Chemical Engineering Thermodynamics
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Lecture – 10
Thermodynamic Properties of Fluids

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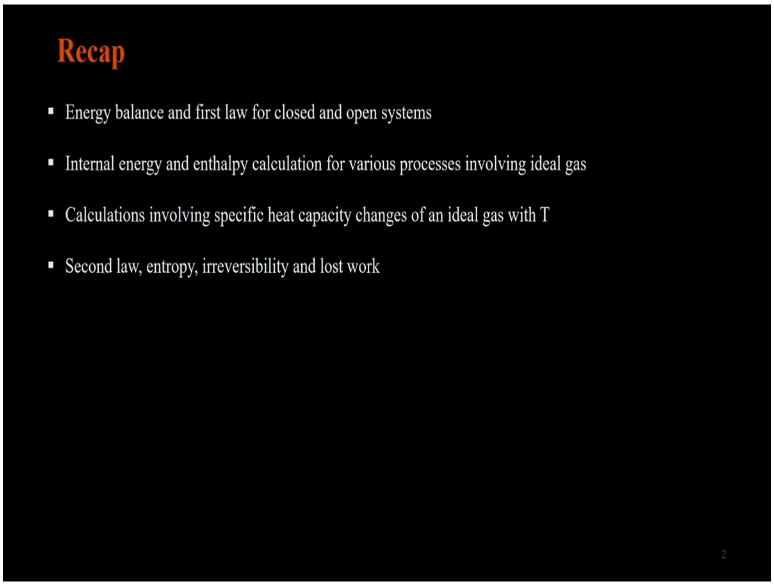

Recap

- Energy balance and first law for closed and open systems
- Internal energy and enthalpy calculation for various processes involving ideal gas
- Calculations involving specific heat capacity changes of an ideal gas with T
- Second law, entropy, irreversibility and lost work

Hello and welcome back. In the previous lectures, we have looked at energy balance and the first law for both closed and open systems. We have looked at internal energy and enthalpy calculations for various processes that involve an ideal gas. We have looked at use in the specific heat capacity for these calculations, and how to use temperature dependency of the specific heat capacity in these calculations. We have also looked at the second law, the entropy calculations, the calculations for irreversible processes, and the calculation for lost work.

What we will do today is try to extend our discussion as we noted earlier, the work and heat requirements for a process involve calculation changes in enthalpy, internal energy, entropy etcetera, but these calculations we have done earlier are for ideal gasses, now we will try to extend them to real fluids. So, how does one determine these real fluids.

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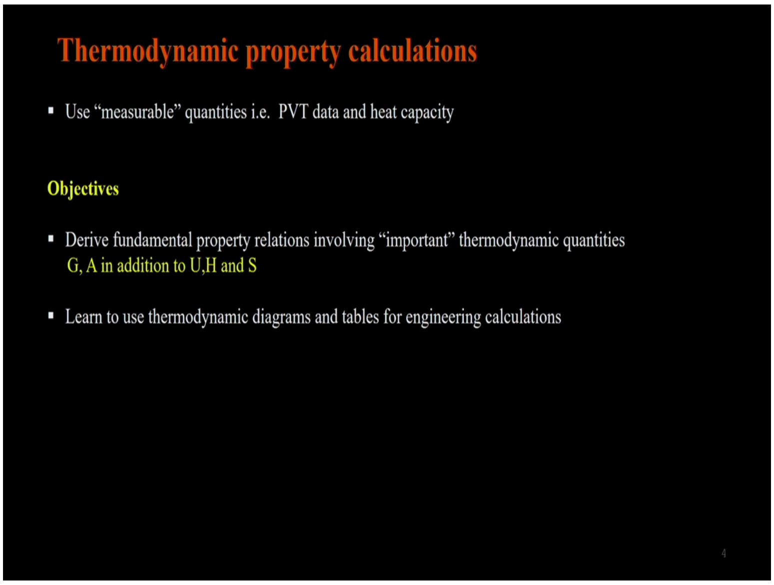

Thermodynamic property calculations

- Use “measurable” quantities i.e. PVT data and heat capacity

Objectives

- Derive fundamental property relations involving “important” thermodynamic quantities
  G, A in addition to U,H and S
- Learn to use thermodynamic diagrams and tables for engineering calculations

Turns out that it is fairly easy the trick is to be able to use measurable quantities to determine these changes; remember that was a very first slide we have used in this course. The idea of all these calculations is to be able to calculate something that cannot be measured directly using and expressing it as in terms of quantities that I can go to a lab and measure.

So, what we will try to do is a try to extend the discussion of calculating the changes in these thermodynamic properties based on measurable quantities such as PVT data, and heat capacity right. And while we are at it, we are going to also look at a couple of other thermodynamic quantities which are important in engineering calculations, and we are going to call them as Gibbs free energy and Helmholtz free energy, G and A in addition to what we have already done for internal energy, enthalpy and entropy.

So, we are going to derive a few fundamental property relations that involve these thermodynamic properties, and then we will try to learn to use thermodynamic diagrams and thermodynamic tables for engineering calculations. So, then the essence of this section in the course is to be able to express these changes in a various thermodynamic quantities in terms of PVT data or relating them somehow to PVT data and heat capacity, and try to use either tables or thermodynamic diagrams and calculate these changes for various engineering applications. So, let us begin our discussion with the internal energy change for a closed system.

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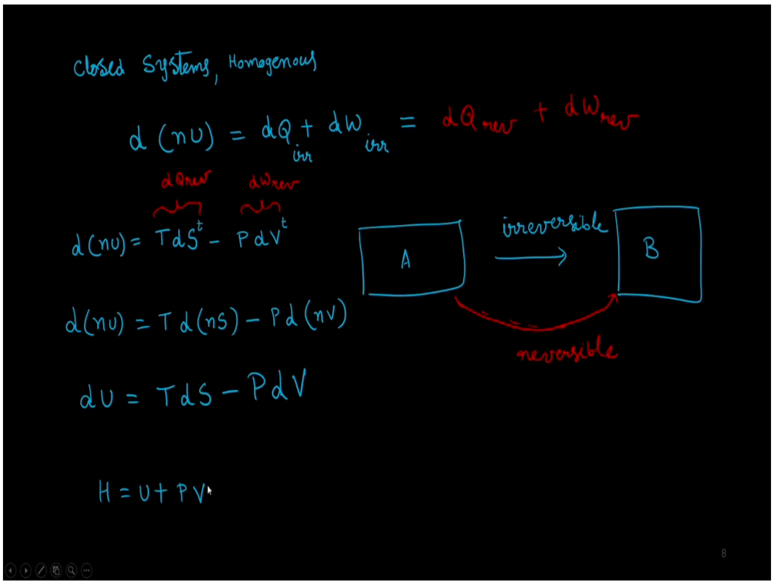

Closed Systems, Homogenous

$$d(nU) = dQ_{irr} + dW_{irr} = dQ_{rev} + dW_{rev}$$

$$d(nU) = \underbrace{TdS^t}_{dQ_{rev}} - \underbrace{PdV^t}_{dW_{rev}}$$

$$d(nU) = Td(nS) - Pd(nV)$$

$$dU = TdS - PdV$$

$$H = U + PV$$

So, I have a closed system, and homogeneous systems right. So, for such a system, the total change or the change in the total internal energy according to the first law is dQ plus dW. And remember internal energy is a state property, so it does not matter whether the process itself is reversible or irreversible. So, let me elaborate that in terms of this equation what we mean is this d n U is going to be dQ for an irreversible process plus dW for an irreversible process. And it will also be exactly equal to dQ for a reversible process plus dW for a reversible process.

So, what we are saying is if I have a process which takes a system at state A to state B, if this is an irreversible path, then I can construct an alternate reversible path right. I can construct an alternate reversible path, and in both scenarios then so let us change this colour to match for previous for the reversible path.

So, this is dQ for the reversible path plus dW for the reversible path. And because internal energy itself is a state property, it is independent of the path I choose, and dQ plus dW along both the paths is going to be exactly same which will give me d n U. Now, this has a significance in the sense that because I can also use the reversible path dQ and dW for calculating d U. What I can do is, remember how dQ is related to the entropy change, it is T dS right, because it is along the reversible path.

So, I am going to replace dQ for the reversible path with T dS and dW for the reversible path, remember dW along a reversible path is negative P dV. So, dW along reversible path is negative P dV. So, d n U then in terms of entropy and volume changes is T dS minus P dV right. Because this is a n this is actually going to be the total entropy and total volume or in terms of the number of moles I can write it as T d of number of moles multiplied with the moral value P d of number of moles multiplied with the molar value.

So, this is my fundamental property relation for change in internal energy in terms of changes in entropy and volume. If for 1 mole, obviously, this equation reduces to d U is T dS the mole of quantity S and P d V. If I use one mole of the system, then d U is going to be T dS minus P dV for n moles it will be the total internal energy, so d n U is T d nS minus P d n V. Now, I can replace U, we recall that H as U plus P V. Let us go to the next slide.

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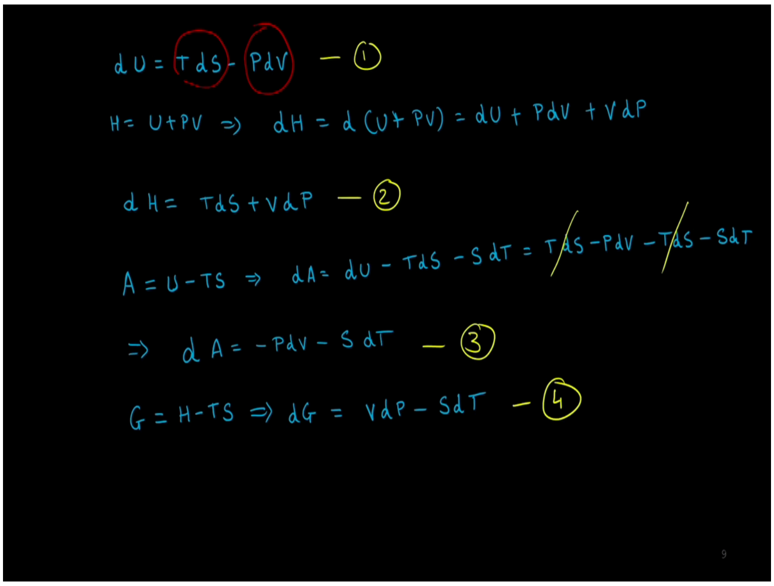

$$dU = TdS - PdV \quad — ①$$

$$H = U + PV \Rightarrow dH = d(U+PV) = dU + PdV + VdP$$

$$dH = TdS + VdP \quad — ②$$

$$A = U - TS \Rightarrow dA = dU - TdS - SdT = T\cancel{dS} - PdV - T\cancel{dS} - SdT$$

$$\Rightarrow dA = -PdV - SdT \quad — ③$$

$$G = H - TS \Rightarrow dG = VdP - SdT \quad — ④$$

Let us write what we had earlier. Now, we will just deal with the molar quantities, we can always write the total quantity is when the need arises, but for now what we derived in the previous slide is d U is T dS minus P d V right. Since H is U plus P V this implies d H is d of U plus P V. So, this will be d U plus P d V plus V dP. And then I can use the expression for d U in terms of entropy and volume, what that resolves an as d H is going to be T dS negative of P dV and positive of P dV cancel out plus V d P. So, d H is going to be T dS plus V dP.

So, what we have done in this exercise is relate various thermodynamic quantities we have had so far; internal energy, entropy, volume, pressure and temperature to one another or changes in these quantities to one another. Now, the way we have achieved it is by using a reversible path as I showed to you earlier, if the path is reversible, then this quality and this quantity are the heat and work changes during along the path. If they are not reversible, if it the actual process does not occur along the reversible path, then T dS and P dV do not correspond to heat and work changes. If it occurs along the reversible path then T dS and P dV correspond to the heat and work changes along the path.

So, remember this irrespective of the path, it is always T dS minus P dV. When the path is reversible each of those two terms represent heat and work requirements; when the path is irreversible they do not send the heat and work for that particular process. And then finally, I can transform the variable from U to H, and get d H as T dS plus V dP.

Now, at the beginning of this lecture, we said we are going to introduce two other thermodynamic variables which are important just like enthalpy and internal energy, the other two thermodynamic variables we introduce are important and the consequences of using these variables become clearer as the progress with this course. Specially, Gibbs free energy has a lot of importance for chemical engineering applications in terms of vapor-liquid equilibrium calculations, chemical reaction equilibrium calculations etcetera.

So, this is a good time to introduce these two variables and then carry on with the calculations involved in these two variables until we reach a point where we can start using them for chemical engineering applications. The first variable we are going to introduce is what we call as Helmholtz free energy, a some of the books use F for this free energy, we are going to use A, and it is defined as U minus T S. What this means is I can take a derivative dA is going to be equal to d U minus T dS minus S d T. And since d U from equation 1 above is T dS minus sd T sorry minus P d V minus T dS minus S d T. What this means is dA is dA is this and this will get cancelled and dA will be minus P d V minus S dT. So, this will be our fundamental property relation number 3 for today right.

And finally, introduce another variable called as Gibbs free energy or G, remember all of these are molar quantities I can always multiply them with the number of moles to get the total quantity. G similar to A is defined as H minus T H the T S. So, we replace you with H in this expression for G. So, G is going to be H minus T S or d G we can do a similar exercise as above and get d G to be V d P minus S d T. And this will be our equation number 4 for today. So, I have four fundamental property relations, one is for dU, the second one for dH, the third one for dA, and the fourth one for dG. So, we call these groupings right.

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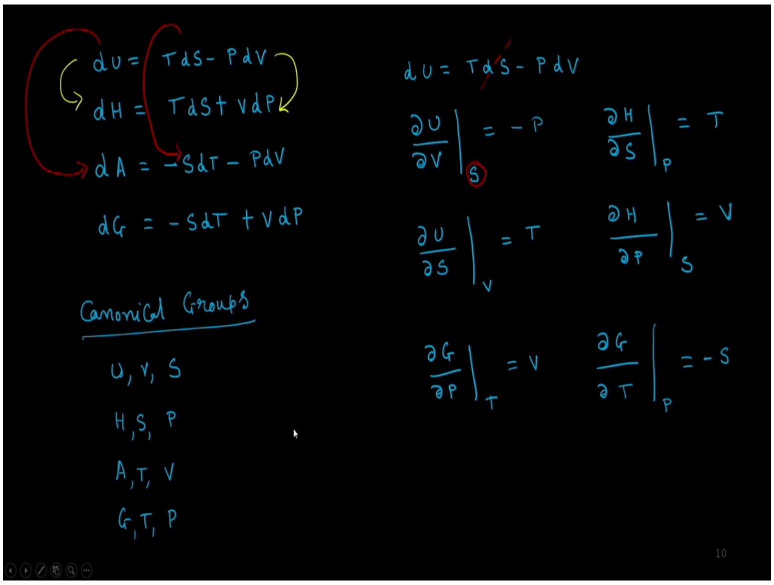

$dU = TdS - PdV$

$dH = TdS + VdP$

$dA = -SdT - PdV$

$dG = -SdT + VdP$

Canonical Groups

U, V, S

H, S, P

A, T, V

G, T, P

$dU = T\cancel{d}S - PdV$

$\left.\frac{\partial U}{\partial V}\right|_{S} = -P \qquad \left.\frac{\partial H}{\partial S}\right|_{P} = T$

$\left.\frac{\partial U}{\partial S}\right|_{V} = T \qquad \left.\frac{\partial H}{\partial P}\right|_{S} = V$

$\left.\frac{\partial G}{\partial P}\right|_{T} = V \qquad \left.\frac{\partial G}{\partial T}\right|_{P} = -S$

So, let us some quickly write the four of them again, dU is T dS minus P d V; d H is T dS plus V d P; dA is minus S d T minus P d V, and d G is minus S d T plus V dP. So, these are the four fundamental property relations we derived. And notice that each one of these transformations results in a flip of the term one flip for one of the terms on the right hand side. For example, when I go from d U to dH, the T dS term remains the same, but dV becomes dP and of course, there is a change in additional change in the sign right.

When I go from similarly dU to dA, the negative P dV term remains the same, but there is a flip in dS to dT right and so on. And for the last one both the terms and a flipping right, both dS becomes dT and dV becomes dP for the last one. This has a important consequences it helps us to express a several quantities in terms of directly in terms of measurable properties. So, such thermodynamic transformations or mathematical transformations help us to determine quantities that cannot be directly related or measured in the sense that they can be related to other measurable quantities. But before we try to express those relations between quantities, that cannot be so directly measured to quantities that can be directly measured.

Let us quickly revise our knowledge on calculus when using these equations. Now, remember all these four equations are for closed homogeneous systems. And what the first equation also means for example, if I take this first equation d U as T dS minus P d V, and if I pose the question, what is the change in internal energy with respect to volume right. What is dou U over dou V the change in internal energy with respect to volume that is very not very convenient to answer, but if I tell that I take this partial derivative holding entropy constant, S constant, then it is pretty straight forward.

Because S is constant the first term in the above equation disappears and dou U by dou V simply becomes right, because of this reason this term disappears, and dou U by dou V simply becomes negative P. Similarly, if I want to know what the change in internal energy with respect to entropy is holding volume constant, I can do a similar exercise and because I am holding the volume constant, the second term disappears. And when I take the derivative of U with respect to S, it would be T.

In a similar fashion for the other three equations also, I can write these derivatives. For example, for the second equation, derivative of H with respect to S at constant P will result in T; derivative of H with respect to P at constant S will equal V. Similarly, if I take the last equation for Gibbs free energy derivative of G with respect to P at constant T will be V; and derivative of G with respect to V, I am sorry with respect to T at constant pressure will equal negative S, derivative of G with respect to T at constant pressures so the second term drops out here. And I have what I have left is negative of S and so on.

This is the first observation we can make using these four fundamental property relations and because these derivatives turn out to be variables which are nice like these for example, for the first one derivative of U with respect to V at constant S is negative P. If I take this partial derivative not holding S constant, but holding some other thermodynamic variable constant, then the resulting value or the quantity will not be such a nice thermodynamic quantity as pressure it might be I can always derived that what it will be, but it may not be such a nice expression. Because these fundamental property relations yield this partial derivatives ending up with these nice quantities we call them as canonical groups.

So, meaning they formed simple groups which will result in partial derivatives being thermodynamic quantities which are straight forward. So, U, V and S form a canonical group; H, S and P form a canonical group a T; and V form a canonical group; similarly G T and P form a canonical group. And when I take partial derivative of one holding the other variable constants, it is results in the thermodynamic quantity which is can be straight forward related to a thermodynamic single thermodynamic variable. This is the first consequence of these fundamental property relations.

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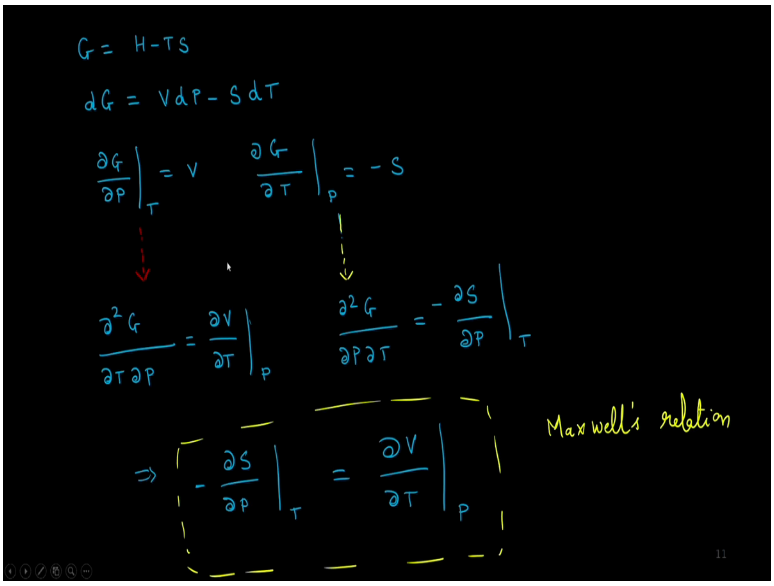

$$G = H - TS$$

$$dG = VdP - SdT$$

$$\left.\frac{\partial G}{\partial P}\right|_T = V \qquad \left.\frac{\partial G}{\partial T}\right|_P = -S$$

$$\frac{\partial^2 G}{\partial T \partial P} = \left.\frac{\partial V}{\partial T}\right|_P \qquad \frac{\partial^2 G}{\partial P \partial T} = -\left.\frac{\partial S}{\partial P}\right|_T$$

$$\Rightarrow \boxed{-\left.\frac{\partial S}{\partial P}\right|_T = \left.\frac{\partial V}{\partial T}\right|_P}$$

Maxwell's relation

The second thing that is more important is through what is known as Maxwell's relation. Let us take an example, let us take the example for Gibbs free energy because in chemical engineering applications we are not using this quantity a lot more. G we said is H minus T H T S, and the way we have written d G was V d P minus S d T. And then we do the first derivatives like we have done earlier derivative of G with respect to P holding T constant is volume derivative of G with respect to T holding the pressure constant is negative S.

Now, when I say this quantity, if I pose the question, how does Gibbs free energy change with temperature, it is entropy. Again entropy is not a quantity which I can measure directly. So, is there a way to express this derivative in terms of quantity, I can measure it terms out, we can do a little mathematical exercise to come up with that answer.

Now, what we do is take the second derivative. For example, to this expression here on the left if I take the second derivative with respect to temperature, and because I am taking the derivative with respect to temperature, it automatically means I am holding the pressure constant, then this will be derivative of V over T that constant pressure. The right hand side also I have to take derivative with respect to temperature and holding the pressure constant. And for this expression here, I will again take the second derivative, but this time with respect to pressure, so that I get derivative of G with respect to dou P dou T, it will be negative derivative of S with respect to pressure at constant temperature.

Now, because of the condition for exactness of the second derivatives, I can equate these two quantities the second derivatives irrespective of the order of differentiation. And what that means, is derivative of S with respect to P at constant temperature negative of that quantity is derivative of V with respect to temperature at constant pressure. So, the whole idea of this exercise, then trying to take the second derivatives etcetera is to relate how entropy changes with pressure dS dou S by dou P. When I hold the temperature constant to properties or quantities I can measure.

So, look at the quantity is on the right hand side, it is a derivative of volume with respect to temperature at constant pressure volume temperature pressure or all the quantities, I can directly measure in a lab. On the left hand side, I have derivative of a quantity, I cannot directly measure in a lab entropy right. So, however, I can relate these derivative of entropy, two quantity I can measure as expressed on the right hand side. We call this as a Maxwell's relation. Now, in this exercise, we have use the fundamental property relation for Gibbs free energy right. I can similarly use other fundamental property relations and I can get this is one fundamental property relation for one Maxwell's relation.

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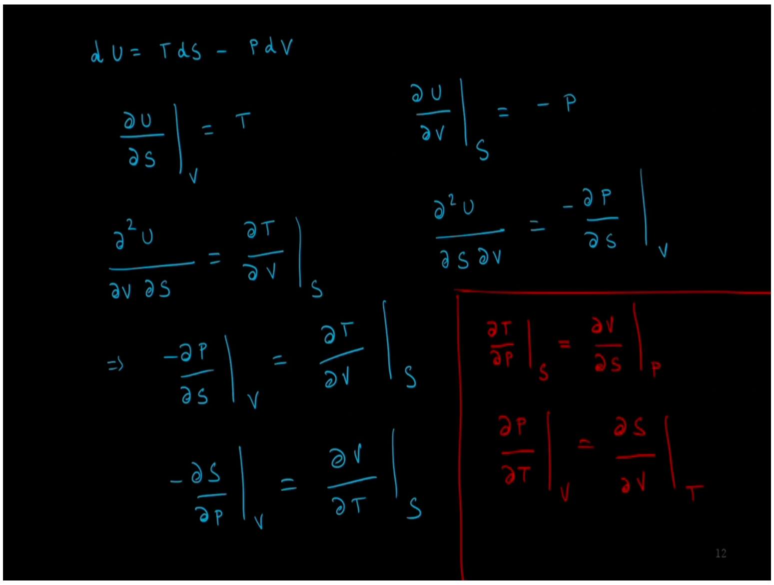

$$dU = TdS - PdV$$

$$\left.\frac{\partial U}{\partial S}\right|_V = T \qquad \left.\frac{\partial U}{\partial V}\right|_S = -P$$

$$\frac{\partial^2 U}{\partial V\,\partial S} = \left.\frac{\partial T}{\partial V}\right|_S \qquad \frac{\partial^2 U}{\partial S\,\partial V} = -\left.\frac{\partial P}{\partial S}\right|_V$$

$$\Rightarrow \quad -\left.\frac{\partial P}{\partial S}\right|_V = \left.\frac{\partial T}{\partial V}\right|_S$$

$$-\left.\frac{\partial S}{\partial P}\right|_V = \left.\frac{\partial V}{\partial T}\right|_S$$

$$\left.\frac{\partial T}{\partial P}\right|_S = \left.\frac{\partial V}{\partial S}\right|_P$$

$$\left.\frac{\partial P}{\partial T}\right|_V = \left.\frac{\partial S}{\partial V}\right|_T$$

I can use other three to get three more Maxwell's relations. Let us quickly run through one more for the sake of clarity. Let us take let us take dU dU was T dS minus P d V on one side we say that derivative of U with respect to S at constant volume is T. And on the other side derivative of U with respect to volume at constant S is negative of P.

Now, I take the second derivatives derivative of U with respect to volume and entropy there is derivative of T with respect to volume at constant entropy, because I am taking the second derivative with respect to volume, it means entropy have constant, so that would be derivative of T with respect to V at constant S. And on this side when I take the second derivative, it will be with respect to S, the first one was with respect to volume. And because I am taking the second derivative with respect to S it means I am holding the volume constant derivative of P with respect to S at constant, constant volume.

Now, what this means is I can equate again applying the criteria for exactness, I can equate the two second derivatives. And what I have done is negative derivative of P with respect to S at constant volume is derivative of T with respect to volume at constant S. And again on the left hand side I have something I cannot measure a derivative of P with respect to S or I can invert it and call it as derivative of S with respect to P in which case I can also invert the right hand side.

So, for example, this would be derivative of S with respect to P at constant volume there will be derivative of volume with respect to temperature at constant S. The left hand side is a quantity I cannot measure, the right hand side is something I can measure in terms of V and T. So, again the idea of deriving these Maxwell's relations is to be able to express quantities, I cannot measure in the lab directly, two quantities I can relate to with our P V T properties or something else I can measured in the lab. So, this is the second Maxwell's relation. I can derive two more Maxwell's relations similarly, one involving H and other involving the Helmholtz free energy using the Helmholtz free energy.

So, I am quickly going to just write them down here. So, if you want to derive them, you can and compare the result it would be constant as would be dou V by dou S at constant P. And the last one is dou P dou T at constant volume is dou S dou V at constant T. Again on one side you have an entropy term; on the other side it is either P V or T terms of we can measure them in the lab. So, these are the four Maxwell's relations and the four fundamental property relations. Now, we will use this idea, and try to see how I can derive an expression for d H in terms only in terms of quantities I can measure.

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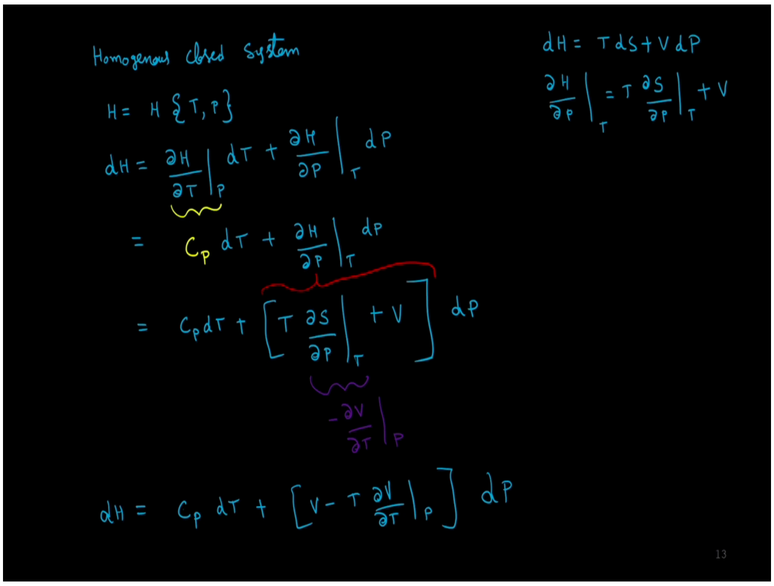

Homogenous closed System

$H = H\{T, P\}$

$$dH = \underbrace{\left.\frac{\partial H}{\partial T}\right|_P} dT + \left.\frac{\partial H}{\partial P}\right|_T dP$$

$$= C_p\, dT + \overbrace{\left.\frac{\partial H}{\partial P}\right|_T} dP$$

$$= C_p dT + \left[T \underbrace{\left.\frac{\partial S}{\partial P}\right|_T}_{-\left.\frac{\partial V}{\partial T}\right|_P} + V\right] dP$$

$$dH = C_p\, dT + \left[V - T\left.\frac{\partial V}{\partial T}\right|_P\right] dP$$

$dH = T dS + V dP$

$$\left.\frac{\partial H}{\partial P}\right|_T = T\left.\frac{\partial S}{\partial P}\right|_T + V$$

Remember originally d H was in terms of dS. Now, we want to replace that and express it in terms of measurable quantities right. For a homogeneous closed system H although the canonical grouping says that d H is T dS plus V d P, I can write H as a function of any two variables. So, what I will do is I will write H as a function of T and P, so that the total derivative d H is going to be derivative of H with respect to T at constant pressure times d T plus derivative of H with respect to P at constant temperature times dP right.

So, partial derivative times dT plus the second partial derivative times dP that would be the total change in H or d H right.

The first term is something which we readily identify. We are calling this guy as the specific heat capacity C p d T right plus derivative of H with respect to P at constant temperature dP. Derivative of H with respect to P at constant temperature is derivative of H, if I use this relation derivative of H with respect to P, when I hold the temperature constant because the temperature is (Refer Time: 28:54) constant, it can come out of the derivative it will be derivative of S with respect to P at constant temperature plus V dou P by dou P S V, so that the second term would be V.

So, derivative of H with respect to P at constant temperature is T derivative of S with respect to P at constant temperature plus V. So, I will use that it will be C p dT plus plus T derivative of S with respect to P at constant temperature plus v, so times dP. So, I have replaced the derivative of H with respect to P with this term, which I can get from the fundamental property relation for d H. And finally, in one of the Maxwell's equation we have derived earlier derivative of S with respect to P at constant temperature or may be in the previous one, here derivative of S with respect to P at constant temperature is negative derivative of V with respect to temperature at constant pressure.

So, I will use this Maxwell's relation right, and I am going to replace this right from the I am going to replace this with negative V over T at constant pressure. So, what done does to my expression, then is it will be C p dT plus V minus T times negative V by sorry derivative of V with respect to T at constant pressure times dP, this will be my expression for a d H right.

Now, look at where we have started either the fundamental property relation where I had T dS plus V d P or in terms of some two other variables where I had express where I had express it in terms of T and P. Irrespective of where I have started things did not look very promising when I went ahead. But then once I manipulate it I have perform the mathematical manipulation, and I have use the Maxwell's relation what I get on the right hand side is something I can measure directly pressure, volume, temperature all measurable and the specific heat capacity C p.

So, finally, I was successful in expressing the change in enthalpy only in terms of quantities I can measure C ps, volume, pressure, and temperature. So, the whole idea of this exercise is to be able to express this thermodynamic quantity in terms of PVT and the specific heat capacity which is what I have done here right. We still have a while to go before we can it start using it for real fluids. We still do not know how the specific heat capacity C p for real fluids can be calculated we know that there are tables for C p for ideal gas like condition, but for real gases C p is still something which we need to work on. This equation also will reduce to what we have seen earlier for an ideal gas right.

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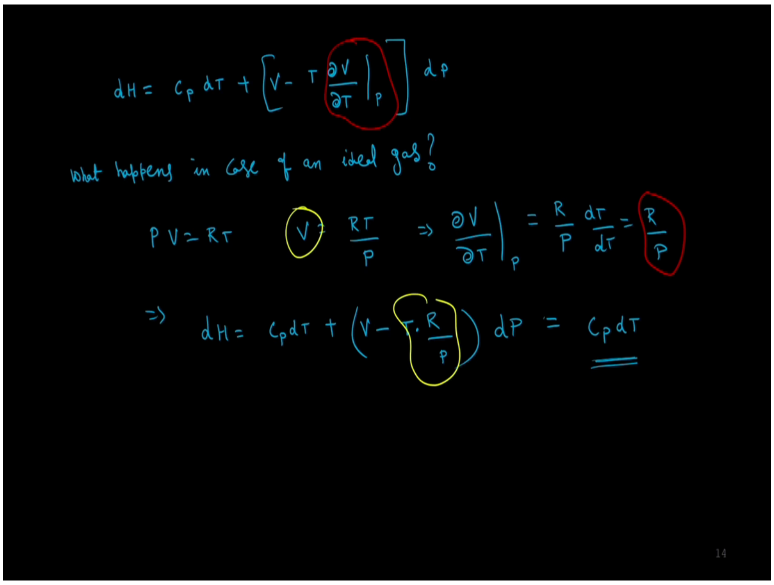

$$dH = C_p\, dT + \left[V - T \left.\frac{\partial V}{\partial T}\right|_P\right] dP$$

What happens in case of an ideal gas?

$$PV = RT \qquad V = \frac{RT}{P} \quad \Rightarrow \left.\frac{\partial V}{\partial T}\right|_P = \frac{R}{P}\frac{dT}{dT} = \frac{R}{P}$$

$$\Rightarrow \quad dH = C_p dT + \left(V - T.\frac{R}{P}\right) dP = \underline{\underline{C_p dT}}$$

It has to, for example, the equation I had derived in the previous slide is the derivative of H was C p dT plus V minus T derivative of V with respect to T at constant pressure times dP. What happens in case of an ideal gas. For an ideal gas, we know that P V is R T right. So, V is R T by P right, V is R T by P. So, derivative of V with respect to T right at constant pressure, so I am holding the pressure constant both R and P are then constant right. And when taking the derivative with respect to temperature, so it will be d T by d T right which is 1, so this is R over P right. So, derivative of volume with respect to temperature at constant pressure will be R over P for an ideal gas which means d H is going to be C p d T plus V minus T times right this derivative here.

Now, I am going to replace it this value for an ideal gas which will be R over P right times d P. Now, R T by P again for an ideal gas is volume. So, volume minus volume will then result in 0. So, this will simply be C p d T. Remember what we said for an ideal gas enthalpy is only a function of temperature. So, it does not matter whether the pressure changes or not, d H will always be equal to C p dT for an ideal gas and that is what we ended up using the expression we just derived.

So, whenever I derive these sort of expressions for the limiting cases, we need to get the expressions which we have already derived for an ideal gas. If that does not happen, then obviously, there is something wrong with our logic. But for now it works out dH happens only to be a function of temperature which is which is a good sign.

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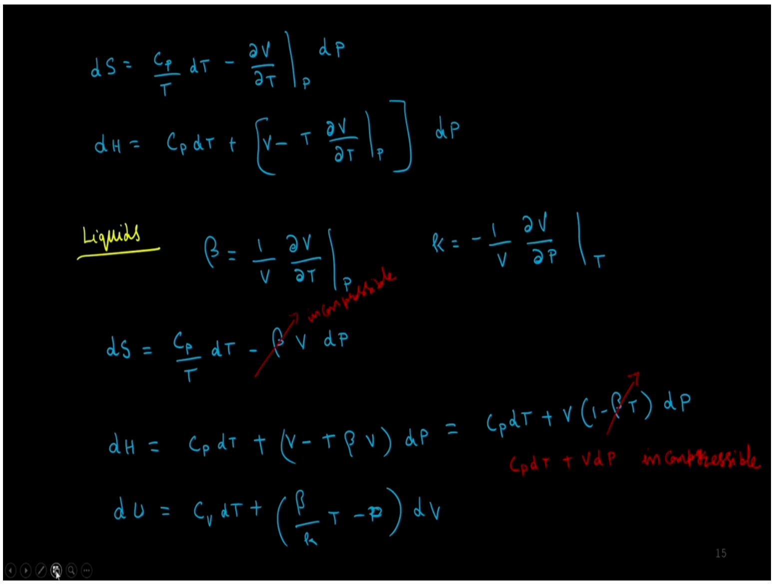

$$dS = \frac{C_p}{T} dT - \left.\frac{\partial V}{\partial T}\right|_P dP$$

$$dH = C_p dT + \left[V - T \left.\frac{\partial V}{\partial T}\right|_P\right] dP$$

Liquids

$$\beta = \frac{1}{V} \left.\frac{\partial V}{\partial T}\right|_P \qquad k = -\frac{1}{V} \left.\frac{\partial V}{\partial P}\right|_T$$

$$dS = \frac{C_p}{T} dT - \cancel{\beta} V dP \quad \text{incompressible}$$

$$dH = C_p dT + (V - T\beta V) dP = C_p dT + V(1 - \cancel{\beta} T) dP$$

$$C_p dT + V dP \quad \text{incompressible}$$

$$dU = C_v dT + \left(\frac{\beta}{k} T - P\right) dV$$

Now, I can work on similar expressions or I can derive similar expressions, what I will do is give out a few expression, and now let you guys derive those dS will be C p by T d T minus d V dT P dP this is with the change in entropy with changes in temperature and pressure. Now, I can derive similar expressions for dU, dG when the need arises I know the trick on how to handle these expressions. What happens to an ideal gas again is something I can look at for dS similar to what we have done for dA d H or the change in enthalpy. Apart from ideal gases there is one other example which we want to discuss about right.

So, let us write that expression previously we have for dH it was C p dT plus V minus T derivative of V with respect to T at constant pressure dP. And we know how to reduce these equations for ideal gases. Let us talk about one other scenario which is of interest and pretty easy to handle what happens in case of liquids, what happens in case of liquids, when I use these equations right. To answer that question we take the help of two quantities which we have already used earlier or a defined earlier. The first one is volume expansivity which we defined as derivative of volume with respect to temperature at constant pressure 1 over V of that, we call it as beta. And the other one is the isothermal compressibility kappa which is negative 1 over V derivative of V with respect to P at constant temperature.

So, if I use this expression, then dS for liquid will be C p by T d T the first term can be left in terms of the specific heat capacity. And the second term derivative of V with respect to T at constant pressure, I can use beta times the volume dP. So, this will be dS. And similarly if I want to write d H it will be C p d T plus V minus T times derivative of V with respect to T at constant pressure is again beta times V times d P or a better way of writing that is C p d T plus V 1 minus beta T dP that will be T H. So, for liquids I can use the isothermal compressibility and volume expansivity we have defined earlier, and try to come up with expressions for dS d H etcetera.

Similarly, dU is going to be C v d T plus beta over kappa tau minus P d V and so on. So, depending on what data, I have at hand I could use one of these expressions. We have derived a general expression which applies for all fluids, then we have we have seen how to reduce those expressions for special cases of an ideal gas or for a liquid where I have information about volume expansivity and isothermal compressibility. For a more extreme case of a completely incompressible liquid what happens is beta is going to be 0. So, dS is going to be simply C p over T d T. And similarly over here, it will be C p dT plus V dP for an incompressible liquid. So, we can start using these equations, and applied them to special cases and derive as the need arises. Let us quickly look at one example on how to handle these equations or use them for liquids.

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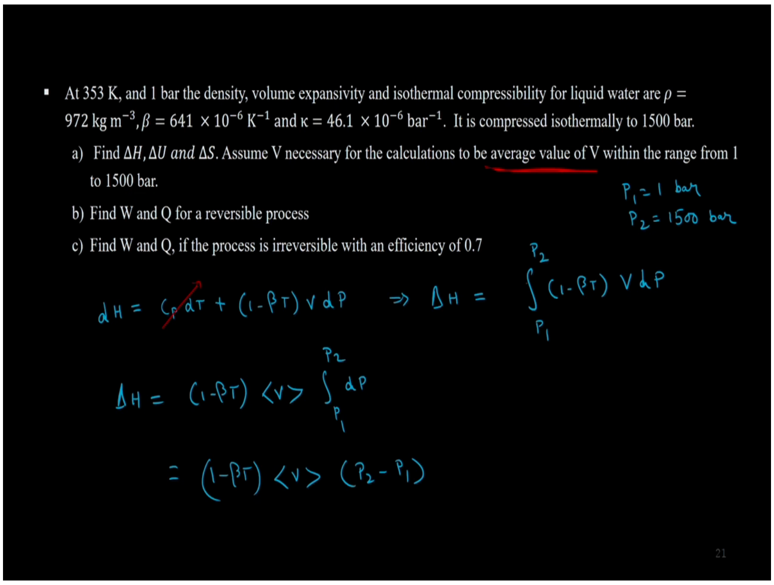

- At 353 K, and 1 bar the density, volume expansivity and isothermal compressibility for liquid water are $\rho = 972\ \text{kg m}^{-3}, \beta = 641 \times 10^{-6}\ \text{K}^{-1}$ and $\kappa = 46.1 \times 10^{-6}\ \text{bar}^{-1}$. It is compressed isothermally to 1500 bar.
  a) Find $\Delta H, \Delta U$ and ΔS. Assume V necessary for the calculations to be average value of V within the range from 1 to 1500 bar.
  b) Find W and Q for a reversible process
  c) Find W and Q, if the process is irreversible with an efficiency of 0.7

$P_1 = 1$ bar
$P_2 = 1500$ bar

$$dH = \cancel{C_p\, dT} + (1-\beta T) V\, dP \Rightarrow \Delta H = \int_{P_1}^{P_2} (1-\beta T) V\, dP$$

$$\Delta H = (1-\beta T) \langle V \rangle \int_{P_1}^{P_2} dP$$

$$= (1-\beta T) \langle V \rangle (P_2 - P_1)$$

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What I have is water at 353 Kelvin and 1 bar the volume expansivity and isothermal compressibility are given to us. The density is given. Now, if we compress at isothermal into 1500 bar, we want to calculate the changes in H U and S, and then we are going to calculate w and q for a reversible and an irreversible process. Let us see how we can do this. It says calculate delta H, delta U and delta S. So, let us see if I can first write the expressions for delta H and delta S.

Delta H as we have seen for a liquid or let us write it as dH for a liquid was 1 minus beta T V (Refer Time: 41:21), it was C p dT plus 1 minus beta T V dP. Now, this liquid is compressed isothermally. So, the first term disappears. I do not need that, because there is no change in temperature. So, dH is simply 1 minus beta T V dP. Now, if I am interested in calculating delta H, then delta H then I simply need to integrate this equation 1 minus beta T V dP from the initial pressure to the final pressure P 1 S 1 bar and P 2 S 1500 bar.

When I perform this integration, beta is constant or it is just one value is given for beta. So, I am going to assume that it is constant, I can integrate this except what is the deal with volume, how do I know, how what do I know about volume or how it changes with pressure. It definitely changes with pressure, it is not given that the liquid is completely incompressible. If it changes with pressure, then I can I need to know how it changes with pressure and perform this integration, alternatively if the changes pretty small, then

I can use an average value over this pressure range that is what is given in the problem statement. Assume V necessary for the calculations to be the average value of V within the range from 1 to 1500 bar.

So, what we want to do is use an average value of V, and assume that it is constant and bring it out of the integral. So that means, what I have done is delta H is 1 minus beta T some sort of average value of for the volume times integral of P 1 to P 2 dP, or this will be 1 minus beta T the average volume times P 2 minus P 1. So, I have everything else I need to calculate this delta H. The only thing I need to do is calculate the average volume right.

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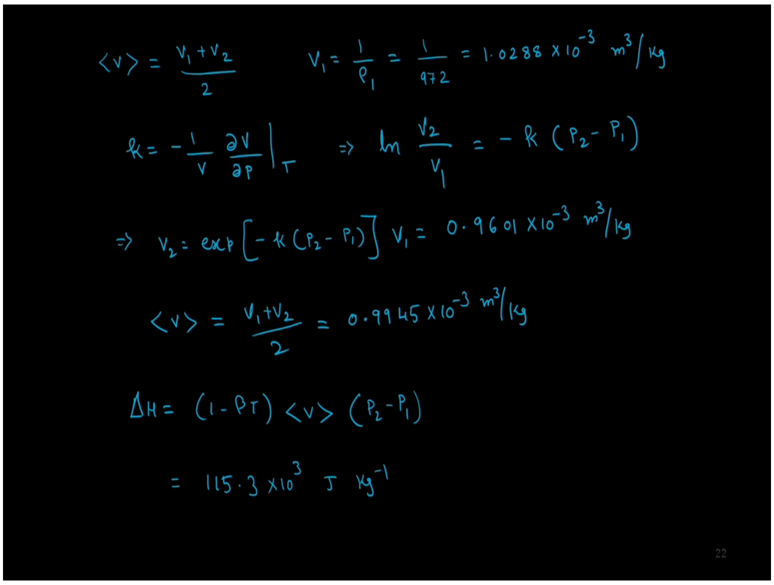

$$\langle v \rangle = \frac{V_1 + V_2}{2} \qquad V_1 = \frac{1}{\rho_1} = \frac{1}{972} = 1.0288 \times 10^{-3} \ m^3/kg$$

$$\kappa = -\frac{1}{V} \left.\frac{\partial V}{\partial P}\right|_T \Rightarrow \ln \frac{V_2}{V_1} = -\kappa (P_2 - P_1)$$

$$\Rightarrow V_2 = \exp\left[-\kappa (P_2 - P_1)\right] V_1 = 0.9601 \times 10^{-3} \ m^3/kg$$

$$\langle v \rangle = \frac{V_1 + V_2}{2} = 0.9945 \times 10^{-3} \ m^3/kg$$

$$\Delta H = (1 - \beta T) \langle v \rangle (P_2 - P_1)$$

$$= 115.3 \times 10^3 \ J \ kg^{-1}$$

So, let us see how we calculate the average volume. The average volume we are going to say that it is average of the volume at the two ends 1 bar and 1500 bar. So, it is V 1 plus V 2 over 2. V 1 is going to be the inverse of density at the condition one which is given to me, so that happens to be 1 over 972 kg per meter cube, so that will be 1.0288 into 10 power minus 3 meter cube per kg. This is the specific volume at condition 1. For condition 2, what we will do is use the definition for kappa; it is negative 1 over V dou V by dou P at constant T right.

So, I can integrate this and end up with an expression which says ln of V 2 over V 1 is negative kappa P 2 minus P 1 right. I know everything in their V 2 is going to be exponential of negative kappa P 2 minus P 1 times V 1 right. I know all the quantities on the right hand side kappa is given P 1 P 2 are given and I have just calculated V one. So, I can plug them in to get the volume at 1500 bar to be 0.96 o 1 10 power negative 3 meter cube per kg. And because now I know both V 1 and V 2 I can calculate the average value for the volume to be 0.9945 10 power negative 3 meter cube per kg right.

And once I have the average volume, I can go back and calculate the change in the enthalpy, it is, this quantity right here 1 minus beta T the volume times the pressure. We just need to be careful in using consistent units the pressure is in bar. So, we need to convert it into Pascal's to be to be able to use a S I units throughout. And it turns out the value we get is 115.3 into 10 power 3 joules per kg. This will be the value for delta H. And now beta I know the average volume I know P 1 and P 2, so we can get this value for delta H.

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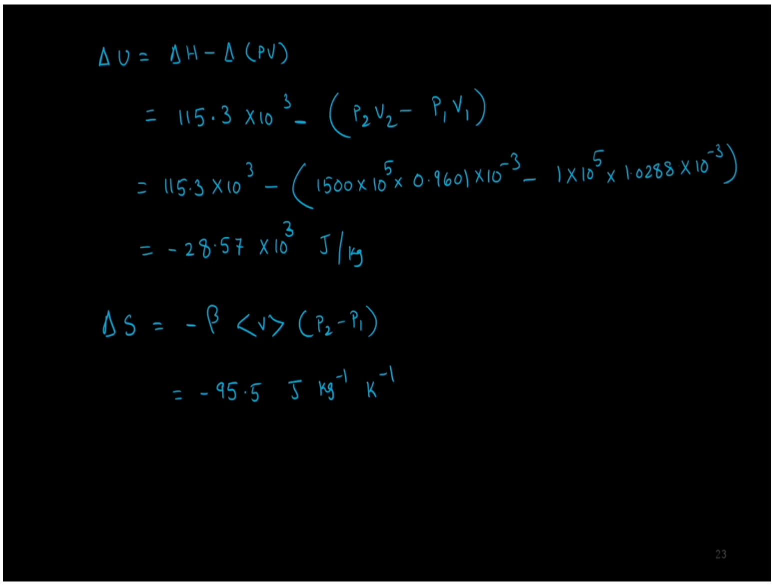

$$\Delta U = \Delta H - \Delta (PV)$$

$$= 115.3 \times 10^{3} - (P_2V_2 - P_1V_1)$$

$$= 115.3 \times 10^{3} - (1500 \times 10^{5} \times 0.9601 \times 10^{-3} - 1 \times 10^{5} \times 1.0288 \times 10^{-3})$$

$$= -28.57 \times 10^{3} \ J/kg$$

$$\Delta S = -\beta \langle v \rangle (P_2 - P_1)$$

$$= -95.5 \ J \ kg^{-1} \ K^{-1}$$

To calculate delta U, I can use seen I can use the expressions we derived earlier, but an easier way in this scenario is simply to take it to be H minus P V or delta U is going to be equal to delta H minus delta of P V. So, this will be delta H which we calculated earlier 115.3 10 cube minus P 2 V 2 minus P 1 V 2. So, this will be negative 115.3 sorry 115.3 10 power negative sorry it should be positive 3 right, I am sorry that is a positive 3 joules per kg minus 1500 10 power 5 Pascal times the final volume which is 0.9601 10 power minus 3 that is 1 bar is the initial pressure multiplied with the initial volume which was

1.0288 10 power negative 3. I can simplify this whole expression and what I have is negative 28.57 10 cube, 10 cube joules per kg. This will be my delta, delta U.

And finally, delta S is going to be negative beta the average volume times P 2 minus P 1. Again convert the pressures into Pascal's and use SI units throughout to get delta S to be 95.5 joule per kg per Kelvin. So, once I find the average volume, the other calculations are pretty straight forward to do. So, this is how I use the beta and kappa values to calculate delta H, delta U and delta S. So, I am done with the first part. The next thing we need to calculate is Q and W.

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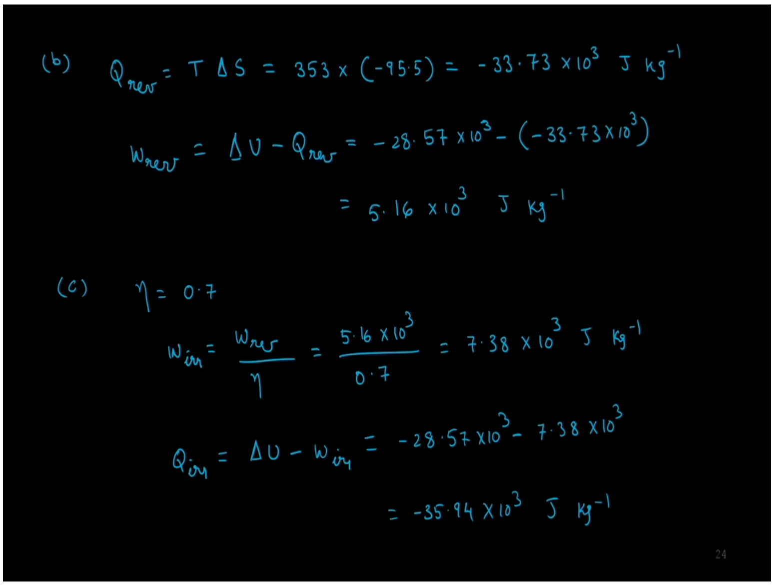

(b) $Q_{rev} = T \Delta S = 353 \times (-95.5) = -33.73 \times 10^3 \text{ J kg}^{-1}$

$W_{rev} = \Delta U - Q_{rev} = -28.57 \times 10^3 - (-33.73 \times 10^3)$

$= 5.16 \times 10^3 \text{ J kg}^{-1}$

(c) $\eta = 0.7$

$W_{irr} = \frac{W_{rev}}{\eta} = \frac{5.16 \times 10^3}{0.7} = 7.38 \times 10^3 \text{ J kg}^{-1}$

$Q_{irr} = \Delta U - W_{irr} = -28.57 \times 10^3 - 7.38 \times 10^3$

$= -35.94 \times 10^3 \text{ J kg}^{-1}$

What we will do is we will try to calculate Q for the reversible process it is simply T dS or T delta S, because the process is isothermal. And I already know the value of delta S temperature is 353 Kelvin times negative 95.5. So, this value turns out to be negative 33.73 times 10 cube joules per kg. Once I have Q, I can apply the first law and say that W for the reversible process is going to be delta U minus Q for the reversible process. Delta U was negative 28.57 times 10 cube, and this guy Q who was negative 33.73 times 10 cube. So, there will be 5.16 joules per kg so that is how I calculate Q and W for the reversible process because I know the other quantities.

And finally, if I want to calculate the values for the irreversible process, I know the efficiency is given to me, it is 0.7 right. So, W for the irreversible process, I need to do more work. It will be W for the reversible process over the efficiency or it is going to be

5.16 10 power 3 over 0.7 which turns out to be 7.38 10 power 3 joules per kg. And the Q for the irreversible process then comes from the first law; it will be delta U minus Q for the irreversible plus sorry W for the irreversible process. Delta U does not change its same irrespective of the nature of the process, it is 28.57 10 power minus 10 power 3 minus minus 7.38 10 power 3, so that is going to be negative 35.94 10 cube joules per kg.

So, once we calculate this quantities, delta H, delta U, delta S, etcetera, the other quantities the heat and work requirements for the process is can be calculated fairly easily and that is the essence of calculating the changes in various thermodynamic quantities, ultimately we want to transfer relate them to heat and work requirements for a given process or heat and work produced from a given process. This is where we are going to stop. Now, we would not go into heat and work calculations for the remainder of this section, but our main focus then is going to be on calculating the changes in the actual thermodynamic properties itself delta H, delta U, etcetera. And once we do that as in this example we have seen we can related to Q and W alright.

So, we will stop therefore it now. When we come back in the next lecture what we will look at is how to calculate these changes if the fluid is not either an ideal gas or a liquid, how do I handle calculation of these changes, what we will do is we will try to use a thermodynamic tables and thermodynamic diagrams first to be able to do these calculations.

Thank you.