

Chemical Engineering Thermodynamics
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Lec 10
First law of thermodynamics: Examples

Welcome back. In this lecture we are going to make use of ideal gas and first law of thermodynamics to solve some simple problems.

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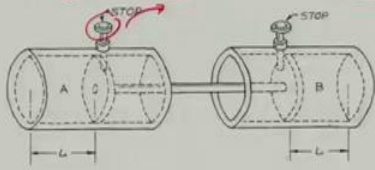
Example 1

Two well-insulated cylinders are placed as shown below. The pistons in both cylinders are of identical construction. The clearances between piston and wall are also made identical in both cylinders. The pistons and the connecting rod are metallic.

Cylinder *A* is filled with gaseous helium at 2 bar and cylinder *B* is filled with gaseous helium at 1 bar. The temperature is 300 K and the length *L* is 10 cm. Both pistons are only slightly lubricated.

The stops are removed. After all oscillations have ceased and the system is at rest, the pressures in both cylinders are, for all practical purposes, identical.

Assuming the gases are ideal with a constant *C_v* and, for simplicity, assuming that the masses of cylinders and pistons are negligible, what are the final temperatures?



Composite *A+B* isolated

$$\Delta U_A + \Delta U_B = 0$$

$$N_A C_v (T_{Af} - T_{Ai}) + N_B C_v (T_{Bf} - T_{Bi}) = 0$$

$$N_A C_v T_{Af} + N_B C_v T_{Bf} = N_A C_v T_{Ai} + N_B C_v T_{Bi}$$

$$(N_A + N_B) T_{Af} = N_A T_{Ai} + N_B T_{Bi}$$

$$\Rightarrow T_{Af} = \frac{N_A T_{Ai} + N_B T_{Bi}}{N_A + N_B}$$

So, we will have 2 examples. To start with we will take the first one. So, what we have is two well-insulated cylinders which are placed as shown below. So you have these two cylinders. The pistons in both the cylinders are identical construction. The clearance between the piston and walls are also made identical in both the cylinders. The pistons and the connecting rods are metallic, ok. So, this is a piston here they are connected and they are metallic which means basically there is transfer of heat from this region to another this region through the rod here.

Cylinder A is filled with a gaseous liquid at 2 bar. Cylinder B is filled with a gaseous helium at 1 bar. The temperature is 300 Kelvin and the length is 10 centimeters. So this is the length which is given here is 10 centimeters both piston are only slightly lubricated. The stops are removed after all oscillations have ceased and the system is at rest and the pressure in both cylinders are for practical purpose identical.

So once the stop is released, so this one you take it out. So, basically it will oscillate. And eventually it will reach an equilibrium point as we know from our postulates and then, at that condition the pressures in both the system can be considered to be same. So, the question is now assuming the gases are identical, so gases are ideal with a constant heat capacity and for simplicity assuming that the mass of cylinders and piston are negligible then what is the final temperature in these 2 particular cylinders?

So this is a very simple question. How do you solve it? One way is, of course, we take system different and try to understand each sub systems or system A and B. The other possibility is that we simply apply the first law to the composite here. So, if we consider the composite A plus B composite system. Rather than applying this to compartment, probably this would make much easier then. Now this is insulated. Remember that this is well insulated, so essentially whatever the changes occurs in the internal energy which remains in here.

So there is no transfer of energy through any boundary. So in that case, one can consider if you consider the composite A + B, then it is going to be isolated. And then we can have:

$$\Delta U_A + \Delta U_B = 0$$

Now, it is an ideal gas and hence, I can make use of the expression of U in terms of heat capacity. So, $N_A C_V (T_{Af} - T_{Ai}) + N_B C_V (T_{Bf} - T_{Bi}) = 0$ where T_i is initial temperature and T_f is final temperature.

Now the other thing is that we assuming the gases with a constant C_V , so both have the constant C_V . So, change in the, total change in the internal energy in the compartment B plus that in A need to be 0 for an isolated composite system here. Because it is insulated and we are ignoring all other losses and then we making use of ideal gas expression to write it in terms of C_V .

Now rearranging we get,

$$T_{Af} = \frac{N_A T_{Ai} + N_B T_{Bi}}{N_A + N_B}$$

This means T_{Af} final temperature is nothing but weighted average of temperature with respect to moles. So this is something which is an expression. So this is first part. That is what exactly what is a final temperatures. Now, you know the temperature which was given. The temperature is 300 so you also know N_A . This N_A you can write, use the ideal gas to find it out. Ideal gas equation of state to find it out and you can obtain the expressions.

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Example 2

Consider the situation described in the earlier example, but with well-insulated pistons and connecting rods of low thermal conductivity. What are the final temperatures after the oscillations have ceased and the pressures have equalized?

no longer simple system
internal adiabatic wall

$$\Delta U_A + \Delta U_B = 0$$

$$N_A C_V (T_{Af} - T_{Ai}) + N_B C_V (T_{Bf} - T_{Bi}) = 0$$

$$N_A T_{Af} + N_B T_{Bf} = N_A T_{Ai} + N_B T_{Bi}$$

Compartment A

$$dU_A = \delta W = -P_A dV_A ; \quad V = \frac{NRT}{P}$$

$$N_A C_V dT = -P_A \left[\frac{NR dT}{P_A} - \frac{NR T dP_A}{P_A^2} \right] \quad \begin{aligned} dW &= \frac{NR dT}{P} \\ &- \frac{NR T dP}{P^2} \end{aligned}$$

$$N_A C_V dT = -P_A \left[\frac{NR P_A dT - NR T dP_A}{P_A^2} \right]$$

$$= - \left[NR dT - \frac{NR T dP_A}{P_A} \right]$$

$$(C_V + R) dT = \frac{RT dP_A}{P_A}$$

$$\frac{(C_V + R) dT}{T} = \frac{dP_A}{P_A} \quad R/(C_V + R)$$

$$\Rightarrow \frac{T_{Af}}{T_{Ai}} = \left(\frac{P_{Af}}{P_{Ai}} \right)^{R/(C_V + R)}$$

$$V_{Af} + V_{Bf} = V_{Ai} + V_{Bi} = V_T$$

$$(N_A T_{Af} + N_B T_{Bf}) R/P_f = V_T$$

So, I can move to the next question. Now, consider a situation described in the, consider the situation described in the earlier example but with well insulated piston and connected rods of low thermal conductivity. Now, which essentially means that, well that the heat will not get transfer from one region to another region. So our assumption, our consideration of temperature equality cannot be imposed on it.

So, since, the process is fast and essentially heat transfers can be neglected through the rod so we can consider this to be now that final temperature is going to be different. So, what we are being asked is what are the final temperatures after the oscillations have ceased and the pressures have equalized. Pressure still is different because of this connecting rod is going to be, is having a low thermal conductivity.

So, now how do you solve this problem? Again we go back to the fact that this is a well-insulated. So we should consider again a composite A plus B. but it is no longer a simple system. It has an internal adiabatic wall, ok. So, it is no longer simple system, ok. It has an internal adiabatic wall but still the composite A + B, if you apply the first law you will get this. The first law can be applied to the composite system and essentially the expression is going to be: $\Delta U_A + \Delta U_B = 0$.

$$\text{And thus, } N_A C_V (T_{Af} - T_{Ai}) + N_B C_V (T_{Bf} - T_{Bi}) = 0$$

Now, what we are assuming is there is no friction in the composite A process is slow and causes static. If that is the case then, here the process is slow then essentially you have an insulated system and this is also adiabatic.

Essentially, so in this case you can simply consider such a case as dU is equal to nothing but dW or delta W because there is no heat transfer. So, in that case, I can write: $dU_A = \delta W = -P_A dV_A$

So, what I have to do is I have to get rid of this, the volume part. Here, we have to eliminate the volume so how do you do that here. So this is only for the compartment A.

So, we can make use of ideal gas here.

$$V = \frac{NRT}{P}$$

$$dV = \frac{NRdT}{P} - \frac{NRTdP}{P^2}$$

Thus,

$$N_A C_V dT = -P_A \left[\frac{N_A R dT_A}{P_A} - \frac{N_A R T_A dP_A}{P_A^2} \right]$$

$$\frac{(C_V + R)}{R} \frac{dT_A}{T_A} = \frac{dp_A}{p_A}$$

Integrating,

$$\frac{T_{Af}}{T_{Ai}} = \left(\frac{P_{Af}}{P_{Ai}} \right)^{\frac{R}{C_V + R}}$$

So, this is the expression you are going to get by solving. So, this was only the first compartment. So, we still have to get the P_f ratio. This we do not know at this point, so we can now make use of the fact that even though the process is occurring the total volume of both the compartment remains constant. So, we are going to make use of that.

So, volume is constant which means: $V_{Af} + V_{Bf} = V_{Ai} + V_{Bi} = V_T$

$$(N_A T_{Af} + N_B T_{Bf}) \frac{R}{P_f} = V_T$$

Similarly, that is for the volume of B. P_f is constant because of the fact that the pressure will eventually, when the piston oscillation stops that will lead to the equality of the pressure.

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Example 2

Consider the situation described in the earlier example, but with well-insulated pistons and connecting rods of low thermal conductivity. What are the final temperatures after the oscillations have ceased and the pressures have equalized?

No longer simple system - internal adiabatic wall $\Delta U_A + \Delta U_B = 0$

$$N_A C_V (T_{Af} - T_{Ai}) + N_B C_V (T_{Bf} - T_{Bi}) = 0$$

$$\boxed{N_A T_{Af} + N_B T_{Bf} = N_A T_{Ai} + N_B T_{Bi}} \quad *$$

Compartment A

$$C_V U_A = \delta W = -P_A dV_A \quad ; \quad V = \frac{NRT}{P}$$

$$N_A C_V dT = -P_A \left[\frac{NR dT}{P_A} - \frac{NRT dP_A}{P_A^2} \right] \quad ; \quad dW = \frac{NR dT}{P} - \frac{NRT dP}{P^2}$$

$$\begin{aligned}
 N_A C_V dT_A &= -P_A \left[\frac{N_A R P_A dT_A - N_A R T_A dP_A}{P_A^2} \right] \\
 &= - \left[N_A R dT_A - \frac{N_A R T_A dP_A}{P_A} \right] \\
 (C_V + R) dT_A &= \frac{R T_A dP_A}{P_A} \\
 \frac{(C_V + R) dT_A}{T_A} &= \frac{dP_A}{P_A} \quad R/(C_V + R) \\
 \Rightarrow \frac{T_{Af}}{T_{Ai}} &= \left(\frac{P_{Af}}{P_{Ai}} \right)
 \end{aligned}$$

$$\begin{aligned}
 V_{Af} + V_{Bf} &= V_{Ai} + V_{Bi} = V_T \\
 (N_A T_{Af} + N_B T_{Bf}) \frac{R}{P_f} &= V_T
 \end{aligned}$$

$$P_f = \frac{(N_A T_{Af} + N_B T_{Bf}) R}{V_{Ai} + V_{Bi}}$$

From *

$$P_f = \frac{N_A T_{Ai} + N_B T_{Bi}}{V_{Ai} + V_{Bi}} = \frac{P_{Ai} V_{Ai} + P_{Bi} V_{Bi}}{V_{Ai} + V_{Bi}} = 1.5 \text{ bar}$$

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$$T_{Af} = \left(\frac{1.5}{2} \right)^{R/(C_V + R)} \quad C_V = 12.6 \text{ J/mol K}$$

$$= 267 \text{ K}$$

$T_{Bf} = 364 \text{ K}$

From first law sup.

Now that means: $P_f = \frac{(N_A T_{Af} + N_B T_{Bf}) R}{V_{Ai} + V_{Bi}}$

It is total volume so that comes directly from this expression. V_T is nothing but the sum of the initial volume. Now this can also be connected to the initial temperatures. Since, this if you go back to earlier statement here, this is nothing but $N_A T_{Ai} + N_B T_{Bi}$. So, from this earlier statement we can write P_f as $N_A T_{Ai} + N_B T_{Bi} + V_{Ai} + V_{Bi}$, but this is nothing but $P_{Ai} V_{Ai} + P_{Bi} V_{Bi} / V_{Ai} + V_{Bi}$.

So, what we have done is we have simply converted everything in the form of the initial conditions here. Now, we will plug in the value as the pressures and the volume you are going to get 1.5 bar. In that case once you have the P_f you can go back to the expression here. So from double star we

have T_{AF} is 1.5, was the final pressure initially is 2 bar in the compartment A and then you have to plug in R and C_V values. R and $C_V + R$ now with C_V . You can C_V , let us say if you consider C_V is 12.6 joule per mole kelvin then this value comes out to be 267.

Similarly, from the first law you can plugin back the expressions so from here you can get T_{BF} . So T_{BF} comes out to be 366 kelvin. So this is from the first law. So, that was the end of the exercises where we have used the first law and as well as the ideal expression to solve a simple set of examples. And that would be the end of today's class. We will look forward to have you in my next class. Thank you.