

**Material and Energy Balances**  
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**Lecture - 69**  
**Unsteady State Energy Balances**

Hello everybody. Welcome back to the last topic and last lecture for the NPTEL course on material and energy balances. So in the last lecture we talked about unsteady state material balances. Today we will talk about unsteady state energy balances.

**(Refer Slide Time: 00:34)**

## Unsteady State Energy Balances

- General energy balance equation is given as

$$\text{Accumulation} = \text{Input} - \text{Output}$$

- Consider an infinitesimally small interval of time  $\Delta t$  between time points  $t$  and  $t + \Delta t$

- Accumulation =  $\Delta E_{sys} = \Delta U_{sys} + \Delta E_{k,sys} + \Delta E_{p,sys}$

- Input =  $\dot{m}_{in} \left( \hat{H}_{in} + \frac{u_{in}^2}{2} + gz_{in} \right) \Delta t + \dot{Q} \Delta t$

- Output =  $\dot{m}_{out} \left( \hat{H}_{out} + \frac{u_{out}^2}{2} + gz_{out} \right) \Delta t + \dot{W}_s \Delta t$

So let us go back to the general balance equation for energy balances. So the general balance equation would be given as input – output = accumulation. As energy can neither be created nor be destroyed you do not have the generation and consumption terms.

And if you were to consider an infinitesimally small time interval of time delta t between the time points of t and t + delta t you would have the term accumulation as delta E sys which is the total energy of the system or change in total energy of the system or during this period of time which would be the accumulation term. So the total energy of any system as we had already learnt has 3 components.

You have the kinetic energy, potential energy and the internal energy. So it has been represented here as  $\Delta U_{\text{sys}} + \Delta E_{k, \text{sys}} + \Delta E_{p, \text{sys}}$ . So the next term you have is the input term. So the input streams can have energy. So the input stream energy multiplied by the rate of input of energy times  $\Delta t$  will give you the total energy input. So that would be given as  $\dot{m}_{\text{in}}$  which is the mass flow rate of the inlet stream times  $H_{\text{cap in}} + u_{\text{in}}^2/2 + gz_{\text{in}}$ .

So this would be the enthalpy change, the kinetic energy and the potential energy of the inlet stream and multiplying that with the mass gives you the total energy of the inlet stream times  $\Delta t$  gives you the total energy which is entering into the system during the time period  $\Delta t$  through the streams which are flowing in. you could also have heat that can be supplied to the system. We have considered heat supplied as positive so we will have this as  $+Q \dot{\Delta t}$ .

So your output streams again can have the overall energy of the output streams which would be  $\dot{m}_{\text{out}}$  times  $H_{\text{cap out}} + u_{\text{out}}^2/2 + gz_{\text{out}}$  times  $\Delta t$ . so we have considered work done by the sys to be positive. So we will take  $W_s \dot{\Delta t}$  in the output stream. So this gives us all the energies which are processed by the sys that could change over time in terms of accumulation.

All the energies which can come into the system in the form of inlet streams and heat supplied and all the energy which could leave the sys in the form of outlet streams and the work which can be done by the system. So now that we have these equations or these terms we can substitute them into the general energy balance equation we have.

**(Refer Slide Time: 03:24)**

## Unsteady State Energy Balances

- Substituting these terms in the general energy balance equation,

$$\Delta U_{sys} + \Delta E_{k,sys} + \Delta E_{p,sys}$$

$$= \dot{m}_{in} \left( \hat{H}_{in} + \frac{u_{in}^2}{2} + gz_{in} \right) \Delta t + \dot{Q} \Delta t - \dot{m}_{out} \left( \hat{H}_{out} + \frac{u_{out}^2}{2} + gz_{out} \right) \Delta t - \dot{W}_s \Delta t$$

- Dividing the equation by  $\Delta t$  and assuming  $\Delta t \rightarrow 0$ , we get

$$\frac{dU_{sys}}{dt} + \frac{dE_{k,sys}}{dt} + \frac{dE_{p,sys}}{dt}$$

$$= \dot{m}_{in} \left( \hat{H}_{in} + \frac{u_{in}^2}{2} + gz_{in} \right) + \dot{Q} - \dot{m}_{out} \left( \hat{H}_{out} + \frac{u_{out}^2}{2} + gz_{out} \right) - \dot{W}_s$$

And we would end up with this equation which is  $\Delta U_{sys} + \Delta E_{k,sys} + \Delta E_{p,sys} = m \dot{in} \text{ times } \hat{H}_{in} + u_{in}^2/2 + gz_{in} \text{ times } \Delta t + \dot{Q} \Delta t - m \dot{out} \text{ times } \hat{H}_{out} + u_{out}^2/2 + gz_{out} \text{ times } \Delta t - \dot{W}_s \Delta t$ . So this is basically your accumulation = input – output term.

So if you were to divide this equation by  $\Delta t$  and assume  $\Delta t$  tends to 0 and apply the limits then you would have  $dU_{sys}/dt + dE_{k,sys}/dt + dE_{p,sys}/dt = m \dot{in} \text{ times } \hat{H}_{in} + u_{in}^2/2 + gz_{in} + \dot{Q} - m \dot{out} \text{ times } \hat{H}_{out} + u_{out}^2/2 + gz_{out} - \dot{W}_s$ .

**(Refer Slide Time: 04:37)**

## Unsteady State Energy Balances

- If several input and output streams are present,  $\dot{m} \left( \hat{H} + \frac{u^2}{2} + gz \right)$  should be accounted for all streams
- This equation is very complex to solve unless a number of simplifications are made
  - The system has at most one input stream and one output stream, each with the same mass/molar flow rate
  - Kinetic and potential energy changes are negligible
- The equation simplifies to

$$\frac{dU_{sys}}{dt} = \dot{m}(\hat{H}_{in} - \hat{H}_{out}) + \dot{Q} - \dot{W}_s$$

So this equation is actually quite complex and it can get even more complicated if you have more than one input or output streams. You would have to account for the  $\dot{m} \left( \frac{H_{cap}}{2} + \frac{u^2}{2} + gz \right)$  for all the streams. If there are multiple inlet streams, you might have multiple of these terms, the summation of all these have to be accounted for as the inlet energy and similarly for the outlet streams you would have to find the summation of these terms for all the outlet streams.

So because of this, the equation can get extremely complex and cannot be solved unless a number of simplifications are made. So in general, there are many simplifications which are commonly done. We will describe what these are. So first simplification which is done is the system has to have at most one input and one output, each with the same mass or molar flow rate.

So you cannot have multiple inlets and outlets and they cannot be, even if it is only one inlet and one outlet, the mass or molar flow rates have to be the same which means the total mass of the system cannot change with respect to time. Kinetic and potential energy changes have to be negligible. So this is a very reasonable assumption to make. In the earlier lectures, we have actually done this exercise where we have calculated change in enthalpy and change in internal energy, change in kinetic energy and potential energy and compare these values.

Usually they are much smaller for most chemical processes compared to the change in enthalpy. So these terms which are the kinetic and potential energy terms can be ignored. So if you were to do this, the equation then simplifies to form  $dU_{sys} dt = \dot{m} (H_{cap, in} - H_{cap, out}) + \dot{Q} - \dot{W}_s$ . So this equation seems simple and neat.

**(Refer Slide Time: 06:27)**

# Unsteady State Energy Balances

- The previous equation is also difficult to solve
- Further simplifications are usually necessary
  - Temperature and composition of the system contents do not vary with position within the system (i.e. the system is perfectly mixed)
    - Outlet stream ( $T_{out}$ ) and system contents ( $T_{sys}$ ) must be at the same temperature ( $T$ )
  - No phase change or chemical reactions take place
  - $\hat{U}$  and  $\hat{H}$  are independent of pressure
  - Mean heat capacities ( $C_p$  and  $C_v$ ) of the system contents are independent of composition and temperature, hence, unchanged with time

However, even this equation is quite difficult to solve. So further simplifications are actually required. So the further simplifications which are usually done are given here. Temperature and composition of the system contents should not vary with position within the system. That is the system should be perfectly mixed. So if you have a system there should not be any effect on the position or the spatial distribution should not be a factor when we are talking about temperature or composition.

So this means that the outlet stream temperature and the system temperature would be the same. So your  $T_{out}$  would be equal to  $T_{sys}$  and both of them would be equal to  $T$  which is the general temperature for the outlet stream and the system. There cannot be any phase change or chemical reactions taking place. So if those are there, then the equation becomes more and more tedious. And  $H_{cap}$  have to be independent of pressure.

So if there are going to be pressure dependency then the problem would require many other correlations to be brought in which will make it extremely difficult to solve. The mean heat capacities of the system  $C_p$  and  $C_v$  which is the  $C_p$  mixture which we calculated earlier have to be independent of the composition and temperature and hence unchanged with time.

So that is important. So even if there is some change in composition, you have to assume that the  $C_p$  and  $C_v$  for the system is remaining a constant. And only with that kind of a system you will be able to solve this equation.

**(Refer Slide Time: 08:04)**

## Unsteady State Energy Balances

- Using these simplifications,

$$U_{sys} = M\hat{U}_{sys} = M[\hat{U}(T_r) + C_v(T - T_r)]$$

- Assuming  $M$ ,  $\hat{U}(T_r)$ , and  $C_v$  are a constant,

$$\frac{dU_{sys}}{dt} = MC_v \frac{dT}{dt}$$

$$\hat{H}_{in} = C_p(T_{in} - T_r)$$

$$\hat{H}_{out} = C_p(T_{out} - T_r) = C_p(T - T_r)$$

- For an open system, the equation simplifies to

$$MC_v \frac{dT}{dt} = \dot{m}C_p(T_{in} - T) + \dot{Q} - \dot{W}_s$$

- For a closed system, the equation simplifies to

$$MC_v \frac{dT}{dt} = \dot{Q} - \dot{W}$$

So using these simplifications, the equation then becomes  $U_{sys} = M$  times  $U_{cap, sys}$ . So the  $U_{cap, sys}$  basically the system internal energy would be the internal energy at a reference temperature +  $C_v$  times  $T -$  the reference temperature. So this specific internal energy times the total mass of the system will give you the total internal energy of the system. Assuming  $M$ ,  $U_{cap}$ ,  $T_r$  and  $C_v$  are constants, you would end up with  $dU_{sys}/dt = MC_v dT/dt$ .

So your  $H_{cap, in}$  which is the enthalpy of the inlet stream can be given as  $C_p$  times  $T_{in} - T_r$  where  $T_r$  is the reference temperature and your  $H_{cap, out}$  would be given as  $C_p$  times  $T_{out} - T_r$ . So  $T_{out}$  as we already mentioned would be equal to the system temperature which is given as  $T$ . So your  $H_{cap, out}$  would be given as  $C_p$  times  $T - T_r$ . So for an open system if you were to substitute these values back into the equation, the equation simplifies to form  $MC_v dT/dt = \dot{m}C_p(T_{in} - T) + \dot{Q} - \dot{W}_s$ .

For a closed system, the equation simplifies to form  $MC_v dT/dt = \dot{Q} - \dot{W}$ . So these are simple equations to work with. So this is what we can actually solve.

**(Refer Slide Time: 09:38)**

# Unsteady State Energy Balances

- Conditions under which these equations are valid
  - Negligible kinetic and potential energy changes
  - No accumulation of mass in the system
  - $\hat{U}$  and  $\hat{H}$  should be independent of pressure
  - No phase change or chemical reactions
  - Uniform system temperature
- Factors that can change with time
  - $T$ : outlet and system temperature
  - $T_{in}$ : inlet temperature
  - $\dot{Q}$ : heat transfer between the system and surroundings
  - $\dot{W}_s$  (or  $\dot{W}$ ): work done on or by the system
- Factors that need to remain a constant
  - $M$ : total mass of the system
  - $\dot{m}$ : mass flow rate
  - $C_p$  and  $C_v$ : heat capacities

So to summarize, for this equation to be used, these conditions have to be valid. There has to be negligible change in kinetic and potential energy. No accumulation of mass has to happen inside the system. The accumulation can happen only for energy.  $\hat{U}$  cap and  $\hat{H}$  cap should be independent of pressure. No phase change or chemical reactions can happen. There has to be uniform system temperature.

So simplifying this and putting them into terms which can change with respect to time and terms which cannot change with respect to time, we can say that the factors that can change with time are temperature which would be the outlet and the system temperature. Temperature of the inlet stream.  $\dot{Q}$  which is the heat transfer between the system and the surroundings. And  $\dot{W}_s$  dot or  $\dot{W}$  dot which would be the work done on or by the system.

The factors that need to remain a constant would be  $M$ , which is the total mass of the system;  $\dot{m}$  dot which is the mass flow rate of the inlet and the outlet streams;  $C_p$  and  $C_v$  which are the heat capacities. So these factors have to remain a constant for these equations to be valid. So we will consider such simplified systems and try to perform a couple of energy balance problems to fully understand how we can apply unsteady state energy balance calculations.

**(Refer Slide Time: 11:03)**

## Example #1: Batch System

- A well-stirred batch reactor wrapped in an electrical heating mantle is charged with a liquid reaction mixture. The reactants must be heated from an initial temperature of 25°C to 250°C before the reaction can take place at a measurable rate. Use the data given below to determine the time required for this heating to take place.
  - Reactants: Mass = 1.50 kg,  $C_v = 0.900 \text{ cal}/(\text{g}\cdot^\circ\text{C})$
  - Reactor: Mass = 3.00 kg,  $C_v = 0.120 \text{ cal}/(\text{g}\cdot^\circ\text{C})$
  - Heating rate:  $\dot{Q} = 500.0 \text{ W}$

Assume negligible reaction and no phase change during the heating. Also, the stirrer adds negligible energy to the system.

So here is the first example. A well stirred batch reactor wrapped in an electrical heating mantle is charged with a liquid reaction mixture. The reactants must be heated from an initial temperature of 25 degree Celsius to 250 degree Celsius before the reaction can take place at a measurable rate. Use the data given below to determine the time required for this heating to take place. Reactants are given as mass of the reactants is 1.5 kg,  $C_v$  for the reactants is also given.

Mass of the reactor and the  $C_v$  for the reactor is also given. The rate of heating  $\dot{Q}$  is given as 500 W. you have been asked to assume negligible reaction and no phase change during the heating. Also, the stirrer adds negligible energy to the system. So making these assumptions, we would be able to use the equations that we derived.

So whatever we had as conditions are met in this problem. So we can use the equations to try and solve this problem. So as you can see it is a batch reactor which means it is a closed system.

**(Refer Slide Time: 12:11)**



## Example #1

$$M C_v \frac{dT}{dt} = \dot{Q} - \dot{W}$$

$$M C_v \frac{dT}{dt} = \dot{Q}$$

$$(C_v)_{avg} = \frac{1500 \times 0.9 + 3000 \times 0.12}{4500}$$

$$(C_v)_{avg} = \frac{1710}{4500} = 0.38 \text{ cal/g}^\circ\text{C}$$

$$(C_v)_{avg} = 1.58992 \text{ J/g}^\circ\text{C}$$

For a closed system we derived an equation as  $M C_v \frac{dT}{dt} = \dot{Q} - \dot{W}$ . So here we have been told that the stirrer does not provide any work so which means  $\dot{W}$  goes to 0. So the equation simplifies to  $M C_v \frac{dT}{dt} = \dot{Q}$ . So we need to use  $C_v$ . So we have been given the  $C_v$  values for the reactor and the reactants. So we have to account for both these components when we are talking about increase in temperature.

So we will have to calculate  $C_v$  for the mixture or average  $C_v$ . So average  $C_v$  can be calculated as the mass fraction for the component times the  $C_v$  for that particular component and get a summation of that. So that would mean it is  $1500/4500$  times  $0.9 + 3000/4500$  times  $0.12$ . So this would give the average  $C_v$  as  $1710/4500$  which  $= 0.38 \text{ cal/g degree C}$ . So this can be converted to joules per gram degree Celsius as  $1.58992 \text{ J/g degree C}$ .

Now we have the  $C_v$  for the system. The  $C_v$  average for the system. So we also have  $\dot{Q}$  dot which has been given as  $500 \text{ W}$ . We have the total mass of the system which is  $4500 \text{ g}$  or  $4.5 \text{ kg}$  because we have  $3 \text{ kg}$  of reactor and  $1.5 \text{ kg}$  of the mixture in the reactor, so giving us  $4.5 \text{ kg}$ . So we have  $C_v$ ,  $M$ , and  $\dot{Q}$  dot. So we need to now find the time taken to increase the temperature from  $25 \text{ degree Celsius}$  to  $250 \text{ degree Celsius}$ . So this can easily be done by performing a simple integration.

**(Refer Slide Time: 14:18)**

## Example #1

$$\int_{25}^{250} M C_v dT = \dot{Q} \int dt$$
$$(4500 \times 1.58992) \int_{25}^{250} dT = 500 t$$
$$t = 3219.6 \text{ s} \quad \boxed{53.66 \text{ min}}$$

So you would have integral 25 to 250  $M C_v dT = \dot{Q} \int dt$ . So now we have the values for  $M$  and  $C_v$  which are constants, not dependent on temperature or time so which would mean 4500 times 1.58992 times integral  $dT$  from 25 to actually it is 250 sorry, 250 would be equal to  $\dot{Q}$  dot which is 500 times  $t$ . So your  $t$  would then be = 3219.6 s or 53.66 min.

So you can heat the system from 25 degree Celsius to 250 degree Celsius within about 54 minutes if you were to provide heat of 500 W. So with this we have solved one example problem which was for a closed system or a batch system. So in the next example problem, we will look at an open system.

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## Example #2: Continuous System

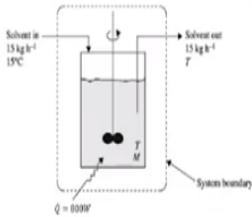
- An electric heating coil is immersed in a stirred tank. Solvent at 15°C with heat capacity 2.1 kJ/(kg.°C) is fed into the tank at a rate of 15 kg/h. Heated solvent is discharged at the same flow rate. The tank is filled initially with 125 kg of cold solvent at 10°C. The rate of heating by the electric coil is 800 W. Calculate the time required for the temperature of the solvent to reach 60°C.

Here is an example for a continuous system. So this problem statement says that an electrical heating coil is immersed in a stirred tank. Solvent at 15 degree Celsius with heat capacity of 2.1 kilo J/kg degree C is fed into the tank at a rate of 15 kg/h. Heated solvent is discharged at the same flow rate. The tank is filled initially with 125 kg of cold solvent at 10 degree Celsius. The rate of heating by the electric coil is 800 W.

Calculate the time required for the temperature of the solvent to reach 60 degree Celsius. So the problem is very similar to what we did in the previous problem except that here it is a continuous system so we need to use the equation we derived for the continuous system instead of using the equation we had for the close system. So let us jump right into the problem, try to solve this problem.

(Refer Slide Time: 16:34)

## Example #2



$$M C_v \frac{dT}{dt} = \dot{m} C_p (T_{in} - T) + \dot{Q}$$

$$\dot{Q} = 800 \text{ W} = 800 \times \frac{3600}{1000} \text{ kJ/h}$$

$$\dot{Q} = 2.88 \times 10^3 \text{ kJ/h}$$

$$125 \times 2.1 \times \frac{dT}{dt} = 15 \times 2.1 (15 - T) + 2.88 \times 10^3$$

$$262.5 \frac{dT}{dt} = 31.5 (15 - T) + 2.88 \times 10^3$$

So the equation we had for the open system was  $M C_v \frac{dT}{dt} = \dot{m} C_p T_{in} - T + \dot{Q}$ . So here  $\dot{Q}$  is given as 800 W and this needs to be converted to kilo joules per kilogram because that is the units for the  $C_p$  and  $C_v$  terms. So we would convert this to kilo joules per hour as 800 times 3600/1000. This would be kJ/h. So this value of  $\dot{Q}$  is then 2.88 times 10 power 3 kJ/h. So now the next step is to substitute the values for  $M$ ,  $\dot{m}$ ,  $C_p$  and  $C_v$ .

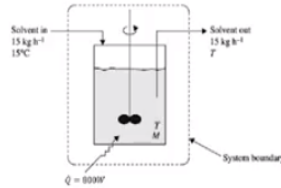
So we have only been given the value for  $C_p$ . So what would be the value for  $C_v$  that we can use? So because it is a liquid system we can assume  $C_p$  is approximately equal to  $C_v$  and use

the same value for both. So substituting the values for the total mass  $C_v$ ,  $C_p$  and mass flow rates and  $\dot{Q}$ , we will be able to get this equation to be 125 times 2.1.

So we are using the same value as  $C_p$  for  $C_v$  as well because it is a liquid system times  $dT/dt = \dot{m}$  which is mass flow rate which is  $15 \text{ kg/h}$  times  $C_p$  which is  $2.1$  times inlet temperature which is  $15 \text{ degree Celsius} - T$  which is the temperature at time  $t$  and this  $+ \dot{Q}$  which is  $2.88$  times  $10^3$ . So this equation can then be simplified as  $262.5 dT/dt = 31.5 \times 15 - T + 2.88 \times 10^3$ .

(Refer Slide Time: 18:48)

## Example #2



$$\frac{dT}{dt} = 1.8 - 0.12T + 10.97$$

$$dT = 12.77 - 0.12T$$

$$\int_{10}^{60} \frac{dT}{12.77 - 0.12T} = \int_0^t dt$$

$$\frac{-1}{0.12} \left[ \ln(12.77 - 0.12T) \right]_{10}^{60} = t$$

$$t = \frac{-1}{0.12} \ln \left( \frac{12.77 - 0.12 \times 60}{12.77 - 0.12 \times 10} \right)$$

$$t = 6.09 \text{ h}$$

So from here you can get  $dT/dt = 1.8 - 0.12T + 10.97$  giving you  $12.77 - 0.12T$ . So  $dT/dt = 12.17 - 0.12T$ . So now, we need to find the time taken for heating the, increasing the temperature from  $10 \text{ degree Celsius}$  which is the system temperature, initial temperature is  $10 \text{ degree Celsius}$  all the way to  $60 \text{ degree Celsius}$ . So for that you would have to integrate this system as  $dT/12.77 - 0.12T$  from  $10 \text{ degree Celsius}$  to  $60 \text{ degree Celsius}$  be equal to integral  $0$  to time taken  $t$  dt.

So this would be  $-1/0.12$  times  $\ln$  of  $12.77 - 0.12 T$  and applying the limits from  $10$  to  $60 \text{ degree Celsius}$  this would be equal to  $t$ . So from here you can solve this equation. So  $t$  would become  $-1/0.12$  times  $\ln$  of  $12.77 - 0.12 \times 60 / 12.77 - 0.12 \times 10$  and solving this equation we would get  $t = 6.09 \text{ h}$ . so it would take  $6.09 \text{ h}$  to heat the given system from  $10 \text{ degree Celsius}$  to  $60 \text{ degree Celsius}$ .

So with this we have been able to perform two very simple problems where we did unsteady state energy balances. So with this we actually come to the end of our course. I hope you enjoyed this course. I hope it was informative and you were able to learn systematic practices and procedures for performing material and energy balances. Thank you.