Basic Principles and Calculations in Chemical Engineering
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Lecture - 28
Unsteady State Energy Balance

Welcome to massive open online course on Basic Principles and Calculations in Chemical Engineering. So in module 9, we were discussing about balances on unsteady state processes. And in the previous lecture we have described about the unsteady state process for material balance.

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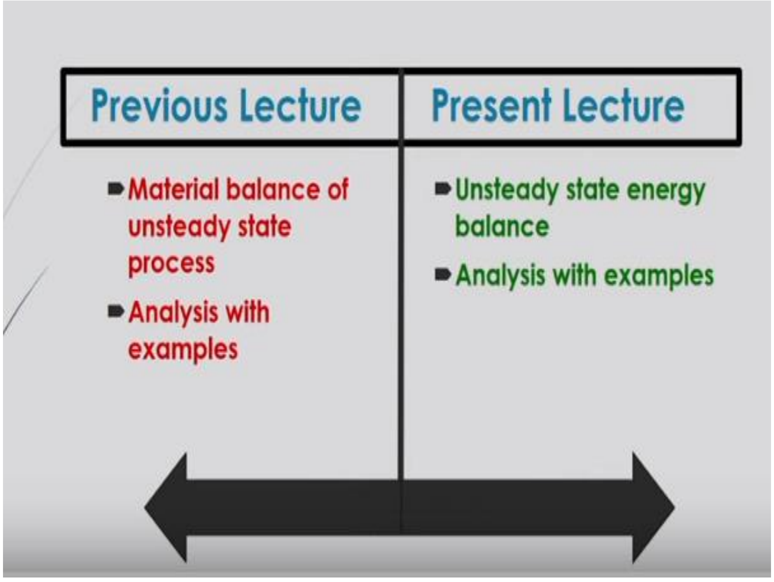

Previous Lecture

- Material balance of unsteady state process
- Analysis with examples

Present Lecture

- Unsteady state energy balance
- Analysis with examples

And also we have discussed those unsteady state material balance with examples. In this lecture we will try to extend those lecture, but it will be with the unsteady state energy balance and we will try to solve some problems where this unsteady state energy balance are involving. Now what are those you know unsteady state processes that already we have described in our previous lecture.

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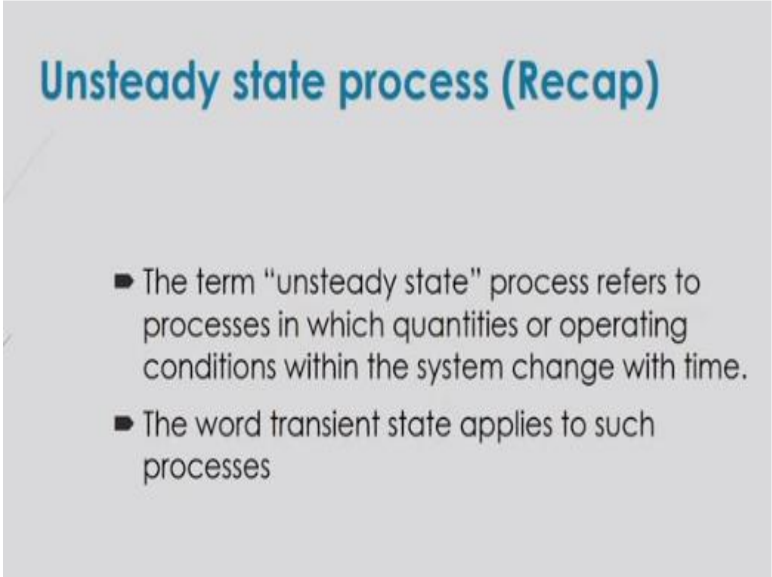

Unsteady state process (Recap)

- The term "unsteady state" process refers to processes in which quantities or operating conditions within the system change with time.
- The word transient state applies to such processes

We know that the term unsteady state process that refers to processes in which quantities or opening conditions or operating conditions within the system that change with the time and in that case, another one important terms like transient state, which also applies to such processes. This transient state is basically unsteady state process.

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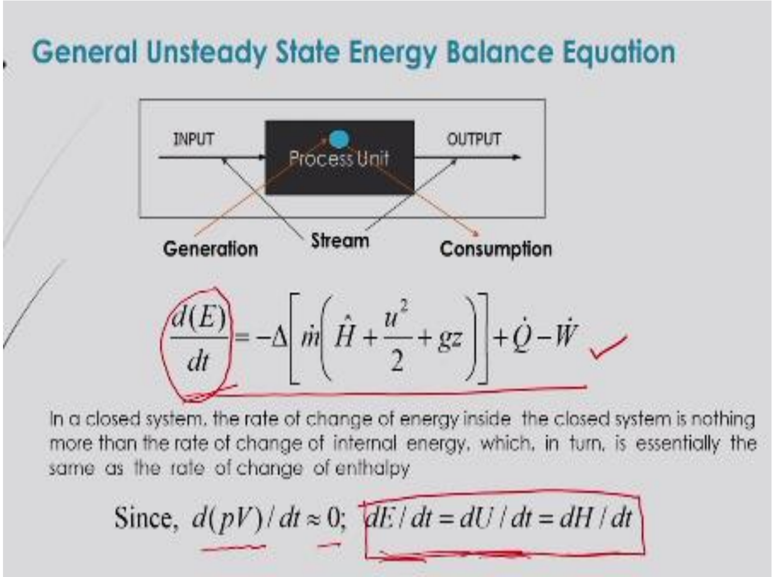

General Unsteady State Energy Balance Equation

$$\frac{d(E)}{dt} = -\Delta\left[\dot{m}\left(\hat{H}+\frac{u^2}{2}+gz\right)\right]+\dot{Q}-\dot{W}$$

In a closed system, the rate of change of energy inside the closed system is nothing more than the rate of change of internal energy, which, in turn, is essentially the same as the rate of change of enthalpy

Since, $d(pV)/dt \approx 0$; $\boxed{dE/dt = dU/dt = dH/dt}$

And general unsteady state energy balance equation how we can write. We know that general energy balance equation where there is no accumulation terms, we have already described in our earlier lecture. So if we consider that accumulation terms in you know general you know energy balance equation, then you can you know write this final form of you know unsteady state energy balance equation.

Where you will see that this dE by dt is basically the energy you know that accumulated or energy loss with respect to time or change of energy with respect to time that we can have. So this energy change with respect to time we can calculate form the enthalpy change of that you know process as well as if there is a flow in open system then what should be the kinetic energy change.

And also if there is the elevation you know of the you know process you need and the flow is with the elevation then we can say that there will be some potential energy change from the you know batch potential energy. So based on which there will be a summation of that you know potential energy change, enthalpy change and kinetic energy change.

And also you will see that this energy change of course will be coming based on that, you know what will be the heat energy supplied to the system and also work done by the system there. And based on that, if there is suppose overall change of that energy with respect to time, based on this change of this enthalpy, kinetic energy, potential energy and even heat supplied to the system, work done by the system.

And based on which we can say that the change of that you know energy with respect to time, which will be regarded as that you know unsteady state energy balance. So that unsteady state energy balance equation, we can write by this format. Now in a closed system, the rate of change of energy inside the closed system is nothing more than the rate of change of internal energy.

So in closed system we know that there will be no you know flow work, there will be no potential energy, there will be no kinetic energy change and also since there will be no you know flow work then we can say that there will be only energy change with respect to time will be based on that internal energy change.

So which in turn is essentially the same as the rate of change of enthalpy here. Since we can say that this flow work rate that is d p V by dt equals to zero. And hence we can say that dE by dt that will be is equal to dU by dt upon that you know kinetic energy and potential energy is negligible.

So finally, we can say that this you know energy change will be based on that internal energy change and if there is no flow work, then simply we can say that the enthalpy change based on that no flow work down on the system.

So that is why we can write here this you know rate of energy change that will be is equal to rate of internal energy change and that will be is equal to rate of enthalpy change if there is a condition of no flow work.

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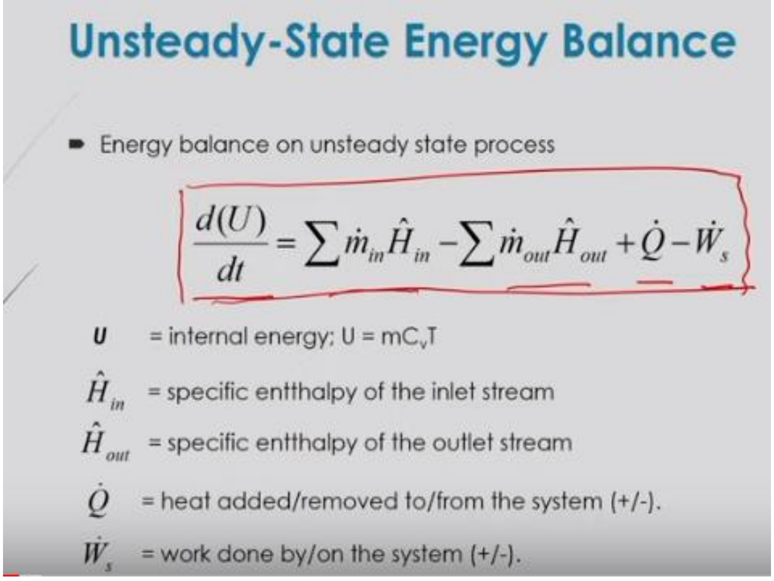

Unsteady-State Energy Balance

- Energy balance on unsteady state process

$$\boxed{\frac{d(U)}{dt} = \sum \dot{m}_{in}\hat{H}_{in} - \sum \dot{m}_{out}\hat{H}_{out} + \dot{Q} - \dot{W}_s}$$

U = internal energy; $U = mC_vT$

$\hat{H}_{in}$ = specific entthalpy of the inlet stream

$\hat{H}_{out}$ = specific entthalpy of the outlet stream

$\dot{Q}$ = heat added/removed to/from the system (+/-).

$\dot{W}_s$ = work done by/on the system (+/-).

Now if we write that energy balance on unsteady state processes, we can simply write based on that this internal energy change with respect to time that will be is equal to dU by dt. Then what should be the enthalpy at the inlet condition and what will be the enthalpy at the outlet condition or outlet streams.

And what will be the heat energy supply to the system and also what will be the shaft work done by the system. So from those components, we can write this internal energy change based on these enthalpy change in the inlet and outlet streams and also energy supplied and work done by the system at a rate.

So here from this equation, we can calculate what should be the internal energy change. If you know that what will be the energy you know change, enthalpy change at the inlet and outlet streams provided that heat energy supplied to the system and shaft work done by the system.

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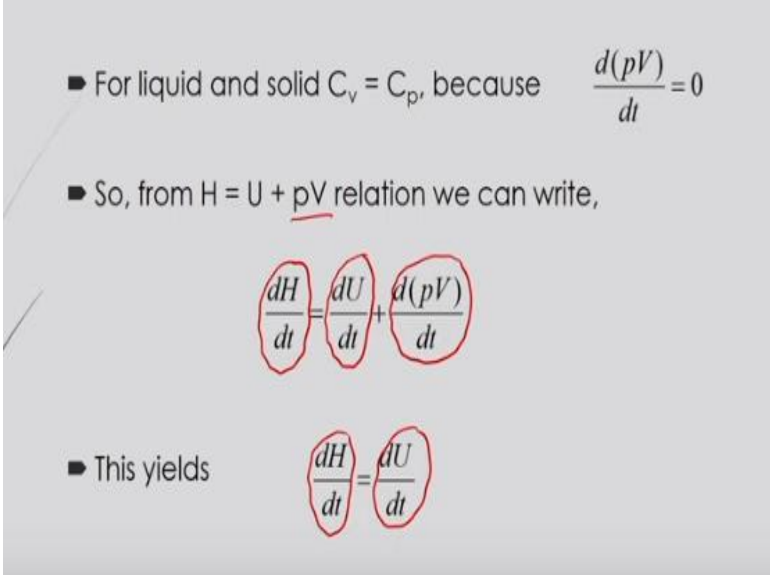

- For liquid and solid $C_v = C_p$, because $\frac{d(pV)}{dt} = 0$
- So, from $H = U + \underline{pV}$ relation we can write,

$$\frac{dH}{dt} = \frac{dU}{dt} + \frac{d(pV)}{dt}$$

- This yields $\frac{dH}{dt} = \frac{dU}{dt}$

And for liquid and solid we know that this specific heat capacity at constant volume and at constant pressure will be equals to 0, sorry will be same to each other. That means C v will be equals to C p. Because in that case, the flow work that is d p V by dt that will be equals to 0.

Therefore, from the relation of enthalpy that is equal to internal energy plus the product of pressure and volume. We can write then dH by dt that will be is equal to dU by dt plus here d p V by dt. So here the rate of change of enthalpy that will be is equal to rate of change of internal energy in addition to the change of flow work with respect to time which yields this dH by dt will be is equal to dU by dt.

That means here enthalpy change will be is equal to internal energy change with respect to time if there is no flow work. That means here d p V by dt will be equals to 0 if it is there.

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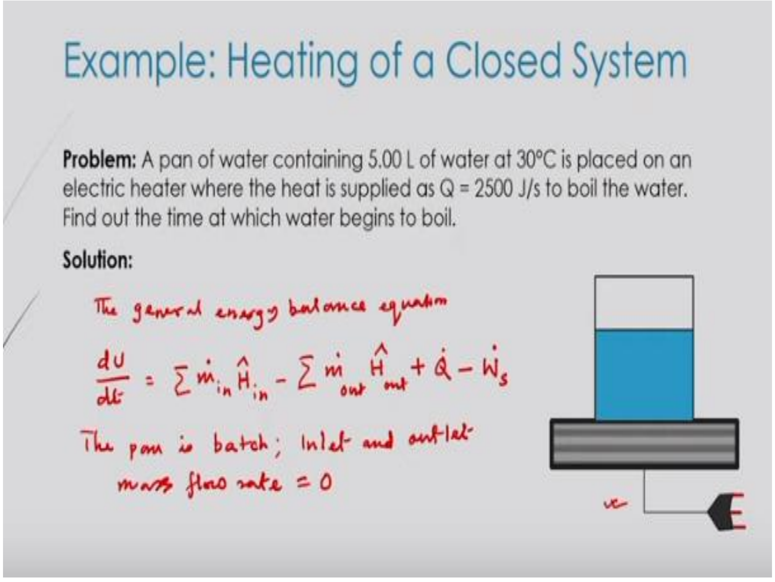

Example: Heating of a Closed System

Problem: A pan of water containing 5.00 L of water at 30°C is placed on an electric heater where the heat is supplied as Q = 2500 J/s to boil the water. Find out the time at which water begins to boil.

Solution:

The general energy balance equation

$$\frac{dU}{dt} = \sum \dot{m}_{in} \hat{H}_{in} - \sum \dot{m}_{out} \hat{H}_{out} + \dot{Q} - \dot{W}_s$$

The pan is batch; Inlet and outlet mass flow rate = 0

Now let us do an example for a closed system where heating is done. Suppose a pan of water containing 5 liter of water at 30 degrees Celsius, which is placed on an electric heater as shown here in the slide where the heat is supplied by this heater to the system as Q which is about 2500 joule per second. Now it is this heat is supplied to boil the water.

Now you have to find out what is the time required at which the water begins to boil. So you can solve this problem based on that unsteady state energy balance equation. In this case you are going to boil this water at 100 degrees Celsius. So the normal boiling point of water you have to know to boil this.

If instead of water other liquids are there, you have to consider there what should be the boiling point of that liquid. Now the general energy balance equation is we know that write that general energy balance equation here. The general energy balance equation can be written as for this unsteady state operation, dU by dt that will be is equal to summation of m dot in into H enthalpy here.

That is specific enthalpy at the inlet, since we are using at minus summation of m dot out specific enthalpy at the outlet condition plus heat supplied to the system here in this pan at a rate Q dot minus work done by the system here as a shaft work W s dot. Now the pan is batch system. In this case inlet and outlet, outlet mass flow rate will be equals to 0.

There is no flow at the inlet and outlet condition. So in that case, we do not need any shaft work to, shaft work by this system to be considered.

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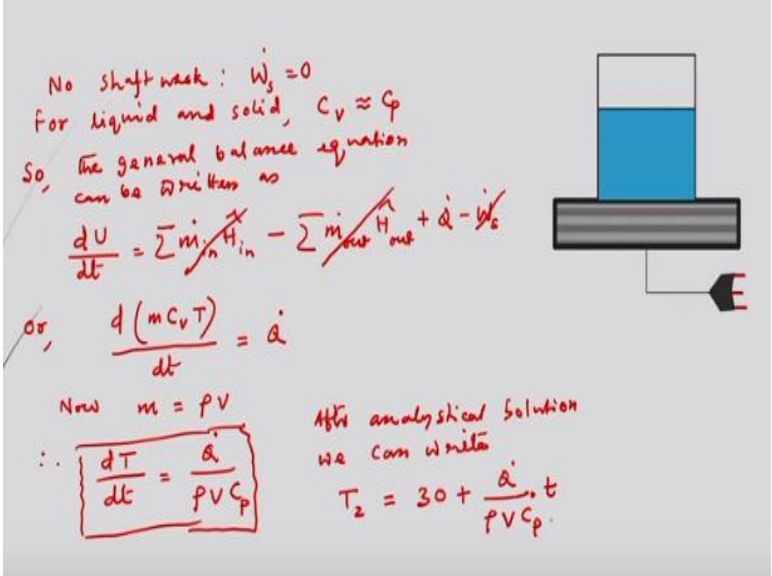

No shaft work : $\dot{W}_s = 0$

For liquid and solid, $C_v \approx C_p$

So, the general balance equation can be written as

$$\frac{dU}{dt} = \cancel{\sum \dot{m}_{in} \hat{H}_{in}} - \cancel{\sum \dot{m}_{out} \hat{H}_{out}} + \dot{Q} - \cancel{\dot{W}_s}$$

or,

$$\frac{d(mC_vT)}{dt} = \dot{Q}$$

Now $m = \rho V$

$$\therefore \boxed{\frac{dT}{dt} = \frac{\dot{Q}}{\rho V C_p}}$$

After analytical solution we can write

$$T_2 = 30 + \frac{\dot{Q}}{\rho V C_p} \cdot t$$

So we can write no shaft work. Therefore, W s dot that will be is equals to zero and also we know that for liquid and solid this C v that will be is equal to C p. So the general balance equation can be written as dU by dt.

That will be is equal to summation of m dot in enthalpy, specific enthalpy at inlet condition minus summation of m dot out into specific enthalpy at the outlet condition plus q dot minus w is dot. So we can delete this w s and also we can delete this inlet enthalpy and outlet enthalpy. Since there is no flow at the inlet and outlet since it is a batch process.

So from this we can write d into m C v into T. This is basically internal energy. This is m C v into T divided by dt. That will be is equal to here simply Q dot. Now we can write m that is basically rho into v. So we can write from this energy balance equation as dT by dt. That will be is equal to Q dot by rho v into C p. C v and C v both are same.

So we can write C p instead of C v here. Then we can get this final equation as per this energy balance equation. Now if we do the analytical solution of this equation, we can get, after analytical solution we can write T 2 that will be equals to 30 plus Q dot by rho v, v is the volume of that system, here C p into t, t is the time.

So from this we can calculate what should be the temperature at this boiling point here for a certain time t. Since we know that temperature is 100 degrees Celsius, since we have to boil this water at 100 degrees Celsius, so here T 2 will be is equal to 100 degrees Celsius. Whereas, this initial temperature is 30 degrees Celsius.

So in that case you can find out this time t after substitution of the T 2 at 100 degrees Celsius and Q dot it is also given to you what will be the heat energy supplied to the system by this heater. It is given as 2500 joule per second and specific heat capacity is also given to you.

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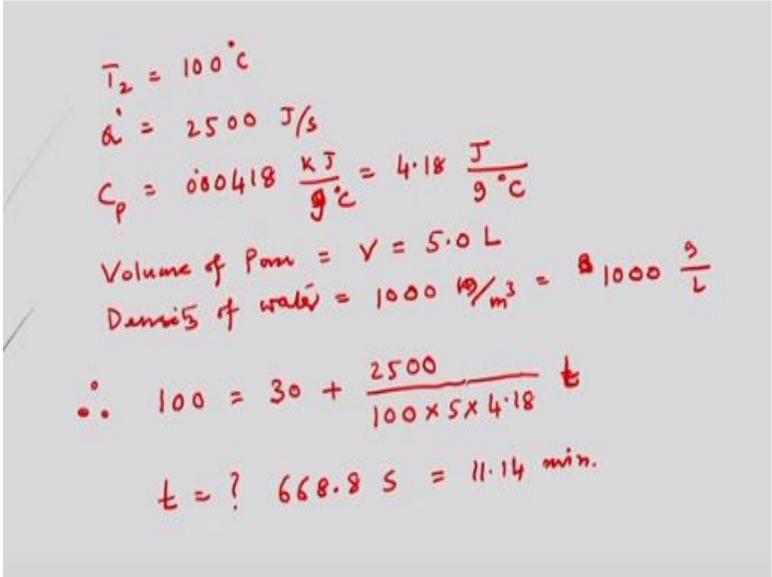

$T_2 = 100\,^\circ C$

$\dot{Q} = 2500\ J/s$

$C_p = 0.00418\ \frac{kJ}{g\,^\circ C} = 4.18\ \frac{J}{g\,^\circ C}$

Volume of Pan $= V = 5.0\ L$

Density of water $= 1000\ kg/m^3 = 1000\ \frac{g}{L}$

$\therefore\ 100 = 30 + \frac{2500}{100 \times 5 \times 4.18}\, t$

$t = ?\ 668.8\ s = 11.14\ min.$

So if we substitute T 2 is equal to 100 degrees Celsius and Q dot that is 2500 joule per second and C p specific heat capacity of water is here, this is 0.0418 0 here, this is you know that zero point, I think it is 0.00418 kilojoule per second. This is simply we can write 4.18 joule per, here this is joule per gram degree Celsius here, joule per gram degree Celsius.

So this is your C p value and volume of pan that will be is equal to V. This is simply given 5.0 liter and density of the water is equal to let it be 1000. This is gram per, this is 1000 kg per meter cube. That means here we can say simply 1000 gram per liter, because kg 1000 gram and then what is that, meter cube means 1000 liter.

1000s, 1000s will be cancelled out. So ultimately it will be 1000 gram per liter. Therefore, we can substitute this value in the previous that energy balance equation as shown here in the slide. And then we have 100 will be is equal to then 30 plus here 2500 divided by 100 into 5 into 4.18 here. So it will be coming as, this is into t.

So from this t will be is equal to what; t will be is equal to ultimately 668.8, this is in second. So it will be coming as 11.14 minute. At 11.14 minute you know that your water will be starting to boil.

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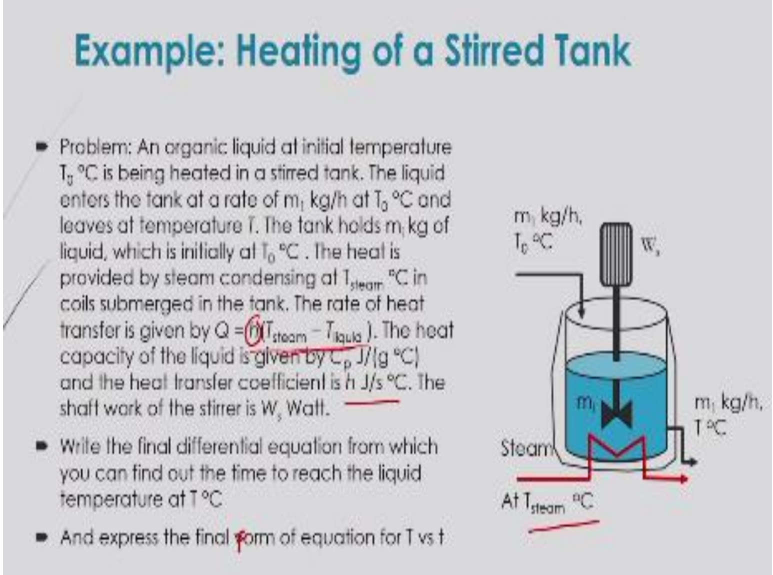

Example: Heating of a Stirred Tank

- Problem: An organic liquid at initial temperature T_0 °C is being heated in a stirred tank. The liquid enters the tank at a rate of m_i kg/h at T_0 °C and leaves at temperature T. The tank holds m_l kg of liquid, which is initially at T_0 °C . The heat is provided by steam condensing at T_{steam} °C in coils submerged in the tank. The rate of heat transfer is given by $Q = h(T_{steam} - T_{liquid})$. The heat capacity of the liquid is given by C_p J/(g °C) and the heat transfer coefficient is h J/s °C. The shaft work of the stirrer is W_s Watt.
- Write the final differential equation from which you can find out the time to reach the liquid temperature at T °C
- And express the final form of equation for T vs t

Let us do another example here, in this case heating of a stirred tank. You know that in chemical engineering process where in a reaction sometimes you need to you know stir the solution to execute the reaction at a certain temperature and pressure.

And if it is done at a continuous mode, then there will be a certain you know flow rate at which the stream will go into the reactor and at a certain rate the product will be coming out and at a temperature to be maintained for that reaction.

Now let us consider this problem here where are we will do this you know energy balance to find out certain expression of you know this process based on which you can calculate what should be the time required to reach the liquid temperature at a certain temperature or what should be the profile of the equation for the temperature change with respect to time inside the reactor.

Now let us consider an organic liquid which is at initial temperature T 0 degree Celsius is being heated in a stir tank. The liquid enters the tank at a rate of suppose m 1 kg per hour at this temperature of T 0 degrees Celsius. And the stream leaves out at temperature T from this reactor at time T.

The tank holds this m 1 kg of liquid which is initially at T 0 degree Celsius. The heat is provided by steam considering at temperature T steam degree Celsius in coils which is submerged in the tank. The rate of heat transfer is given by Q will be equals to here some expression is given that heat transfer will be actually basically based on that temperature difference of steam and the temperature of that liquid inside the stir tank.

So if there is a temperature difference and that heat transfer basically will be based on that temperature difference and this heat transfer will be proportional to that heat transfer, heat differences or temperature differences. So that proportionality constant of that heat transfer based on that temperature difference will be called as heat transfer coefficient.

That we have already described in our lectures that very beginning of this course, where we were discussing about the rate of you know transfer or transfer equation or rate of processes, where we have described this heat transfer rate, mass transfer rate, even some other you know fluid flow rate systems that we have described.

So accordingly we can say that here the rate of heat transfer is proportional to that temperature difference of this steam and the liquid inside the tank. And since this heat rate is proportional to the temperature difference, the proportionality constant will be regarded as that heat transfer coefficient.

And that heat transfer coefficient is denoted by this h here. That units are joule per second degree Celsius. Now heat capacity of the liquid is given by C p and in this case the shaft work of that stirrer is W s watt is given to you. So at this rate this, you know that bubble will you know stirring that, you know that liquid inside the reactor.

Now in this case you have to write the final differential equation from which you can find out the time to reach the liquid temperature at T degree Celsius and also express the final form of equation for temperature as a function of time.

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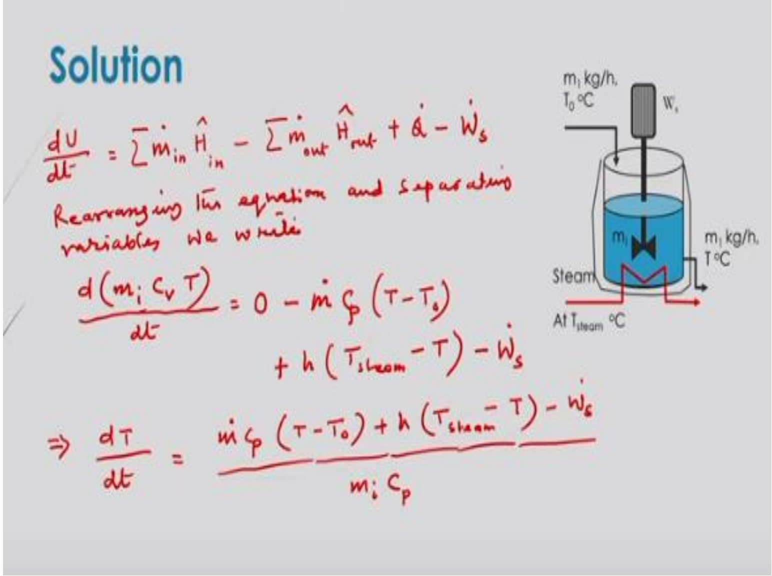

Solution

$$\frac{dU}{dt} = \sum \dot{m}_{in} \hat{H}_{in} - \sum \dot{m}_{out} \hat{H}_{out} + \dot{Q} - \dot{W}_s$$

Rearranging the equation and separating variables we write

$$\frac{d(m_i C_v T)}{dt} = 0 - \dot{m} C_p (T - T_0) + h(T_{steam} - T) - \dot{W}_s$$

$$\Rightarrow \frac{dT}{dt} = \frac{\dot{m} C_p (T - T_0) + h(T_{steam} - T) - \dot{W}_s}{m_i C_p}$$

So let us solve this problem here. Based on that general energy balance equation for unsteady state, we can write dU by dt. That will be is equal to summation of m in dot H hat in enthalpy here, minus summation of m dot that is, mass flow rate at out into H hat again at outlet streams plus Q dot heat transferred to the system minus W s dot that is heat is sorry, shaft work done by the system.

Now rearranging this equation and separate variables, separating variables we can write d of m i, i is for here initial amount of mass, C v into T, this is basically internal energy change with respect to time T dt, That will be is equal to here inlet condition. Inlet flow rate is zero.

Whereas we can write output flow rate as a certain you know rate of that heat you know transfer there. Here it will be simply minus, what is that m out. It is let it be here m dot into C p and temperature difference is T minus basically T 0and then plus heat energy supplied to the system as Q dot.

That will be simply h into T steam minus temperature at time T minus here W dot s which implies the final form of equation like this after separation as dT by dt. That will be is equal to m dot C p into T minus T 0 plus h into T steam minus T minus W s dot. Since it is rate, so we are giving a dot there and divided by m i initial mass into specific heat capacity of the fluid.

Here you can write C v also no problem, because C v and C p will be same for liquid. Now after integration, what we can write?

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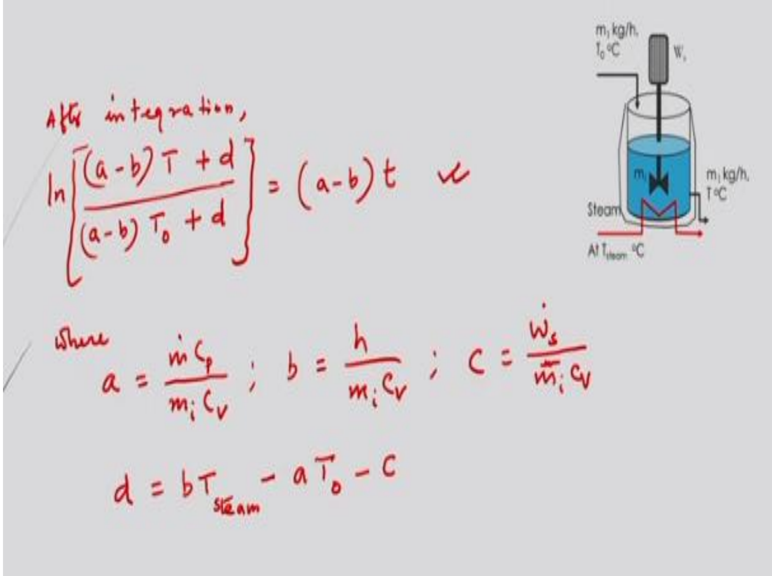

After integration,

$$\ln\left[\frac{(a-b)T + d}{(a-b)T_0 + d}\right] = (a-b)t$$

Where

$$a = \frac{\dot{m} C_p}{m_i C_v} \; ; \; b = \frac{h}{m_i C_v} \; ; \; C = \frac{\dot{W}_s}{\cancel{\dot{m}_i} C_v}$$

$$d = bT_{steam} - aT_0 - C$$

After integration we can write ln here a –b into capital T into d divided by a – b into T 0, T 0 is the initial temperature plus d. That will be is equal to a – b into small t, small t is the time. In this case we have brought here a, b and d. These are coefficients from that equation of that integration. After integration, we have simplified as this.

Where we have defined this a as m dot C p by m i here C v and b is equal to h by m i C v and C is equal to here W s dot by m i dot sorry m i only, mi into C v. Here it will not be dot. So m i into C v. And d is defined as b into T steam minus a into T 0 minus c. So this is your d.

So after substitution of this a, b, c, d here in this equation you can have this final form of equation for the temperature as a function of time. So if you know this m i value initial mass, if you know that C v value, if you know that heat transfer coefficient, if you know that shaft work, if you know that you know that m dot that means here at you know outlet condition at a certain rate, then we can easily find out what should be the temperature for a certain time.

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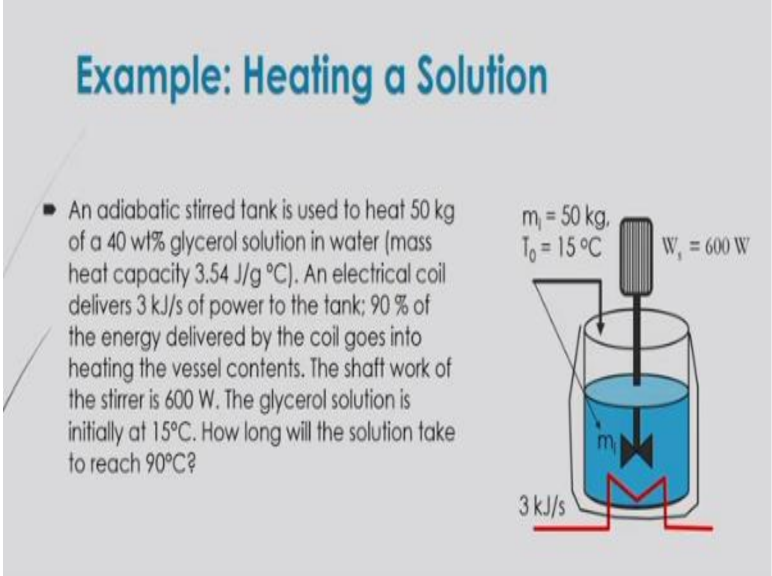

Example: Heating a Solution

- An adiabatic stirred tank is used to heat 50 kg of a 40 wt% glycerol solution in water (mass heat capacity 3.54 J/g °C). An electrical coil delivers 3 kJ/s of power to the tank; 90 % of the energy delivered by the coil goes into heating the vessel contents. The shaft work of the stirrer is 600 W. The glycerol solution is initially at 15°C. How long will the solution take to reach 90°C?

Let us do another example, with this you know unsteady state energy balance equation. There again if we consider that an adiabatic stir tank is used to heat 50 kg or a 48% glycerol solution in water. Here mass capacity, mass heat capacity is given as 3.54 joule per gram degree Celsius and electrical coil which delivers certain amount of power, here it is given 3 kilojoule per second of power to the tank.

And it is seen that 90% of the energy delivered by the coil goes into hitting the vessel contents and remaining 10% will be lost to the atmosphere. Now the shaft work to rotate that you know stirrer is 600 watt. The glycerol solution is initially at 15 degrees Celsius. Now you have to find out how long will the solution take to reach its temperature to 90 degrees Celsius.

So here interesting that m i value is given to you, initial amount 50 kg and temperature also given to you 15 degree Celsius. Shaft work is given to you to heat that solution (()) (33:55) kilojoule per second. This amount of heat is supplied to that system where 90% will be utilized, other 10% will be lost.

Now at this condition you have to find out how long it will take to reach this solution to a temperature of 90 degree Celsius. So again we will do it by general energy balance equation. What is that general energy balance equation?

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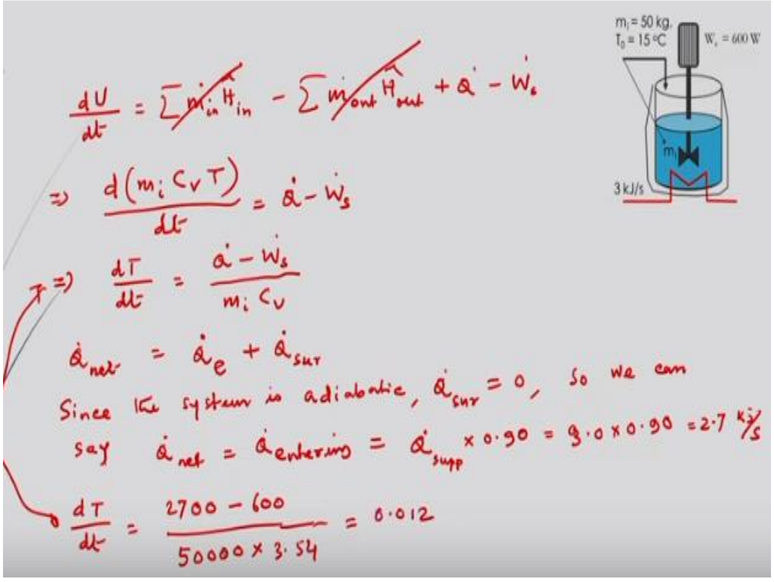

$$\frac{dU}{dt} = \cancel{\sum \dot{m}_{in} \hat{H}_{in}} - \cancel{\sum \dot{m}_{out} \hat{H}_{out}} + \dot{Q} - \dot{W}_s$$

$$\Rightarrow \frac{d(m_i C_v T)}{dt} = \dot{Q} - \dot{W}_s$$

$$\Rightarrow \frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s}{m_i C_v}$$

$$\dot{Q}_{net} = \dot{Q}_e + \dot{Q}_{sur}$$

Since the system is adiabatic, $\dot{Q}_{sur} = 0$, so we can say $\dot{Q}_{net} = \dot{Q}_{entering} = \dot{Q}_{supp} \times 0.90 = 3.0 \times 0.90 = 2.7$ kJ/s

$$\frac{dT}{dt} = \frac{2700 - 600}{50000 \times 3.54} = 0.012$$

We know dU by dt that will be is equal to summation of here m i dot in H i here in we can write in minus summation of m out dot H hat out plus Q dot minus W s dot. In this case again this inlet and outlet streams to be neglected because there is no stream. This is batch wise process so simply we can write this equation as here d (m i C v T) by dt.

That will be is equal to Q dot minus W s dot which implies dT by dt that will be is equal to Q dot minus W s dot divided by m i into C v. In this case Q dot net that means net energy supplied to that solution to heat that solution to 90 degrees Celsius is Q net. It will be basically what is that Q dot e that is you know entered to that solution plus what is the heat energy lost to that surroundings.

Since the system is adiabatic, system is adiabatic, that means no heat energy is lost is you know is going to that surrounding from that. So Q surrounding here dot will be equals to zero. So we can say that Q dot net that will be is equal to Q dot entering to the solution. This is basically 90% of that utilized there which is added to that solution.

So here we can write it will be is equal to that is Q dot which is supplied into 0.90. This is basically zero sorry 3.0 into 0.90. So this is basically 2.7 kilojoule per second. So this amount of net heat to be supplied to the solution to heat up that solution to 90 degrees Celsius.

Now if we substitute this value we can write here dT by dt that will be is equal to Q is 27, since it is kilojoule, so we can convert it to joule here 2700 minus here W s is what? It is given 600. So we are substituting here in this equation. So divided by m i it is given here 50,000 50 liter means 50,000. I think, here it is given 50,000 yes there into what is that?

No this is 50 kg it is given, am I right? This is m i so 50,000 gram and into C p is given, what is the value of C p it is given 3.54 joule per gram per degree Celsius. So finally it will be coming as 0.012.

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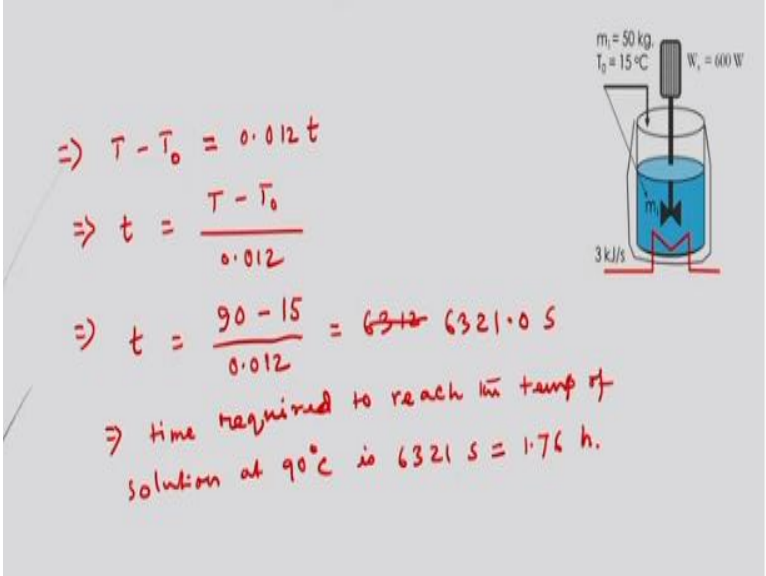


$$\Rightarrow T - T_0 = 0.012\,t$$

$$\Rightarrow t = \frac{T - T_0}{0.012}$$

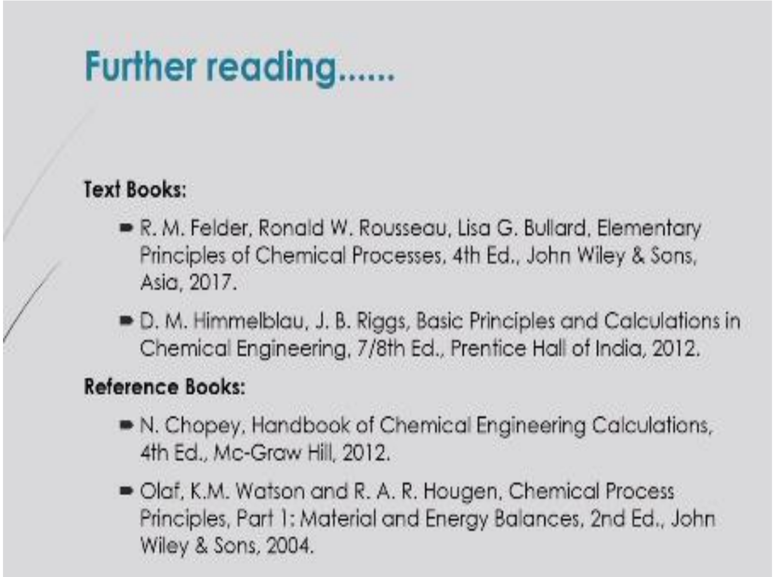
$$\Rightarrow t = \frac{90 - 15}{0.012} = \cancel{6312}\ 6321.0\ s$$

⇒ time required to reach the temp of solution at 90°C is 6321 s = 1.76 h.

So from which we can write T – T 0. It will be is equal to 0.012 small t, this is time from which we can calculate t will be is equal to T – T 0 divided by 0.012. Which implies t will be is equal to this is 90 degree Celsius, your final temperature minus initial temperature is 50 degrees Celsius and then this 0.012. It will be coming as 6312 sorry 621 6321.0 this is second.

So finally, we can say that the time required to reach the temperature of solution at 90 degree Celsius is 6321 second, which is equals to 1.76 hour. So 1.76 hour time will be taking to reach the solution temperature to 90 degree Celsius.

(Refer Slide Time: 41:00)



Further reading……

Text Books:

- R. M. Felder, Ronald W. Rousseau, Lisa G. Bullard, Elementary Principles of Chemical Processes, 4th Ed., John Wiley & Sons, Asia, 2017.
- D. M. Himmelblau, J. B. Riggs, Basic Principles and Calculations in Chemical Engineering, 7/8th Ed., Prentice Hall of India, 2012.

Reference Books:

- N. Chopey, Handbook of Chemical Engineering Calculations, 4th Ed., Mc-Graw Hill, 2012.
- Olaf, K.M. Watson and R. A. R. Hougen, Chemical Process Principles, Part 1: Material and Energy Balances, 2nd Ed., John Wiley & Sons, 2004.

So we have given different, you know examples to understand the unsteady state energy balance equation and how to solve those equations even in general form and also we have given some examples numerically. So I think you understood this, you know the energy balance and how to apply it to the chemical engineering processes.

I would suggest you to go further and solve some problems given in examples in the textbook even in exercise. So it will be you know easier to understand based on this concept and it will be you know more useful for you.

In the next lecture we will try to start another module of that you know computer techniques and based on which we will discuss about the degree of freedom and analysis for that processes and thank you for your attention for this lecture.