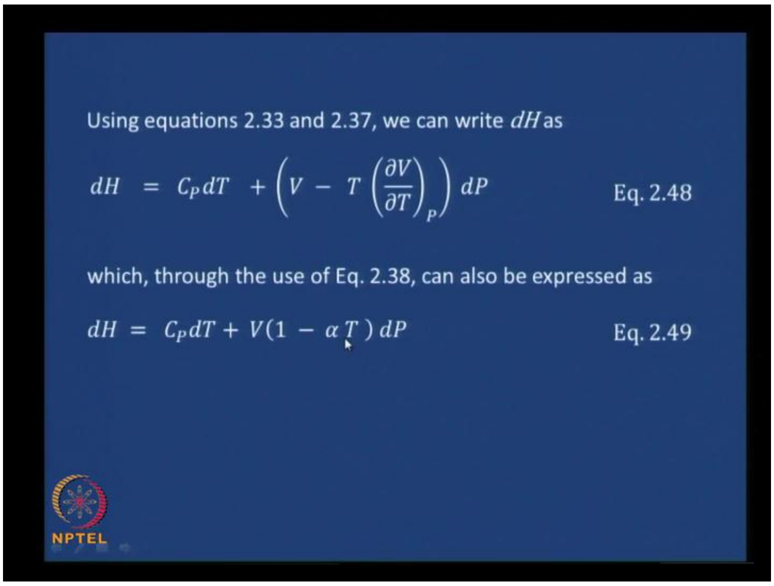

Using equations 2.33 and 2.37, we can write dH as

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which, through the use of Eq. 2.38, can also be expressed as

$$dH = C_P dT + V(1 - \alpha T)\, dP \qquad \text{Eq. 2.49}$$

Now, look at the thing here, we have enthalpy … the variation and enthalpy - the total variation in enthalpy as … expressed as C P, in terms of that is C P, V, alpha, and t. So, this is easily computable.

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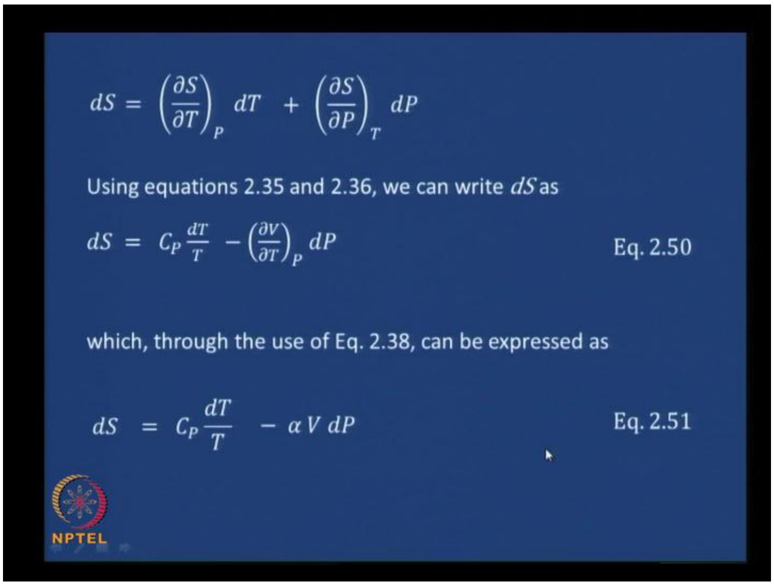

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Using equations 2.35 and 2.36, we can write dS as

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{Eq. 2.50}$$

which, through the use of Eq. 2.38, can be expressed as

$$dS = C_P \frac{dT}{T} - \alpha V \, dP \qquad \text{Eq. 2.51}$$

Similarly, let us consider d S equals dou S dou T at constant P … d T plus dou S dou P at constant T d P. Again as you may recall, or if you want you can go back, and check equations 2.35 and 2.36; they are essentially going to replace these partial differentials in terms of the easily, more easily measurable variables. We have already seen that dou S dou P was C P by T as given by equation 2.35, and that is what we have substituted here. Therefore, d S becomes equal to C P d T by T, and we have seen through equation 2.36 that dou S dou P at constant T could be written as minus dou V dou T at constant P.

So, that is what we have substituted here. Therefore, we get d S equals C P d T by T minus dou V by … dou V dou T at constant P times d P; we will call this equation 2.50, which can be expressed as – we are going to use the equation 2.38, now; d S equals C P d T minus alpha V d P. Note that this is d V … dow V dou T at constant P; therefore, this is variation of volume with temperature at constant pressure, expansivity – related to expansivity. And … 1 by V is actually the expansivity. And therefore, this becomes alpha times V. We will call that equation 2.51.

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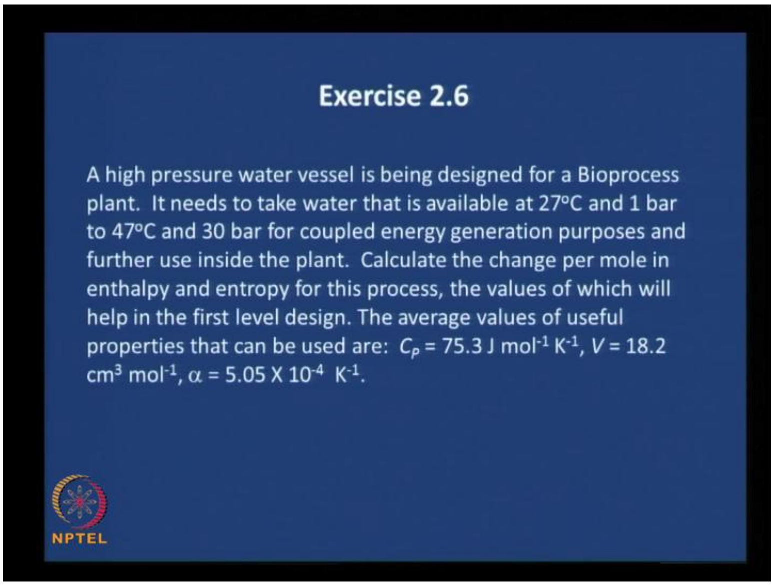

Exercise 2.6

A high pressure water vessel is being designed for a Bioprocess plant. It needs to take water that is available at 27°C and 1 bar to 47°C and 30 bar for coupled energy generation purposes and further use inside the plant. Calculate the change per mole in enthalpy and entropy for this process, the values of which will help in the first level design. The average values of useful properties that can be used are: $C_P = 75.3$ J mol^{-1} K^{-1}, $V = 18.2$ cm^3 mol^{-1}, $\alpha = 5.05 \times 10^{-4}$ K^{-1}.

Now, that we have the expressions for the variations in enthalpy and entropy of 1 mole of a pure substance, in terms of T, P, and other easily measurable variables, we will look at an exercise, where we can get more comfortable with the use of those equations. As earlier, I am going to present the exercise, then I will give you some time maybe 10 minutes to work things out … think through it - first think through it. There is a whole aspect of problem solving. If we have time we will get into that a little later. We first need to think about the problem – see what is given? What is required? How do you relate what is given to what is required? And then workout what is required. Simple to say, but it is not very easy in practice unless somebody … has a lot of experience or is very good.

Let us get to this exercise. A high pressure water vessel is being designed for a bioprocess plant. It needs to take water that is available at 27 degrees C and one bar to 47 degrees C and 30 bar for coupled generation … energy generation purposes, and further use inside the plant. This is a very typical scenario. Calculate the change per mole in enthalpy, and entropy for this process, the values of which will help the … in the first level design – we are in the design stage now. The average values of useful properties that can be used are C P equals 75.3 joules per mole per kelvin. Specific volume or molar volume is 18.2 centimeter cube per mole; nice number to remember – this is for water H 2 O, 18.2 centimeter cube per mole; alpha is 5.05 into 10 power minus 4 kelvin.

Please go ahead take about 10 minutes and work this out, and then I will present a part of the solution for you to go forward.

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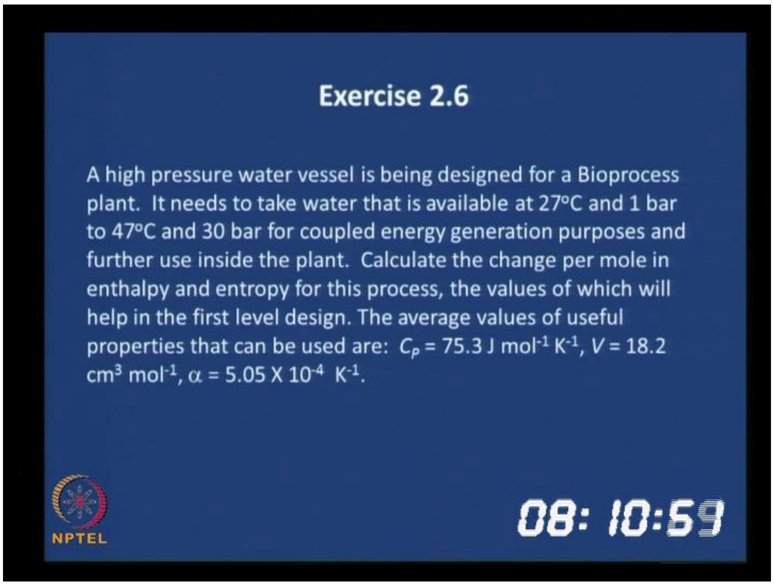

Exercise 2.6

A high pressure water vessel is being designed for a Bioprocess plant. It needs to take water that is available at 27°C and 1 bar to 47°C and 30 bar for coupled energy generation purposes and further use inside the plant. Calculate the change per mole in enthalpy and entropy for this process, the values of which will help in the first level design. The average values of useful properties that can be used are: $C_p = 75.3$ J mol^{-1} K^{-1}, $V = 18.2$ cm^3 mol^{-1}, $\alpha = 5.05 \times 10^{-4}$ K^{-1}.

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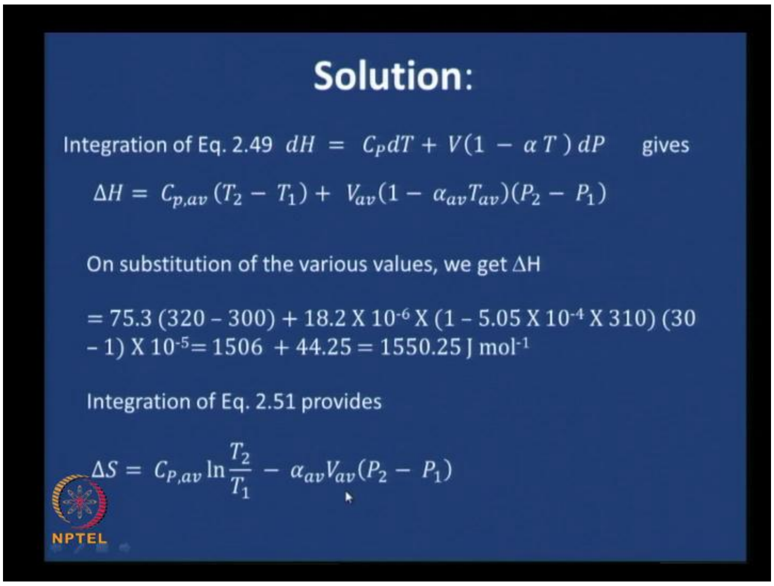

Solution:

Integration of Eq. 2.49 $dH = C_P dT + V(1 - \alpha T)\, dP$ gives

$$\Delta H = C_{p,av}(T_2 - T_1) + V_{av}(1 - \alpha_{av} T_{av})(P_2 - P_1)$$

On substitution of the various values, we get ΔH

$= 75.3\,(320 - 300) + 18.2 \times 10^{-6} \times (1 - 5.05 \times 10^{-4} \times 310)\,(30 - 1) \times 10^{-5} = 1506 + 44.25 = 1550.25$ J mol^{-1}

Integration of Eq. 2.51 provides

$$\Delta S = C_{P,av} \ln\frac{T_2}{T_1} - \alpha_{av} V_{av}(P_2 - P_1)$$

Now, let us look at how to go about solving this. I am just going to give you a hint, and then I am going to give you another 10 to 15 minutes to work things out, maybe you should take 15 minutes to figure out, how to go about this. If we integrate 2.49, I hope you recall … you can go back and check out 2.49 is: d H equals C P d T plus V into 1 minus alpha times T d P. If we integrate this … yeah, that is the equation there. We will get delta H here, and this is straightforward integration C P d T; therefore, it is C P average T 2 minus T 1. We have taken C P average, because C P is a function of temperature; that you may recall from the earlier classes in thermodynamics. Therefore, strictly speaking we must express C P as a function of temperature, and then integrate this. Nevertheless for small changes in temperature taking C P to be a constant is not a big error, that'll not result in a big error. Therefore, we take an average value of C P between the 2 temperatures, temperatures of interest; here, there is only a 20 degree change, and we should be fine. Here, if you integrate this; this is molar volume; we will again take this to be a constant, it may not be a bad assumption - times one minus alpha average T average d P is P 2 minus P 1. Now, why don't you substitute the various values to get delta H. Since, there are some calculations involved, where in to take about 15 minutes. Go ahead please.

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Let us go forward. Substituting the values that were given … check the units first; make sure that the units are consistent. In this case, you do not have to worry about it, all the values are given in consistent SI units. So, it is 75.3 C P average, T 2 expressed as kelvin – remember that – expressed as kelvin, 320 minus 300. In this case it does not make a difference, because we are taking the difference. So, whether you take it as in centigrade or in kelvin does not make a difference. But it is good to take it in kelvin where appropriate. And the molar volume, the average value was given, 18.2 into 10 power minus 6; alpha average was given 5.05 into 10 power minus 4. Here it is 1 minus that into the average temperature of 320 and 300, which is 310. And the pressures in the consistent units were 30 and 1, so 30 minus 1 into 10 power minus 5 to get into get it in the consistent set of units.

So, the first set of values would come down to 1506, the second set of values would come to 44.25, it is good to note the relative contributions of these terms. C P average T 2 minus T 1 is 1506; whereas, V into 1 minus alpha T P 2 minus P 1 is only 44.25. It is good to keep noting these relative contributions to be able to make quick estimates which are also reasonably close to what we require. In this case, since we have calculated both we need to calculate both here, this is not too small either its 44 out of 1500, and therefore, it is good to take this. So, 1506 plus 44.25, 1550.25 joule per mole. This is delta H.

Now, why don't you go ahead with the integration of 2.51. Go back into your notes, and integrate 2.51. See what you get. This is for delta S. See what you get in terms of the measurable properties. Substitute the values, and find out what delta S is for this particular case. Take another maybe 10 minutes since you know the scheme now, why don't you take about 10 minutes to find out. Go ahead please.

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Let us go ahead with the solution. Integration of equation 2.51. If you recall it was C P d T by T minus alpha V d P. Therefore, delta S would be … you have a d T by T term there along with a C P; and therefore, if we take the C P average value here, C P average times ln of T 2 by T 1 integral of d T by T is ln T. Therefore, … when you substitute the limits you get ln T 2 minus ln T 1 or ln T 2 by T 1. Here it is straightforward: minus alpha average V average into P 2 minus P 1; substituting the values now we know the … values.

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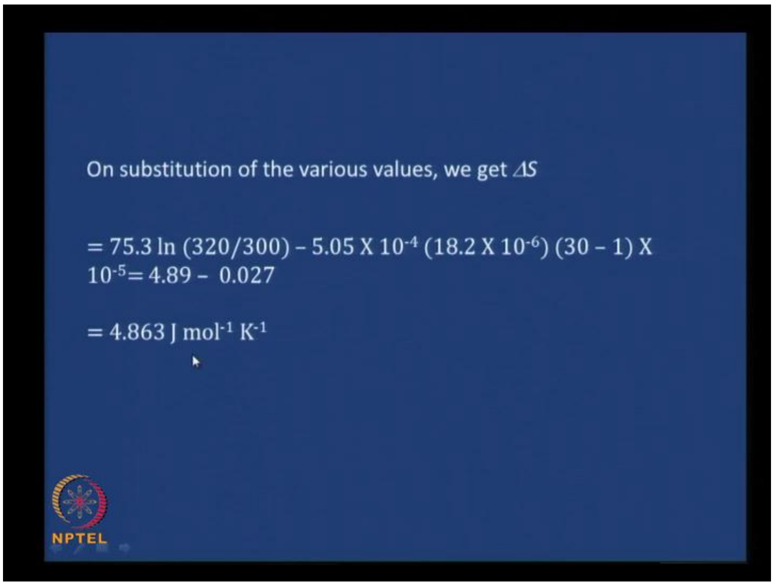

On substitution of the various values, we get ΔS

$= 75.3 \ln (320/300) - 5.05 \text{ X } 10^{-4} (18.2 \text{ X } 10^{-6}) (30 - 1) \text{ X } 10^{-5} = 4.89 - 0.027$

$= 4.863 \text{ J mol}^{-1} \text{ K}^{-1}$

We get 75.3 into ln of T 2: 320, T 1: 300 minus 5.05 into 10 power minus 4 into… This is alpha, this is molar volume V, 18.2 into 10 power minus 6, and this is 30 minus 1 conversion into the proper system of units, we multiply by 10 power minus 5, and 4.89

minus 0.027. Also nice to note the relative contribution of the values. Here you get 4.863 joule per mole per kelvin for delta S, take it on face value now that these are useful values for the design of the process itself. You would have some idea as to how these come in useful for process related aspects from earlier classes, may be we will see some related aspects in the later part of this module itself.