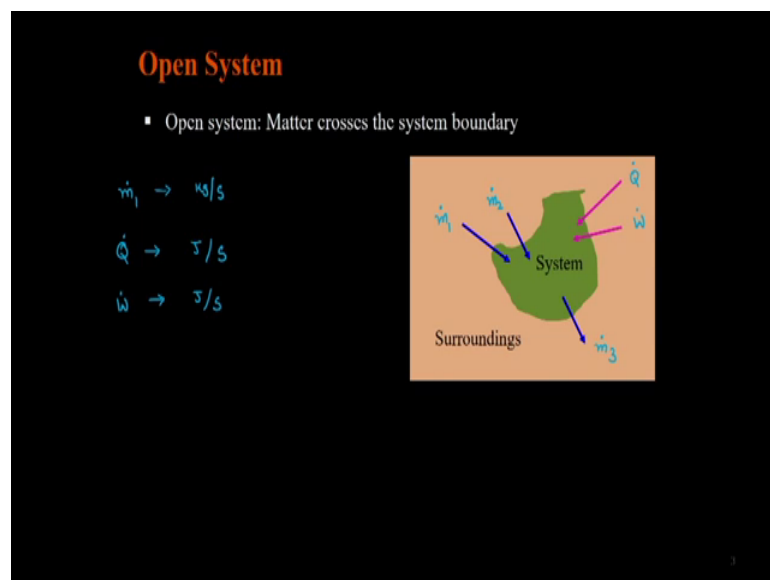


Chemical Engineering Thermodynamics
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Lecture – 03
The First Law of Thermodynamics for Open Systems

Hello everyone and welcome back to this course on Chemical Engineering Thermodynamics. Today we are going to talk about the first law of thermodynamics for open systems.

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In the last class we looked at development of the first law for a closed system which is essentially an energy balance equation. And ultimately it boils down to the fact that the change in the internal energy of a system of a closed system is going to be equal to the heat added and the work done on the system or some of the heat added and work done on the closed system.

Now, if you recall a closed system is one where there is no transfer of mass or matter across the boundary of the system. Today we will try to extend this first law to an open system. In an open system the matter crosses the system boundaries, as opposed to that in a closed system where there is no exchange of matter between the system in the surroundings, in this case the matter can cross the system boundaries the system and

surroundings can exchange mass with one another. And of course, there is also heat and work that can be added or taken away from the system.

Let us say there are 3 streams that can carry mass in or out of the system two of them carrying it into the system. Let us call those streams as m_1 and m_2 , and the third stream that carries mass away from the system will be denoted as m_3 . The heat and work as in the earlier case of a closed system are going to be denoted by Q and W .

Now, typically in an open system we do mass or energy balances for rate of change in mass or rate of change in energy. So, we will actually use the notation \dot{m}_1 , \dot{m}_2 and \dot{m}_3 . Similarly, for the heat and work we will be \dot{Q} and \dot{W} . These dots indicate the rate of change of mass. So, \dot{m}_1 is going to be the amount of mass transferred by the stream to the system in unit time. So, typically its units are going to be something like kilograms per second, the same case for \dot{m}_2 and \dot{m}_3 is going to be the rate of mass, transferred or taken away by stream 3 from the system to the surroundings.

Similarly, \dot{Q} is going to be the rate of heat added to the system in unit time. So, the units are going to be something like Joules per second or watts, and the same thing holds good for \dot{W} as well it is going to be rate of work done on the system in unit time. So, the units are going to be again Joules per second or watts. So, this is the typical notation we follow when we work with open systems. The first thing we will do for an open system is to perform a mass balance on the system. So, we will just look at the 3 streams for now that carry mass in and out of the system. We call them as \dot{m}_1 , \dot{m}_2 and \dot{m}_3 .

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Mass balance on an open system

- Open system: Matter crosses the system boundary

Accumulation = In - out

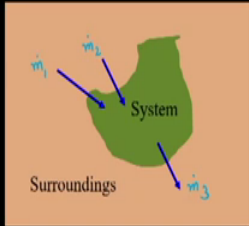
$$\frac{d(m_{cv})}{dt} = \dot{m}_1 + \dot{m}_2 - \dot{m}_3$$

$$\frac{d(m_{cv})}{dt} + \Delta(\dot{m}_{fs}) = 0$$

$\Delta \rightarrow \text{out} - \text{in}$

At S.S. $\Delta(\dot{m}_{fs}) = 0$ $\dot{m}_1 + \dot{m}_2 = \dot{m}_3$

$\dot{m}_i = \rho_i A_i u_i$ $\rho_1 u_1 A_1 + \rho_2 u_2 A_2 = \rho_3 u_3 A_3$



The diagram shows a green irregular shape labeled 'System' surrounded by an orange area labeled 'Surroundings'. Three blue arrows represent mass flow streams: two arrows labeled \dot{m}_1 and \dot{m}_2 point into the system from the left, and one arrow labeled \dot{m}_3 points out of the system to the right.

Now, this is an open system. So, the mass balance equation would be something like accumulation of the mass inside the system boundaries is going to be the mass of coming in minus the mass going out. This is an unsteady state balance. We can have an accumulation term for now, we will see what happens at steady state once we finish this derivation.

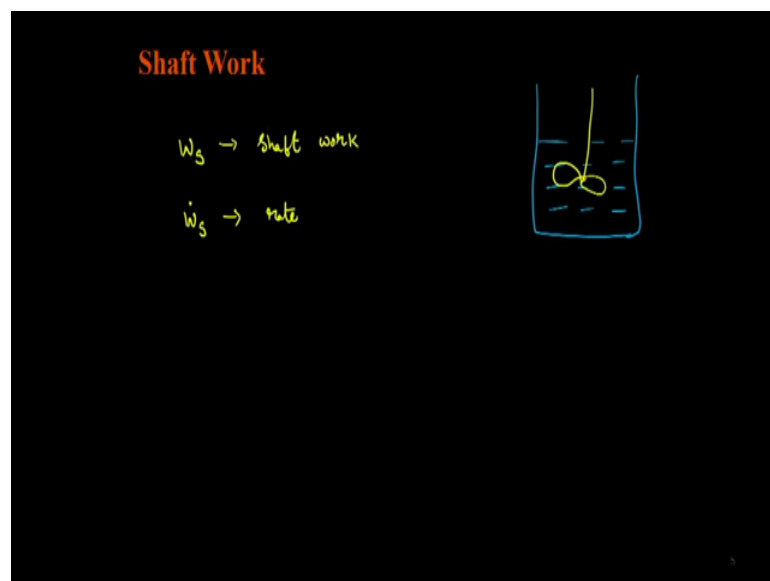
Now, rate of accumulation of mass inside the system boundaries is going to be $d m$ or change in mass of the control volume over dt is going to be equal to the amount going in which is \dot{m}_1 plus \dot{m}_2 minus \dot{m}_3 , right. If there is multiple streams the typical way we write this equation if there are multiple streams is $\frac{d m_{cv}}{dt} + \Delta(\dot{m}_{fs}) = 0$. Notice that this delta notation here indicates out all the streams going out minus all the streams coming in. So, that way they sign in versus and then we have the equation we were looking at which reads $\frac{d m_{cv}}{dt} + \Delta(\dot{m}_{fs}) = 0$. This is the mass balance on the open system.

Of course, at steady state the accumulation term is 0 because steady state implies there is no accumulation within the system boundaries, that implies $\Delta(\dot{m}_{fs})$ is going to be equal to 0. Therefore, the mass balance at steady state conditions or in other words if we are talking about these 3 streams then $\dot{m}_1 + \dot{m}_2$ is going to be equal to \dot{m}_3 at the steady state condition.

I can also write this equation, sometimes it is convenient to write this equation in terms of the velocities and the densities, notice that $m_1 \dot{}$ or any for any stream $m_i \dot{}$ can be written as the density that is in kilograms per meter cube something like that multiplied with the area of cross section for that stream, multiplied with the velocity. So, that would be the volumetric flow rate multiplied with the density will give us the mass flow rate. So, at steady state then this equation would look something like $\rho_1 u_1$ times the area of cross section for stream 1 plus $\rho_2 u_2$ times area of cross section for stream 2 will be equal to $\rho_3 u_3$ times the area of cross section for stream 3. So, instead of the mass flow rates we can write things in terms of densities and velocities as well. So, this is a typical mass balance in a open system.

Now, let us talk about the energy balance. But before we talk about the energy balance a few things are in order we need to define various types of work that can be associated with an open system. The first one is a shaft work.

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For example, in the case where I had a fluid that is mixed well with a stirrer work is done on the fluid which is my system of interest through this tower, and we call this type of work as shaft work. Similarly, in case of a turbine the fluid does work on the turbine or in case of a centrifugal pump it pushes the fluid through the pipes in all these cases there is a shaft work that is being done on the system or delivered shaft work being delivered by the system as in case of a turbine. The essential feature of this shaft work is that there

would be no change in the control volume of our system. So, to differentiate it from other forms of work typically we will denote the shaft work with a subscript s. So, W_s indicates the shaft work or the rate of change or the rate of shaft work is going to be denoted by \dot{W}_s .

The other type of work that is important is what we call as the flow work for an open system. It is a work associated with the flow as the name indicates. For example, when a gas is released from a tank into the atmosphere which is at a lower pressure it is by opening a valve it is going to push the fluid outside so that it can come out. Or in the other case if I have a high-pressure reservoir and I am trying to fill it tank by opening a valve then the fluid in the reservoir is going to push the fluid inside the tank which is the system of my interest so that it can end the tank. In both cases there is a work that is being done by pushing the fluid. In one case the system is doing work on the surrounding fluid, in the other case there is an external work that is being done on the fluid inside the tank, right. This type of work is what we call as flow work, right.

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Flow Work

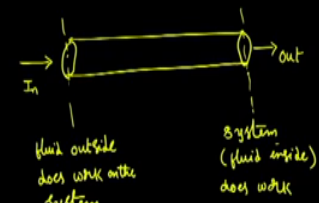
$$\dot{W}_{flow} = F \cdot \dot{z} = PA \dot{z} = P \dot{V}^t$$

$$= PV \dot{m}$$

$$\dot{V}^t = \dot{m} v$$

↓ specific volume ($\frac{m^3}{kg}$)

$$\dot{W}_{flow} = \dot{W}_{flow}|_{in} - \dot{W}_{flow}|_{outlet}$$

$$= \sum \dot{m}_{in} (PV)_{in} - \sum \dot{m}_{out} (PV)_{out}$$


For example, if we have a control volume which is indicated by this tube here if this is my control volume and this is the inlet to my control volume and this is the outlet to the control volume. At the inlet the fluid outside does work on the system and at the outlet the system or the fluid inside is going to do work on the surroundings. Now, I can easily quantify this work, the rate of the flow over \dot{W}_{flow} will call it as \dot{W}_{flow} instead of \dot{W}_s

as we did in case of shaft work to differentiate the two is going to be the rate of flow volts; so, this is going to be force multiplied with the distance per time. So, that is going to be the velocity x dot.

Force is pressure times area, so it will be pressure area times x dot and I can write it as pressure times the volumetric flow rate the total volumetric flow rate V dot t. If I want to write it in terms of molar quantities or specific quantities then it becomes PV m dot, right. This V total dot is going to be m dot times V this is the specific volume. So, it is typically in terms of something like meter cubed per kilogram multiplied the d. Mass flow rate m dot so that will be in meter cube per second which is same as units of V dot t.

So, then the flow work W dot, then there is one stream entering the control volume in another stream taking it out of the control volume is going to be difference between the work done at the inlet minus the work done at the outlet. So, in this case W flow is going to be, W flow at all the inlet streams minus W flow at all the outlet streams. So, I can write it as m dot at the inlet times the PV term at the inlet minus m dot at the outlet times PV term at the outlet. If there are multiple streams then it will be summation over all such streams that would give me the net flow work that is done on the system through all the inlet streams and all the outlet streams.

So, as opposed to that of a closed system in a open system we will have an additional term to account for this flow work.

(Refer Slide Time: 12:57)

Energy Balance on Open System

$$\text{Rate of accumulation} = \frac{d}{dt} (m U_{cv})$$

$$\text{Rate of Energy in} = \dot{m}_1 U_1 + \dot{m}_2 U_2$$

$$\text{Rate of Energy out} = \dot{m}_3 U_3$$

$$\dot{W}_{flow} = \dot{m}_1 (PV)_1 + \dot{m}_2 (PV)_2 - \dot{m}_3 (PV)_3$$

$$\frac{d}{dt} (m U_{cv}) = \dot{m}_1 U_1 + \dot{m}_2 U_2 - \dot{m}_3 U_3 + \dot{Q} + \dot{W}_s + \dot{W}_{flow}$$

$$= \dot{m}_1 [U_1 + (PV)_1] + \dot{m}_2 [U_2 + (PV)_2] - \dot{m}_3 [U_3 + (PV)_3] + \dot{Q} + \dot{W}_s$$

$$\frac{d}{dt} (m U_{cv}) = \dot{m}_1 H_1 + \dot{m}_2 H_2 - \dot{m}_3 H_3 + \dot{Q} + \dot{W}_s$$

Now, with these ideas in mind let us try to develop an equation for energy balance on an open system. So, I have an open system which can exchange mass as well as energy with the surroundings. So, for sake of clarity let us use two streams that will bring mass into the system with flow rates \dot{m}_1 and \dot{m}_2 , and one stream that will take mass away from the system let us call that as \dot{m}_3 . And I have Q which is the heat added to the system \dot{Q} is the rate of heat added to the system, and W_s is the rate of shaft work that is delivered to the system.

So, to differentiate between shaft work and flow work we will just use the shaft work term in there when we do the energy balance, we will of course go through the flow work. So, this is my open system which has two inlet streams one outlet stream \dot{Q} and W_s being the heat and work shaft work done on the system. For this system if I want to write an unsteady state energy balance the first term, I will identify is the rate of energy that is accumulated inside the system. So, let me call that as rate of accumulation of energy in the system is going to be $\frac{d}{dt}$ the change with time of m times U for the control volume. The internal energy for the control volume multiplied that is the more specific internal energy for the control volume multiplied with the mass of the control volume that will be m the total energy of the control volume $\frac{d}{dt}$ of that would be the rate of energy that is getting accumulated inside my control volume.

Now, as far as the energy that is entering the system is concerned that would be \dot{m}_1 the mass flow rate multiplied with the specific internal energy U_1 plus \dot{m}_2 times U_2 . This would be the energy entering the system, the energy leaving the system would of course, be \dot{m}_3 times U_3 . All of these are molar quantities U_1, U_2, U_3 and you multiplied with the mass flow rate, so we get the rate of energy in and rate of energy going out of the system.

Next thing we were going to identify is the flow work as we talked about in case of open systems. The total flow work or the rate of total flow work done on the system in this scenario is going to be \dot{m}_1 multiplied with the PV term at for stream 1 plus \dot{m}_2 multiplied with the PV term for stream 2 minus \dot{m}_3 multiplied with the PV term for stream 3. This is the flow work. If I write a unsteady state balance for this scenario it would be accumulation which is $\frac{d}{dt}$ of $m U_c v$; accumulation is going to be the rate of energy entering through the streams that would be $\dot{m}_1 U_1$ plus $\dot{m}_2 U_2$ minus the rate of energy leaving which is $\dot{m}_3 U_3$ plus all the heat and the work that

are added to the system. So, that would be \dot{Q} plus the shaft work \dot{W}_s plus the flow work that is added to the system \dot{W}_f .

Now, I can substitute the quantities for the flow work in this equation so that this equation simplifies to $\dot{m}_1 U_1 + P_1 V_1 + \dot{m}_2 U_2 + P_2 V_2 - \dot{m}_3 U_3 + P_3 V_3$, right plus \dot{Q} plus \dot{W}_s . Now, notice that $U + PV$ is what we called as enthalpy. So, this will be $\dot{m}_1 H_1 + \dot{m}_2 H_2 - \dot{m}_3 H_3$, all of these are the more specific enthalpies in Joules per kilogram for the 3 streams plus \dot{Q} plus \dot{W}_s this will be the rate of energy accumulating in the system. This is my unsteady state balance.

(Refer Slide Time: 18:09)

Energy Balance on Open System

$$\frac{d(mU_{cv})}{dt} = \sum_{in} \dot{m}_i H_{in} - \sum_{out} \dot{m}_i H_{out} + \dot{Q} + \dot{W}_s$$

P.E. for stream "i" = $\dot{m}_i g Z_i$
 K.E. for stream "i" = $\frac{1}{2} \dot{m}_i u_i^2$

$$\frac{d(mU_{cv})}{dt} = \left\{ \sum_{in} \dot{m}_i \left(H_{in} + \frac{u_{in}^2}{2} + gZ_{in} \right) - \sum_{out} \dot{m}_i \left(H_{out} + \frac{u_{out}^2}{2} + gZ_{out} \right) \right\} + \dot{Q} + \dot{W}_s$$

At S.S. $\frac{d(mU_{cv})}{dt} = 0$ $\dot{m}_{in} = \dot{m}_{out}$ (one inlet & one outlet)

Now, in addition to this there can also be a change in the macroscopic quantities, right. So, the rate of energy accumulating in the system we said is d by dt of $m U_{cv}$ is going to be equal to sigma over all the inlet streams $\dot{m}_i H_{in}$ minus sigma over all the outlet streams $\dot{m}_i H_{out}$ plus \dot{Q} plus \dot{W}_s .

Now, in addition to this there can also be a change in the potential and kinetic energies of the streams entering and leaving the macroscopic potential and kinetic energies, right. So, for example, the potential energy for stream "i" is going to be $\dot{m}_i g Z_i$ and similarly the kinetic energy for stream "i" is going to be half $\dot{m}_i u_i^2$.

If all the streams entering and leaving out at the same location then of course, there will not be any change in potential energy if all the streams entering and leaving are doing so, at the same velocity is again there would be no change in the total kinetic energy macroscopic kinetic energy, but otherwise these quantities will be nonzero. So, if we want to add these quantities also to the energy balance system equation then we do so, by adding them to the enthalpy term the inlet and the outlet streams. And the energy balance equation in such a scenario would look something like this, $\frac{d}{dt} \left(m \left[\sum_i H_i + \frac{u_i^2}{2} + Z_i \right] \right)$ at the inlet minus \sum at the outlet $m \left[\sum_i H_i + \frac{u_i^2}{2} + Z_i \right]$ plus \dot{Q} plus \dot{W}_s . This is the total energy balance equation which also accounts for the changes in the kinetic and potential energy of the inlet and the outlet streams.

Now, at steady state, consider there is only one inlet stream and one outlet stream at steady state the left-hand side will be of course 0, right. And if there is only one inlet and one outlet streams then m_{in} will be same as m_{out} , right, only for one inlet and one outlet streams then m_{in} and m_{out} are going to be same and this equation will reduce to something like this.

(Refer Slide Time: 21:45)

Energy Balance on Open System

S.S. with one inlet & one outlet streams, $\Delta KE=0$ $\Delta PE=0$

$$\dot{m} \Delta H = \dot{Q} + \dot{W}_s$$

↓

$H_{out} - H_{in}$

It will be $\dot{m} \Delta H$ is going to be equal to $\dot{Q} + \dot{W}_s$. This ΔH again stands for H of the outlet stream minus H for the inlet. This is the energy balance on an open system at steady state condition with one inlet and one outlet

streams, otherwise depending and of course we have neglected the kinetic and potential energy changes in this scenario. So, ΔK is 0, ΔP is 0 this is a simplified version of the total equation we have written in the previous case

(Refer Slide Time: 22:37)

Example

- 10 mol/s of air is compressed from 1 bar to 10 bar. The inlet temperature and 300 K and the temperature at the outlet of compressor is 450 K. The velocity at the inlet and outlet of the compressor are 6 and 0.9 ms^{-1} . The compressor delivers power at 75 kW. Assume that the enthalpy does not depend on pressure and $C_p = 3.5 R$, find the rate of heat transfer.

$$\begin{aligned}
 & \left. \begin{aligned} P_1 &= 1 \text{ bar} & T_1 &= 300 \text{ K} & u_1 &= 6 \text{ ms}^{-1} \\ P_2 &= 10 \text{ bar} & T_2 &= 450 \text{ K} & u_2 &= 0.9 \text{ ms}^{-1} \end{aligned} \right\} \\
 & \dot{w} = 75 \text{ kW} \\
 & \dot{Q} + \dot{w} + \dot{m}_{in} \left(h_1 + \frac{1}{2} u_1^2 \right) - \dot{m}_{out} \left(h_2 + \frac{1}{2} u_2^2 \right) = 0 \\
 & \dot{Q} + \dot{w} + \dot{m} \left(h_1 - h_2 + \frac{1}{2} u_1^2 - \frac{1}{2} u_2^2 \right) = 0 \\
 & \dot{Q} = \dot{m} \left(h_2 - h_1 + \frac{1}{2} u_2^2 - \frac{1}{2} u_1^2 \right) - \dot{w} \\
 & \dot{m} = 10 \frac{\text{mol}}{\text{s}} + 29 \frac{\text{J}}{\text{mol}} + \frac{1 \text{ kg}}{1020 \text{ g}} = 0.27 \text{ kg/s}
 \end{aligned}$$

Let us see if we can apply this concept to solve a simple problem. Let us say I have a compressor where air is compressed from 10, from 1 bar to 10 bar and 10 moles per second is the rate at which this air is compressed. Due to the compression the temperature of the air increases from 300 to 450 kelvin. The velocities at the inlet and the outlet are given, and the power that is delivered by the compressor to the fluid which is aid in this case is also given. We want to find the rate of heat transferred in this particular process.

Let us try to summarize the given data in terms of mathematical variables which we are familiar with. So, I have a compressor coming in, going out $P_1 T_1$, $P_2 T_2$ the velocity is U_1 , velocity is here U_2 , right. And other variables whatever we need have the same subscripts 1 and 2 at the inlet and outlet of the compressor. What is given to us is P_1 is 1 bar, T_1 is 300 Kelvin, u_1 is 6 meters per second, P_2 is 10 bar, T_2 is 450 Kelvin and u_2 is 0.9 miter per seconds. What is also given to us is the shaft work that is done in this scenario is 75 kilowatts, and we are required to find the rate of heat transfer or let us just call it as Q dot. Let us write it here that is what we were interested in. So, what is given to us is the values P_1 , T_2 and U_1 at the inlet and the outlet of the compressor, right.

What is also given to us is the work done \dot{W} is 75 kilowatts its work done on the fluid or on our system here, so it is positive. The energy balance equation we have written earlier would look something like this, $\dot{Q} + \dot{W} + \dot{m} (H_1 - \frac{1}{2} u_1^2) - \dot{m} (H_2 + \frac{1}{2} u_2^2) = 0$. Now, for us H_1 and H_2 we can replace them with H_1 and H_2 in this case, right and because it is a steady state process the inlet and outlet mass flow rates are also going to be same. So, this equation would reduce to $\dot{Q} + \dot{W} + \dot{m} (H_1 - H_2 + \frac{1}{2} u_1^2 - \frac{1}{2} u_2^2) = 0$. What we are interested in is \dot{Q} , so this will be $\dot{m} (H_2 - H_1 + \frac{1}{2} u_2^2 - \frac{1}{2} u_1^2) - \dot{W}$.

So, now if we can find all the quantities on the right-hand side of this equation, we would have our result. The first thing to find out is the mass flow rate of the air, it is 10 moles per second multiplied with its molecular weight, let us say the multiple rate of 8 is 29 grams per mole. So, this would be and then 1000 or rather 1 kilogram per 1000 grams. So, that would make it 0.29 kg per second that is the mass flow rate of the air.

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Handwritten calculations on a blackboard:

$$H_2 - H_1 = \Delta H = C_p \Delta T = 3.5 \times 8.314 \times (450 - 300) = 4.365 \text{ kJ/mol}$$

Specific enthalpies

$$H_2 - H_1 = 4.365 \frac{\text{kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{29 \text{ gm}} \times \frac{1000 \text{ gm}}{1 \text{ kg}} = 150.5 \text{ kJ/kg}$$

$$\frac{1}{2} (u_2^2 - u_1^2) = \frac{1}{2} (0.9^2 - 6^2) = -17.595 \text{ m}^2/\text{s}^2$$

$$\dot{Q} = 0.29 \left[150.5 - 17.595 \right] - 75 = -36.45 \frac{\text{kJ}}{\text{s}}$$

Let us look at the other terms. The next thing I have is $H_2 - H_1$. So, H_2 and H_1 are the specific enthalpies, because we are multiplying them with \dot{m} which is the mass flow rate, so H_2 and H_1 are the specific enthalpies. Let us, to get this number let us first calculate the change in the molar enthalpy which is let us call it as ΔH it

would be $C_p \Delta T$. So, this is going to be 3.5 times r which is 8.314 times ΔT is 450 minus 300. So, this will be 4.365 kilo Joules per moles, right.

Now, we want to convert these kilojoules per mole into the specific enthalpies let us say kilojoules per kg. So, we use the molecular weight to achieve this, right. So, it would be $H_2 - H_1$, then would be 4.365 kilojoules per mole times the molecular weight of the fluid or rather divided by the molecular weight of the fluid. So, 1 mole per 29 grams multiplied with 1000 grams for 1 kilogram. So, if we do this math this turns out to be a 150.5 kilo Joules per kg, this is $H_2 - H_1$ in terms of kilo Joules per kg. Notice that we are converting the molar value in $C_p \Delta T$ to the specific value so that we can multiply it with the mass flow rate. So, I have $\dot{m} (H_2 - H_1)$.

The next thing to calculate is the change in the kinetic energies which is half of $U_2^2 - U_1^2$ that would be half of $0.9^2 - 6^2$ which will be negative 17.595 meter square per second square. So, now if I write the energy balance equation it would be $\dot{Q} = \dot{m} (H_2 - H_1) + \dot{m} (U_2^2 - U_1^2) - \dot{W}$ which is 0.29 kilograms per second multiplied with $H_2 - H_1$ which is 150.5 minus 17.595 minus \dot{W} which is 75 kilowatts. And if we simplify this, we get negative 36.45 kilo Joules per second. So, for this particular process it turns out that the heat exchange with the surroundings is negative 36.45 kilojoules per second, it is negative which means the heat is transferred from the system to the surroundings.

So, what we have done in this case is we have used the expression for the first law of an open system, we have deleted the terms that are not applicable such as the potential energy term and use the remainder of the terms to solve our problem and get the heat exchanged with the surroundings.

So, this is how we apply first law in a open system. So, that completes our discussion of the first law of thermodynamics, we looked at an example or a couple of examples for a closed system, we looked at one example for an open system today. When we come back in the next lecture, we will try to apply first law, to a few other processes and see how we can extend these ideas and concepts into solving other types of thermodynamic problems.

Thank you.