Chemical Engineering Thermodynamics
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Lecture – 06
Processes Involving Ideal Gas

Hello and welcome back in the last lecture we looked at derivation of heat and work, in case of Processes that involve Ideal Gas, those derivations essentially the word for mechanically reversible processes, what we will do today is try to solve a few problems based on those concepts for different kinds of processes such as isothermal process, isobaric process, adiabatic process and so on. And then I will introduce the concept of irreversibility and how we calculate the work done, in case of an irreversible process also involving an ideal gas, where the heat capacities are constant they do not change with time.

Then we bring in the concept of temperature dependency for the heat capacity in case of an ideal gas. And then finally, we will start moving towards the second law of thermodynamics and the concept of entropy. Let us first start with a few numerical problems on processes that involve ideal gases.

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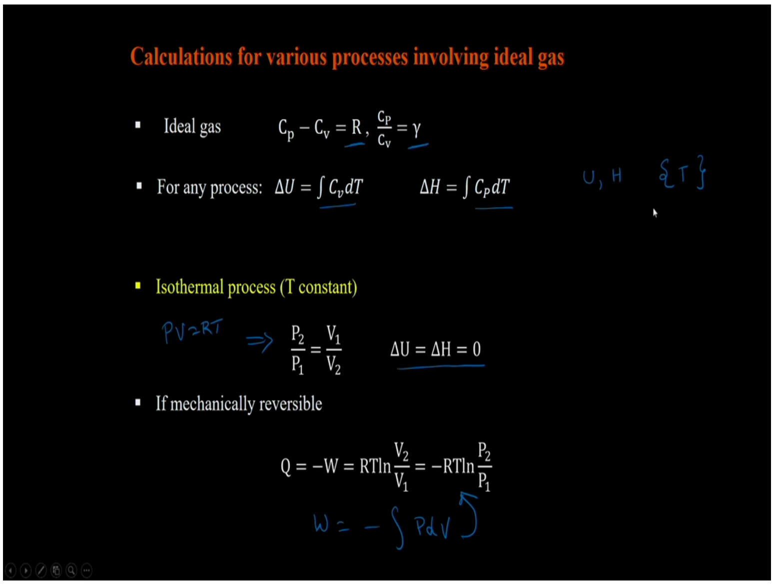

Calculations for various processes involving ideal gas

- Ideal gas $C_p - C_v = \underline{R}, \frac{C_P}{C_v} = \underline{\gamma}$
- For any process: $\Delta U = \int \underline{C_v dT}$ $\Delta H = \int \underline{C_P dT}$

U, H {T}

- Isothermal process (T constant)

$PV = RT \Rightarrow \frac{P_2}{P_1} = \frac{V_1}{V_2}$ $\underline{\Delta U = \Delta H = 0}$

- If mechanically reversible

$$Q = -W = RT\ln\frac{V_2}{V_1} = -RT\ln\frac{P_2}{P_1}$$

$$W = -\int PdV$$

Before that a quick summary of what we have done in the last lecture, we said for an ideal gas the difference in the heat capacities is always equal to the universal gas constant R and then the ratio of heat capacities is what we call as gamma that is the ratio of C p to C v.

And because for an ideal gas both U and H are functions only of temperature, they are independent of pressure it turns out that irrespective of the process delta U and delta H are always integrals of C v d T and C p d T again only for an ideal gas. Now, in case of a isothermal process because delta U and delta H depend only on temperature and in case of an isothermal process the temperature does not change delta U and delta H will be 0 and because of P V T relationship in case of an ideal gas P V is RT. So, that would imply ratio of the pressures will be equal to the inverse ratio of the volumes if the process is isothermal.

On top of this we can derive the work requirement for the process as minus of integral P d V and we substitute the P V T relationship for an ideal gas to get this equations shown here and applying first law that would also be equal to negative of the heat requirement.

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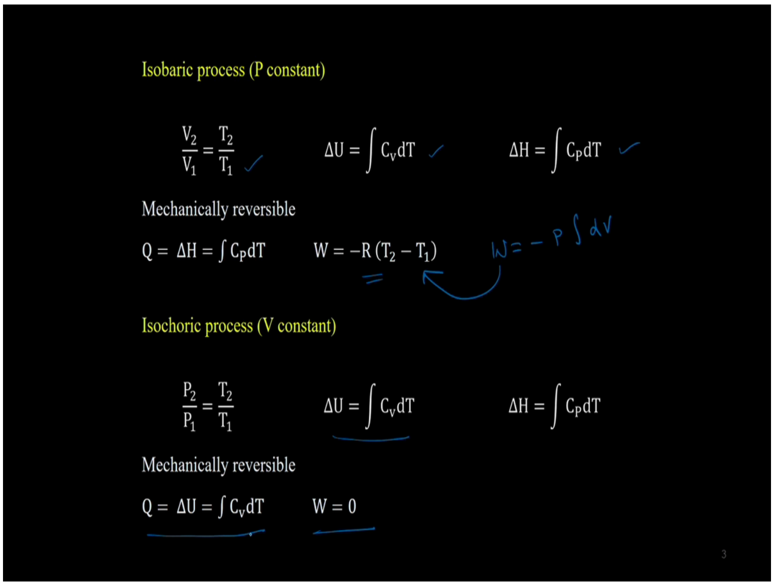

Isobaric process (P constant)

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \checkmark \qquad \Delta U = \int C_v dT \checkmark \qquad \Delta H = \int C_P dT \checkmark$$

Mechanically reversible

$$Q = \Delta H = \int C_P dT \qquad \underset{=}{W = -R\,(T_2 - T_1)} \qquad W = -P \int dV$$

Isochoric process (V constant)

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \qquad \underline{\Delta U = \int C_v dT} \qquad \Delta H = \int C_P dT$$

Mechanically reversible

$$\underline{Q = \Delta U = \int C_v dT} \qquad \underline{W = 0}$$

We can do a similar exercise for other types of processes such as the isobaric process, in case of an isobaric process P V T relationship gives this relation between V and T, because P is constant, these two relations still do not change their integrals of C p d T and C v d T. And then because the process is isobaric we can get W to be equal to integral of minus P integral d V dv is RT by P so, that will turn out to be W will be equal to minus R T 2 minus T 1 and so on. For a isochoric process it is that the work done is minus P d V so, it will be 0 if the process is mechanically reversible and because delta U is integral C v d T Q will also be equal to integral of C v d T.

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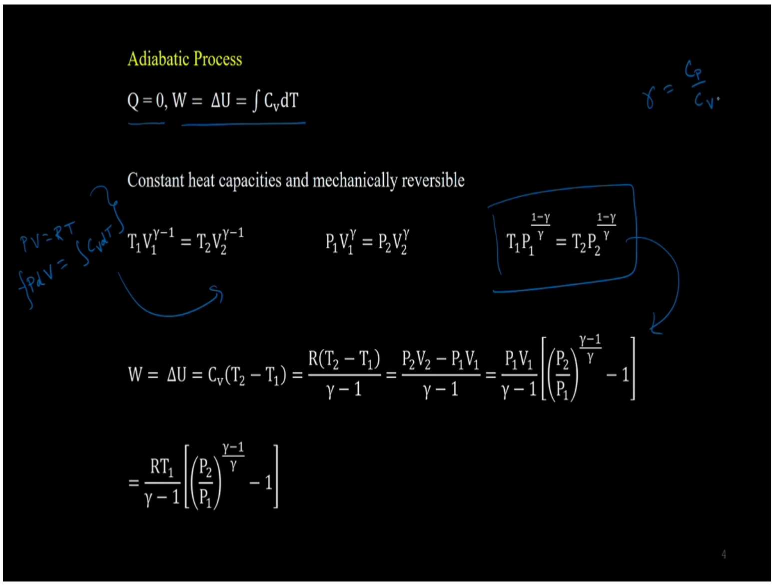

Adiabatic Process

$Q = 0,\ W = \Delta U = \int C_V dT$

$\gamma = \frac{C_P}{C_V}$

Constant heat capacities and mechanically reversible

$PV = RT$

$\int P dV = \int C_V dT$

$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$ $\quad P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$ $\quad \boxed{T_1 P_1^{\frac{1-\gamma}{\gamma}} = T_2 P_2^{\frac{1-\gamma}{\gamma}}}$

$$W = \Delta U = C_V(T_2 - T_1) = \frac{R(T_2 - T_1)}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]$$

$$= \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]$$

And finally, in case of an adiabatic process if the definition requires that the heat exchanged with the surroundings is 0 for a closed system, remember that all through we have been talking about closed systems right.

So, Q is 0 so by virtue of the first law W will be equal to delta U which is integral of C v d T right. And then we can derive the P V T relationships we can apply P V is RT and then since W is also equal to minus P d V or integral of minus P d V, this will be equal to integral of C v d T we can use these two relations in tandem to get these three equations depending on what variable we eliminate whether P V or T. And finally, once we have these relations we can rewrite the expression for work and heat requirement in terms of two of the three variables depending on what we have at hand.

All again these equations will be applicable only for mechanically reversible processes and then when C p and C v are constant that they do not change with temperature, but this in mind these equations are elaborate you can straightaway use them in solving the numerical problems, but what we will do when we solve the numerical problems is just try to go over from the basics and derive either 1 or 2 equations that are necessary to solve that particular problem.

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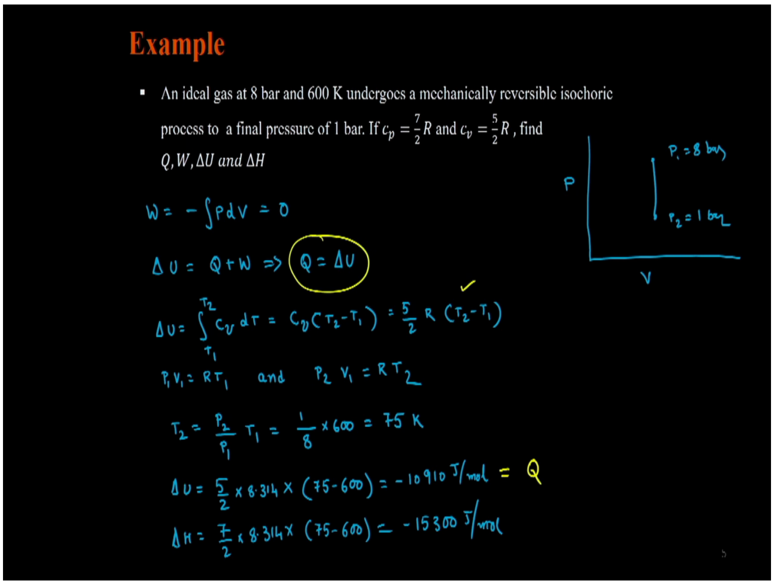

Example

- An ideal gas at 8 bar and 600 K undergoes a mechanically reversible isochoric process to a final pressure of 1 bar. If $c_p = \frac{7}{2}R$ and $c_v = \frac{5}{2}R$, find $Q, W, \Delta U$ and ΔH

$W = -\int P dV = 0$

$\Delta U = Q + W \Rightarrow \boxed{Q = \Delta U}$

$\Delta U = \int_{T_1}^{T_2} C_v dT = C_v(T_2 - T_1) = \frac{5}{2} R (T_2 - T_1)$

$P_1 V_1 = RT_1$ and $P_2 V_1 = RT_2$

$T_2 = \frac{P_2}{P_1} T_1 = \frac{1}{8} \times 600 = 75$ K

$\Delta U = \frac{5}{2} \times 8.314 \times (75 - 600) = -10910$ J/mol $= Q$

$\Delta H = \frac{7}{2} \times 8.314 \times (75 - 600) \simeq -15300$ J/mol

That so look at an example I have an ideal gas at 8 bar and 600 Kelvin it undergoes a mechanically reversible isochoric process to a final pressure of 1 bar, the C p and C v values are constant they are 7 by 2 R and 5 by 2 R respectively we want to find Q W delta U and delta H for this process right. So, if I were to draw a P V curve for this particular process. The volume is constant so, it starts at 8 bar and goes down to 1 bar P 1 is 8 bar and P 2 is 1 bar.

This gas is at 600 Kelvin its an ideal gas and we were to we are required to calculate the 4 quantities asked there. The first thing W it is a mechanically reversible process W is integral of negative P d V, because volume is constant this will be equal to 0 because delta U is Q plus W this also implies Q will be equal to delta U and because this process involves an ideal gas, we can calculate both delta U and delta H from the integrals.

So, delta U will be integral of T 1 to T 2 C v d T or this will be C v of T 2 minus T 1 because C v is constant it is 5 by 2 R. So, it will be 5 by 2 R T 2 minus T 1 so these are the numbers I have. So, this will be the value of delta U what I have at hand is the initial temperature T 1 what I do not know is the final temperature T 2, but what I do know that the is that the process is isochoric which means which means volume is not changing. So, P 1 V 1 is R T 1 and at the final condition P 2 the volume has not changed it is still V 1 will be equal to R T 2 these are the 2 conditions at the initial condition 1 and the final condition 2.

So, then I can find out T 2 from these relations hopefully. So, T 2 then is going to be equal to P 2 over P 1 times T 1 and that would be 1 bar or 8 bar times 600 which is 75 Kelvin. So, once I have T 2 I can go back and calculate delta U; delta U is going to be 5 over 2 times R which is 8.314 times T 2 minus T 1 that is going to be 75 minus 600, which would give me negative 10 9 1 0 in joules per mole.

On the other hand delta H is going to be 7 by 2 R times T 2 minus T 1 and that would give me negative 15300 joules per mole 15300 joules per mole. So, essentially then to solve this particular problem what we have done is first use the ideal gas law, to calculate the unknown condition at the final state T 2 and once we have T 2 we can use C v d T and C p d T to calculate delta U and delta H. And apply the first law to calculate Q and W for this is an isochoric process or d W reversible isochoric process W is 0 and delta U is going to be then equal to Q. So, that completes this particular problem.

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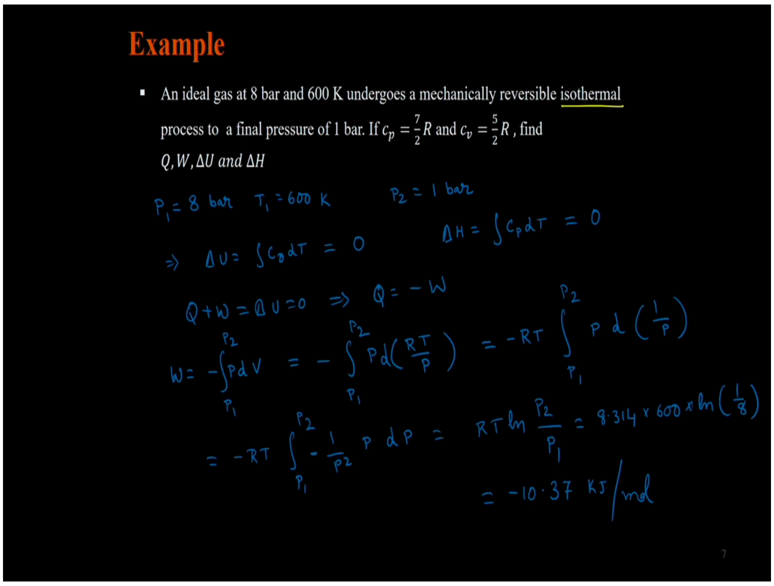

Example

- An ideal gas at 8 bar and 600 K undergoes a mechanically reversible isothermal process to a final pressure of 1 bar. If $c_p = \frac{7}{2}R$ and $c_v = \frac{5}{2}R$, find $Q, W, \Delta U$ and ΔH

$P_1 = 8$ bar $T_1 = 600$ K $P_2 = 1$ bar

$\Rightarrow \Delta U = \int C_v dT = 0$ $\Delta H = \int C_p dT = 0$

$Q + W = \Delta U = 0 \Rightarrow Q = -W$

$$W = -\int_{P_1}^{P_2} P dV = -\int_{P_1}^{P_2} P d\left(\frac{RT}{P}\right) = -RT \int_{P_1}^{P_2} P d\left(\frac{1}{P}\right)$$

$$= -RT \int_{P_1}^{P_2} -\frac{1}{P^2} P dP = RT \ln \frac{P_2}{P_1} = 8.314 \times 600 \times \ln\left(\frac{1}{8}\right)$$

$$= -10.37 \text{ KJ/mol}$$

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This time I still have the initial conditions to be same, I have an ideal gas undergoing a mechanically reversible process the initial conditions are 8 bar and 600 Kelvin, but now the process is isochoric as earlier. So, the other values are of course, the same the final pressure is again 1 bar C p and C v values are constant as in the earlier case and we want to find all the 4 variables Q W delta U and delta H again this process is isothermal.

So, delta U is always integral C v d T because the gas is ideal. So, since the temperature is not changing then this integral will go to 0. Similarly delta H is integral C p d T and again since d T or delta T or change in temperature is 0 this integral also goes to 0. So, now, I am left only with 2 numbers Q and W to calculate by virtue of the first law Q plus W is delta U which happened to be 0 a minute ago which means Q will be equal to negative of W right. So, we will try then proceed to calculate W; W is minus P d V integral of that going from V 1 to V 2 or let us just say because we know the pressures let us see if I can integrate it with respect to pressure P 1 to P 2 right.

So, negative of integral P for an ideal gas V is RT over P this is d right P 1 to P 2. Since temperature is constant this can come out. So, it will be minus RT integral P 1 to P 2 P d of 1 over P right. So, I will be minus RT integral P 1 to P 2 minus of 1 over P square P d V that is minus RT or rather plus now RT ln P 2 over P 1. So, that will be 8.314 times the temperature is constant anyway 600 Kelvin times ln of 1 by 8.

So, that will be equal to negative 10.37 kilojoules per mole like that is also pretty straightforward calculation. So, we know how to handle an isothermal process we know how to handle a isochoric process, let us see what we do in case of an adiabatic process right.

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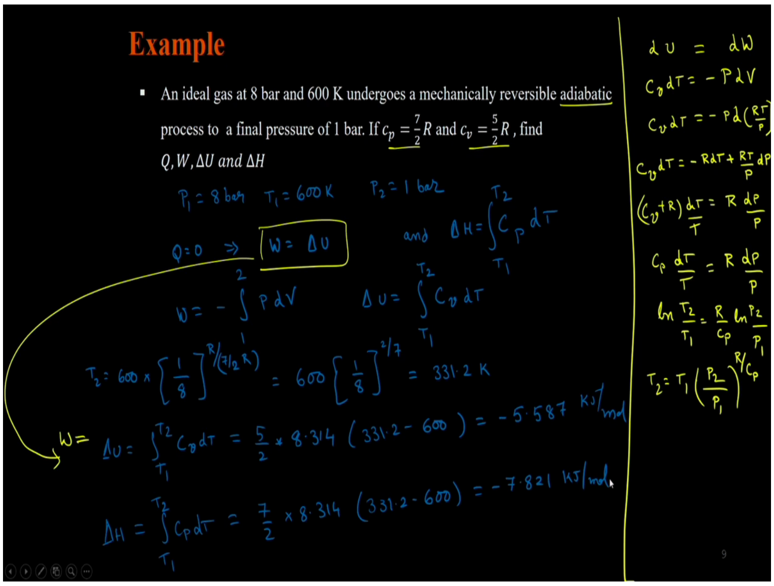

Example

- An ideal gas at 8 bar and 600 K undergoes a mechanically reversible adiabatic process to a final pressure of 1 bar. If $c_p = \frac{7}{2}R$ and $c_v = \frac{5}{2}R$, find $Q, W, \Delta U$ and ΔH

$P_1 = 8$ bar $\quad T_1 = 600\,K \quad P_2 = 1$ bar

$Q = 0 \Rightarrow \boxed{W = \Delta U}$ and $\Delta H = \int_{T_1}^{T_2} C_p\, dT$

$W = -\int_1^2 P\, dV \qquad \Delta U = \int_{T_1}^{T_2} C_v\, dT$

$T_2 = 600 \times \left[\frac{1}{8}\right]^{R/(7/2 R)} = 600\left[\frac{1}{8}\right]^{2/7} = 331.2\ K$

$W = \Delta U = \int_{T_1}^{T_2} C_v\, dT = \frac{5}{2} \times 8.314\ (331.2 - 600) = -5.587\ KJ/mol$

$\Delta H = \int_{T_1}^{T_2} C_p\, dT = \frac{7}{2} \times 8.314\ (331.2 - 600) = -7.821\ KJ/mol$

$dU = dW$

$C_v\, dT = -P\, dV$

$C_v\, dT = -P\, d\left(\frac{RT}{P}\right)$

$C_v\, dT = -R\, dT + \frac{RT}{P}\, dP$

$(C_v + R)\frac{dT}{T} = R\frac{dP}{P}$

$C_p \frac{dT}{T} = R \frac{dP}{P}$

$\ln\frac{T_2}{T_1} = \frac{R}{C_p}\ln\frac{P_2}{P_1}$

$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{R/C_p}$

Again I have the same conditions starting from P 1 is 8 bar to P 2 being 1 bar the temperature initial temperature is still the same, 600 Kelvin P 2 is 1 bar process is adiabatic and the specific heats are again constant with respect to temperature.

Because the process is adiabatic I can use any of the equations, we had earlier depending on the variables I have to get the unknown variable, but let us see if we can actually derive this again. So, for an adiabatic process we know that Q is 0 which implies W is going to be equal to delta U right and delta H is going to be equal to C v d T or integral of that going from T 1 to T 2. And W is negative integral of P d V going from state 1 to 2 whatever variable we choose to integrate it with and delta U is integral of C v I am sorry this is delta H.

So, it should have been it should have been a C p not C v this is delta U is actually C v d T going from T 1 to T 2 right, what we can do is a because these numbers that U is equal to delta, now if I were to integrate this I need some variables at condition two I have pressure I do not have volume I do not have temperature. So, what we do is because we know that W equals delta U what I can do is actually let us just derive that expression here C v d T is minus P d V right this is d U and this is the other side is d W.

So, what we can do is C v d T instead of P because the gas is ideal we can write it as P multiplied with d of RT by P, I can expand that derivative on the right hand side right to get C v d T will be equal to negative R d T plus R T by P dP right. So, if i bring R d T to the other side it will be C v plus R d T by T is R d P by P for an ideal gas C v plus R is C p. So, C p d T by T they will be equal to R d P by P I can integrate this to get ln of T 2 by T 1 equals R by C p ln of P 2 by P 1 or T 2 is going to be equal to T 1 multiplied with P 2 by P 1 to the power R over C p.

So, if I know P 1 P 2 and T 1 I can calculate T 2 and once I know T 2 I can calculate all the other variables. So, what we will do is borrow that equation is T 1 which is 600 Kelvin multiplied by 1 over 8 which is P 2 over P 1 R by C p is 7 by 2 times of R. So, that is 600 1 by 8 to the power of 2 by 7 to the power of 2 by 7 which turns out to be 331.2 Kelvin right that is T 2, once you have T 2 we can calculate all the other variables we need delta U is integral of T 1 to T 2 C v d T that is 5 by 2 times 8.314 times 600 minus 331.2 which turns out to be minus 5.587 kilojoules per mole.

And because in this case this will also be equal to W; W also will be minus 5.587 kilojoules per mole and finally, delta H is integral of C p d T because I know T 1 and T 2 I can readily calculate this integral value to be 7 by 2 times R times you know this should have been actually T 2 minus T 1. So, let us correct that 331.2 minus 600 which will actually give us that negative sign there.

And similarly here as well it is T 2 minus T 1 so, 331.2 minus 600 which is negative 7.821 kilo joules per mole. So, that is how we handle an adiabatic process of course, we can we do not have to do the yellow part of the derivation here those are some of the equations, I showed to you early on in the slide in this lecture right for an adiabatic process this equation is known I know P 1 P 2 and T 1 I can use this equation here gamma of course, as we said is ratio of specific heats since C p and C v are given.

I can use the value of gamma and calculate T 2 directly from this equation or spend a few minutes and derive what we have here on the right hand side and then go about calculating T 2 and finally, delta U and delta H.

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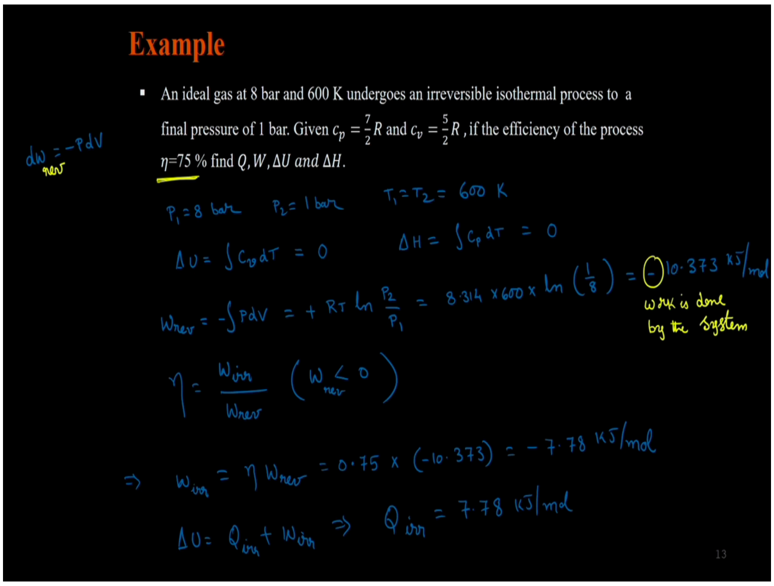

Example

- An ideal gas at 8 bar and 600 K undergoes an irreversible isothermal process to a final pressure of 1 bar. Given $c_p = \frac{7}{2}R$ and $c_v = \frac{5}{2}R$, if the efficiency of the process η=75 % find $Q, W, \Delta U$ and ΔH.

$dW_{rev} = -PdV$

$P_1 = 8$ bar $\quad P_2 = 1$ bar $\quad T_1 = T_2 = 600$ K

$\Delta U = \int C_v dT = 0 \qquad \Delta H = \int C_p dT = 0$

$W_{rev} = -\int PdV = +RT \ln \frac{P_2}{P_1} = 8.314 \times 600 \times \ln\left(\frac{1}{8}\right) = -10.373$ kJ/mol

work is done by the system

$\eta = \frac{W_{irr}}{W_{rev}} \quad (W_{rev} < 0)$

$\Rightarrow W_{irr} = \eta W_{rev} = 0.75 \times (-10.373) = -7.78$ kJ/mol

$\Delta U = Q_{irr} + W_{irr} \Rightarrow Q_{irr} = 7.78$ kJ/mol

Let us see if we can bring some irreversibility into picture and how we handle irreversibility and calculate the work and heat requirements for an irreversible process right. Now, remember all the equations we had earlier for W such as d W is minus P d V this equation is true only for a reversible process.

It is true only for a reversible process if the process is not reversible, then this equation will not hold and we did not look at how we can calculate the work in processes that are not reversible which is what we are going to do in this problem. Let us take the same problem we have dealt with so far the initial state is same as in the previous case P 1 is 8 bar and P 2 is 1 bar the process is an isothermal P 1 is 8 bar P 2 is 1 bar T 1 is T 2 is 600 Kelvin.

What we want to do is calculate the heat and work requirements as well as changes in delta U and delta H for an irreversible process. First stop irrespective of whether the process is reversible or irreversible delta U and delta H do not depend on the path, they depend only on the state going from P 1 T 1 to P 2 T 2. As long as that happens irrespective of whether the path itself is reversible or irreversible delta U will always be integral of C v d T as long as the gas is ideal, even for an irreversible process and because in this case change in temperature is 0 delta U will be 0.

And similarly delta H again is only a state function or H is a state function. So, delta H only depends on the two states initial and final and it will be integral of C p d T for an ideal gas. And because change in temperature is 0 delta H also is going to be equal to 0 for this case, then if the process were reversible we could use the reversible work done to calculate work and by using first law we can calculate the heat requirements, but now the process is not reversible so, how do we calculate the work requirement. So, to be able to handle that we use a quantity called as the efficiency of the process and in this case the efficiency of the process is given as 75 percent.

So, we will see how to use that, but first what we do is we calculate the work done for a reversible process. As earlier for a reversible process the work done is simply integral of P d V and in this case because the gas is ideal it will be negative RT ln or rather positive RT ln P 2 over P 1. So, that will be 8.314 times 600 times ln of 1 over 8 which turns out to be negative 10.373 kilojoules per mole this is the work and the negative sign implies that the system is doing work on the surroundings.

So, this negative sign indicates work is done by the system on the surroundings that is the sign convention, we are following and what this means is that in a reversible process the system is going to do a work of 10.373 kilojoules per mole. If the process were irreversible then the system will not be able to do so, much work it will depend how much work it does on the surroundings will depend on the efficiency of the process. And the way we define efficiency is work done in an irreversible process over work done in a reversible process.

If it is a system that is doing work on the surroundings. So, if W is negative then efficiency is the ratio of the work done in the irreversible process to that of the reversible process, what this means is in this case the work done in an irreversible process is going to be efficiency times the work done in a reversible process, because it is the system that is doing work. So, this will be 0.75 75 percent times negative 10.373. So, that will be equal to negative 7.78 kilojoules per mole.

So, in case of a reverse irreversible process the system will be able to do only negative 7.78 kilojoules per mole of work. And the first law has to hold irrespective of whether the process is reversible or irreversible delta U is still this, what this means is that Q in case of an irreversible process is going to be 7.78 kilojoules per mole notice that W is not P d V its P d V multiplied with whatever the efficiency of the processes and Q accordingly changes for an irreversible process. This is the key if the system is doing work on the surroundings, this is how we use efficiency of a irreversible process.

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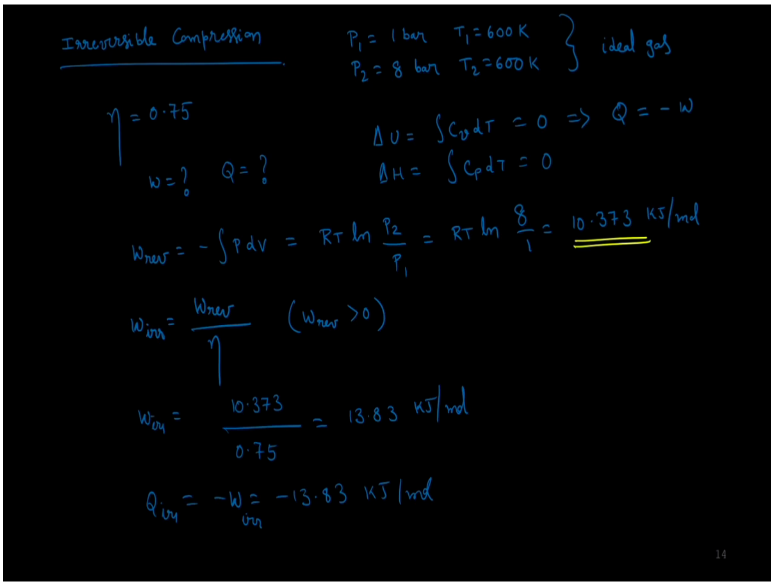

Irreversible Compression

$P_1 = 1$ bar $T_1 = 600$ K

$P_2 = 8$ bar $T_2 = 600$ K

$\}$ ideal gas

$\eta = 0.75$

$W = ?$ $Q = ?$

$\Delta U = \int C_v dT = 0 \Rightarrow Q = -W$

$\Delta H = \int C_p dT = 0$

$$W_{rev} = -\int P dV = RT \ln \frac{P_2}{P_1} = RT \ln \frac{8}{1} = \underline{\underline{10.373}} \text{ KJ/mol}$$

$$W_{irr} = \frac{W_{rev}}{\eta} \quad (W_{rev} > 0)$$

$$W_{irr} = \frac{10.373}{0.75} = 13.83 \text{ KJ/mol}$$

$$Q_{irr} = -W_{irr} = -13.83 \text{ KJ/mol}$$

The earlier one was an irreversible expansion of the gas, where the system is going to do work on the surroundings. Now, let us consider an irreversible compression all right in this case what we are doing is we start with an initial state of 1 bar the temperature is same 600 Kelvin and we go to a final state of 8 bar it is still an isothermal process, it is an ideal gas undergoing this change. Again process is not mechanically reversible, but it is irreversible and the efficiency of the process is 0.75 or 70 percent the question asked is what is the work and heat the requirements for this process.

Now, this looks pretty straightforward and on the first look except once we try to solve it, we see a subtle difference between the earlier expansion case. And this compression case when the process is irreversible notice that since the temperature is same even for this process delta U is integral C v d T it is 0 and delta H is integral C p d T it is also going to be equal to 0, what this also means by through first law is that Q is going to be equal to negative of W.

Now, to use efficiency as earlier what we do is we calculate the work required for a reversible process first, the work required in case of a reversible process in this example is going to be integral of P d V this will be RT ln P 2 over P 1 RT ln 8 over 1 or that will be positive 10.373 kilojoules per mole. Now, notice that this number is the same which makes sense, because it is same as earlier irreversible or reversible expansion the system is going to do 10.373 kilojoules per mole of work.

If it is a reversible compression the surroundings have to do the same amount of work 10.373 kilojoules per mole of work on the system to get back to the original state. So, in case of a reversible process the work requirement during compression is exactly equal to the work produced during expansion, because the process is reversible; however, if the process is irreversible. So, now, if you look at this is a compression what I am saying is we need 10.373 kilojoules per mole of work to be done by the surroundings on the system so, that we can go from 1 bar to 8 bar.

Now, if the process is irreversible then the surroundings have to do more work on the system to get it back to the final state. So, in case of an irreversible process when W is positive the way we define efficiency is the work required in case of an irreversible process is the work required in a reversible process over the efficiency, when W is positive. If the surroundings are doing work on the system then they need to do more work if the process is irreversible, which means in this case it will be 10.373 over 0.75 which will be equal to 13.83 kilojoules per mole.

This is the work required in case of an irreversible process the system, the surroundings have to do more work on the system. And again as earlier the Q will be negative of W the first law still holds so, it will be negative 13.83 kilojoules per mole. So, notice that we used the relation between reverse if the definition for efficiency slightly differently for an expansion versus a compression. So, now, we know that we can handle an irreversible process as well except what I need to know is the efficiency of the process ok.

So, if it is seventy five percent efficient then I can use that efficiency to calculate the work done. So, this efficiency is always used in this calculations as efficiency for the work required or work done by the system.

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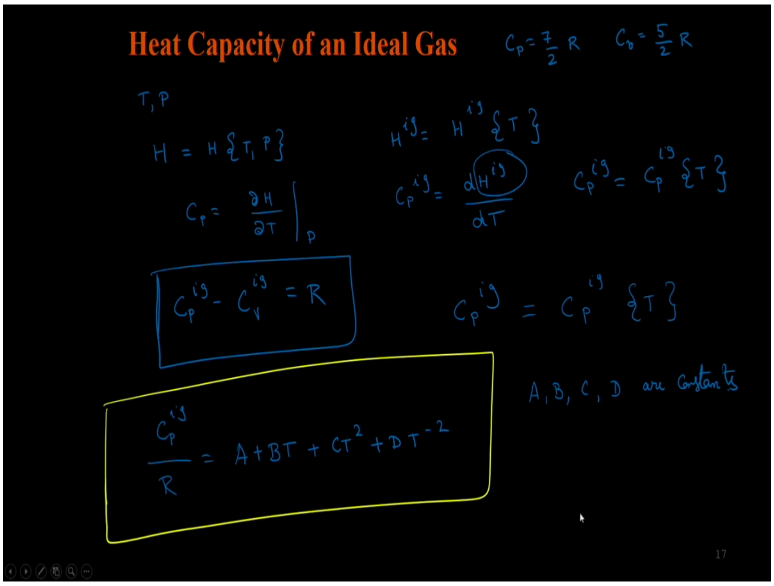

Heat Capacity of an Ideal Gas

$C_p = \frac{7}{2} R$ $C_v = \frac{5}{2} R$

T, P

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

$C_p = \left.\frac{\partial H}{\partial T}\right|_P$

$$\boxed{C_p^{ig} - C_v^{ig} = R}$$

$H^{ig} = H^{ig}\{T\}$

$C_p^{ig} = \frac{d H^{ig}}{dT}$

$C_p^{ig} = C_p^{ig}\{T\}$

$C_p^{ig} = C_p^{ig}\{T\}$

$$\boxed{\frac{C_p^{ig}}{R} = A + BT + CT^2 + DT^{-2}}$$

A, B, C, D are Constants

So, far what we have looked at is processes that involve ideal gases, they can be reversible or irreversible we can handle them, but all through the calculations if you notice what we have used is that the heat capacity C p or C v is constant it was 7 over 2 times R or 5 over 2 times R.

This is rarely the case if we go back to the phase rule to fix the state of a system I need 2 variables let us say temperature and pressure, if I have a gas I need 2 variable and a single component gas, then I need 2 variables to fix the state of the system. So, for example, H will be a function of 2 variables, but for an ideal case it is a special case because the molecules do not interact H will turn out to be a function of only one variable which is the temperature right.

So, because C p if you recall the definition for C p it is derivative of H with respect to temperature at constant pressure and for an ideal gas it will be total derivative with respect to temperature, because it is not dependent on pressure anyway or let us separate them. So, for an ideal gas there will be d H ig over d T. So, since H is a function of temperature C p ig also strictly speaking is going to be dependent on temperature it is not constant, like we have used in the previous problems it is going to be a function of temperature strictly speaking.

So; however, the earlier relations still hold C p minus C v for an ideal gas, we can actually prove this rigorously is always going to be equal to R. Even though both of them are functions of temperature the difference between the 2 is always going to be equal to R. So, if I define one of these two specific heats it is fairly straightforward to calculate the other specific heat. So, what we will do usually what is done is we focus only on one of these quantities usually C p ig is what we are interested in if need be we can always calculate it for an ideal gas by subtracting R from this value.

So, then my focus is on C p ig and its always a function of temperature even for an ideal gas. And usually this functionality for is tabulated experiments have to be performed and then the temperature dependency of this quantity is tabulated in any of the handbooks you want to refer to you should in some of the handbooks, you can refer to find these values and usually the functionalities expressed in terms of a polynomial the last term is inverse quadratic so, d T to the power minus 2.

This is the usual functionality you will find for temperature dependency of C p ig in certain cases one or more of these parameters A B C or D might be 0 usually either C or D might be 0, but you a and b are nonzero values. So, A B C D are constants for a given gas and there is a particular range over which you can use these C p values the range is usually specified in the table next to A B C D values so, be careful about the range where we are applying going to apply this equation to find the specific heat capacity make sure that it falls within the range suggested for use of these A B C D values.

Once you have that you should be it should be pretty straightforward to calculate C p ig at a particular temperature. Usually though what we are interested is not the value of C p ig, rather the integral of that value right remember that in the earlier discussion this is actually not the value of C p ig rather it is the value of C p ig over R right. So, it is not just C p ig but rather it C p ig over R.

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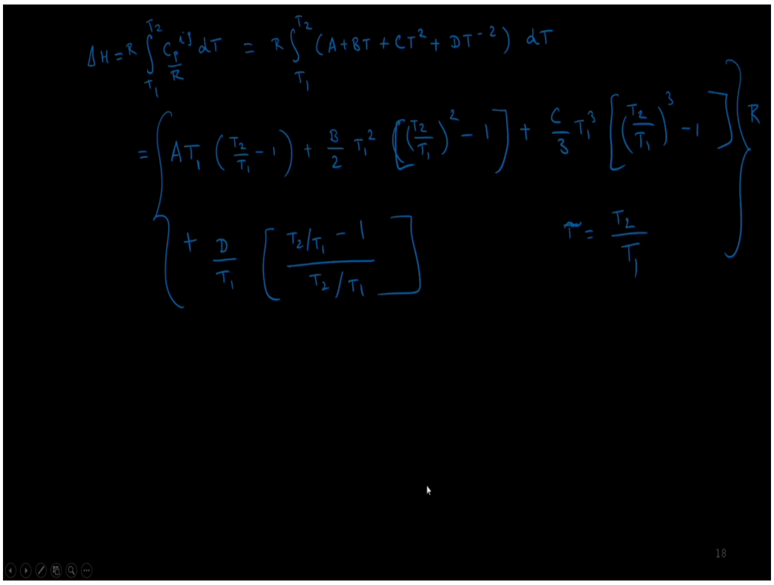

$$\Delta H = R\int_{T_1}^{T_2} \frac{C_p^{ig}}{R}\, dT = R\int_{T_1}^{T_2} (A + BT + CT^2 + DT^{-2})\, dT$$

$$= \left\{ AT_1\left(\frac{T_2}{T_1} - 1\right) + \frac{B}{2}T_1^2\left[\left(\frac{T_2}{T_1}\right)^2 - 1\right] + \frac{C}{3}T_1^3\left[\left(\frac{T_2}{T_1}\right)^3 - 1\right] + \frac{D}{T_1}\left[\frac{T_2/T_1 - 1}{T_2/T_1}\right] \right\} R$$

$$\tau = \frac{T_2}{T_1}$$

So, if we want to calculate for example, delta H, then what we need to do is integrate this with respect to d T right and C p ig is no longer constant, but rather it is a plus B T plus C T squared plus D T to the power minus 2 D T A B C D are constants this is an algebraic expression we can integrate it pretty easily and it turns out that this value is going to be equal to A times T 1 times T 2 minus T 1 minus 1 plus B over 2 T 1 squared T 2 by T 1 whole squared minus 1 plus C over 3 T 1 cube T 2 by T 1 whole cube minus 1 plus d by T 1 T 2 by T 1 minus 1 over T 2 by T 1.

So, this is the suggested expression for delta H involving A B C and D when the temperature changes from T 1 to T 2. Usually T 2 by T 1 is written as tau and then we can use this expression in a pretty straightforward fashion otherwise we can integrate it whenever the need arises.

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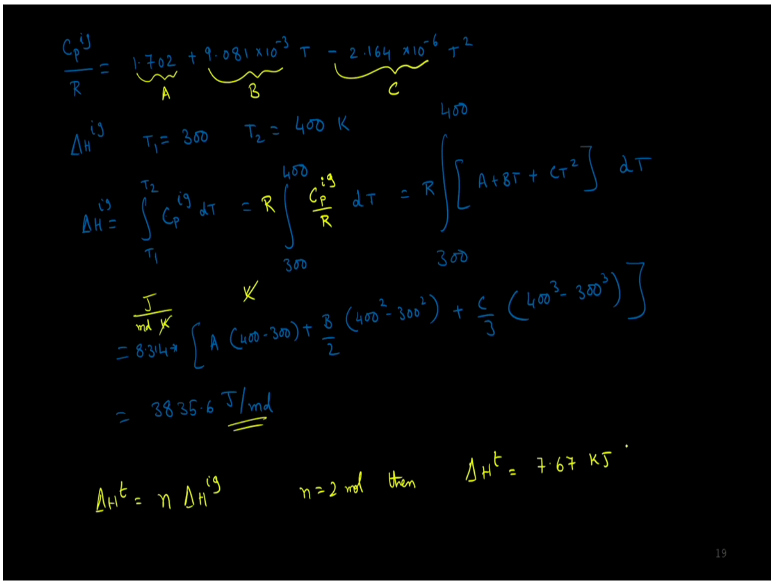

$$\frac{C_p^{ig}}{R} = \underbrace{1.702}_{A} + \underbrace{9.081 \times 10^{-3}}_{B} T - \underbrace{2.164 \times 10^{-6}}_{C} T^2$$

ΔH^{ig} $T_1 = 300$ $T_2 = 400$ K

$$\Delta H^{ig} = \int_{T_1}^{T_2} C_p^{ig}\, dT = R \int_{300}^{400} \frac{C_p^{ig}}{R}\, dT = R \int_{300}^{400} \left[A + BT + CT^2 \right] dT$$

$$\underset{\frac{J}{mol\, \cancel{K}}}{= 8.314} * \left[A(400-300) + \frac{B}{2}(400^2 - 300^2) + \frac{C}{3}(400^3 - 300^3) \right] \cancel{K}$$

$$= \underline{\underline{3835.6 \; J/mol}}$$

$\Delta H^t = n \, \Delta H^{ig}$ $n = 2$ mol then $\Delta H^t = 7.67$ KJ.

So, let us do one quick example based on this idea right we have methane and for methane the C p ig from the tables is given as C p ig over R is 1.702 plus 9.081 10 power minus 3 T minus 2.164 times 10 power minus 6 times T squared.

Notice that we had a multiplication with R here which we missed probably. So, C p ig over R is in terms of A B C and D so, we have a factor of R there. The whole thing if A B C D relate to C p ig over R. This is the case this is C p ig over R what we are interested in is finding delta H ig the change in delta H for an ideal gas, going from 300 to 400 Kelvin we want to find delta H ig, this is a pretty straightforward delta H for an ideal gas is integral C p ig d T going from T 1 to T 2.

So, in this case it will be going from 300 to 400 let us quickly write these this is A this is B and then this is C negative of 2.164 is C into 10 power minus 6 is C. So, this will be C p ig over R times R times d T. So, this is R times A plus B T plus C T squared D T integral of 300 to 400 so, that is 8.314 times A 400 minus 300 plus B T squared or rather 400 squared minus 300 squared over 2 plus V by 3 400 cube minus 300 cube.

And we can put the values of A B and C back in this expression to get 38 35.6 joules per mole. So, this is the value of delta H ig going from 300 to 400 Kelvin notice that these are is in joules per mole per Kelvin and this is in this integral itself is in Kelvin. So, what we get is joules per mole here right. So, this is the change in the molar enthalpy going from T 1 to T 2 given C p ig value, we can always calculate the total enthalpy change delta H total is going to be the number of moles multiplied with the molar value delta H ig.

So, for example if n is 2 moles then delta H total is going to be 7.67 kilojoules etcetera. So, once we have the temperature dependency for C p ig then we cannot consider C p to be constant with temperature anymore, we will have to perform an integration on the polynomial we have for C p ig and then get the final value of delta H after the integration. So, with that we come to an end of the discussion on calculation of a heat and work requirements for various processes involving an ideal gas.

How we do the calculation if the process is irreversible and how do we how we do these calculations, if the heat capacities are not constant, but rather depend on temperature.

Thank you, I will see you in the next lecture.