Advanced Chemical Reaction Engineering

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Lecture-15
Energy Balance-II

So, you are going be looking at the energy balance today.

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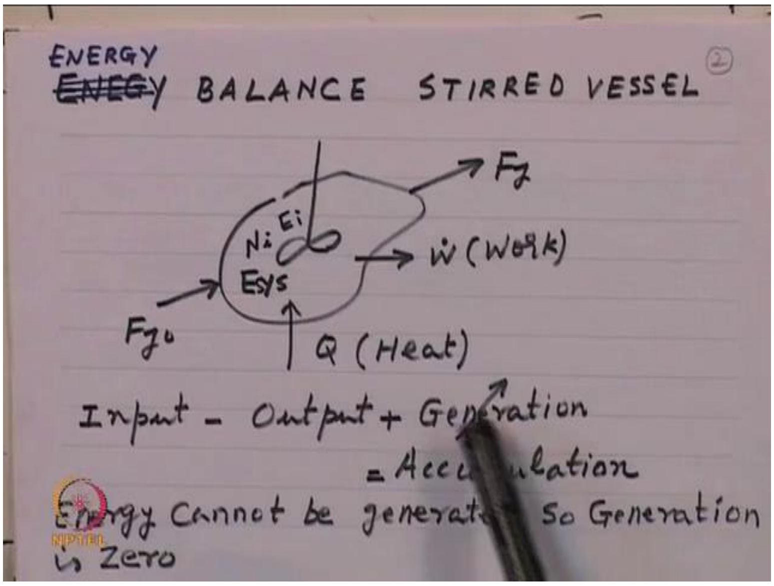

ENERGY
~~ENEGY~~ BALANCE STIRRED VESSEL

Input − Output + Generation = Accumulation

Energy Cannot be generated So Generation is Zero

What we trying do here is look at energy balance for a stirred vessel. Now, stirred vessel in there is stirrer where the composition to the system is uniform at different position. I will say the intensive property of the system is the same everywhere; because of the mixing that we have introduced. Here, F g 0 moles coming in, F g moles going out; you have so much of heat coming in, so much of work coming out. This system itself has N i moles of component i; each of energy E i and the energy of the system we denote as E system. And, the statement of the energy balance is that input minus the output plus generation is accumulation.

What we recognize here is that in energy balance there is no generation of energy or distract of energy. Therefore, generation terms should not appear; unlike, in the material balance where we accept that there is the generation of material; because it can form another product. Therefore, this term is removed; so, the statement the energy balance simply input minus output equal to the accumulation.

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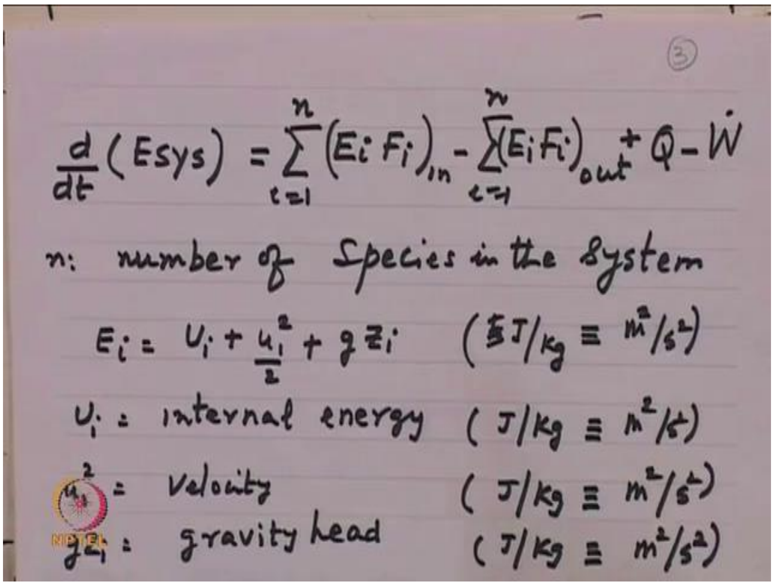

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$$\frac{d}{dt}(E_{sys}) = \sum_{i=1}^{n}(E_i F_i)_{in} - \sum_{i=1}^{n}(E_i F_i)_{out} + Q - \dot{W}$$

n: number of species in the system

$E_i = U_i + \frac{u_i^2}{2} + g z_i$ ($\equiv$ J/kg $\equiv$ m^2/s^2)

U_i : internal energy (J/kg $\equiv$ m^2/s^2)

u_i^2 : velocity (J/kg $\equiv$ m^2/s^2)

$g z_i$: gravity head (J/kg $\equiv$ m^2/s^2)

Stating this in mathematical representation is d by d t (E sys) equal to sigma 1 to n, (E i F i) input. And, then (E i F i) output some do over all species plus Q minus W s; where, Q is heat input, W is work output. This is the energy there is energy coming in with all the species, energy that is going out with all the species. We are neglecting the E mixing that is neglected here; we will include if we required at a later stage. E i is the energy content of each other species; and, this consist of kinetic energy this is the internal energy, kinetic energy, and potential energy. Notice, that the units of this is joules per k g or units or can be also called as meter squared by second squared.

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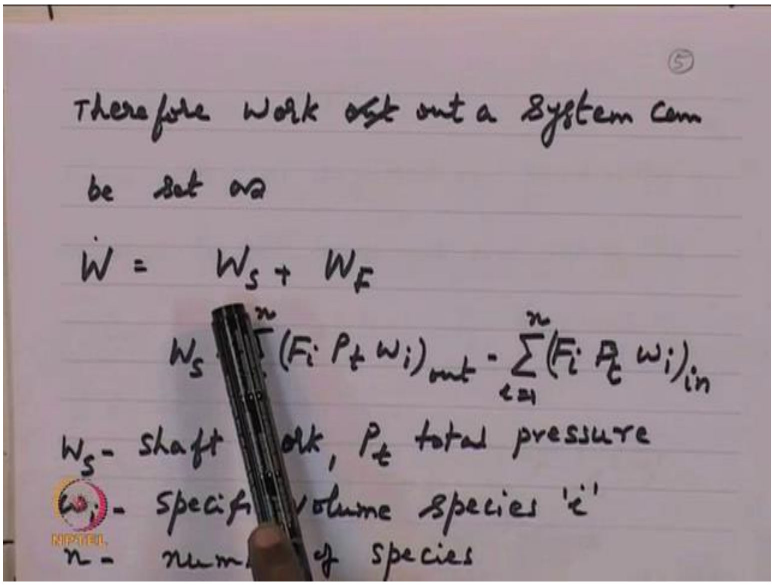

⑤

Therefore work ~~ost~~ out a System can be set as

$\dot{W} = W_s + W_F$

$$W_s = \sum^{n}(F_i P_t w_i)_{out} - \sum_{i=1}^{n}(F_i P_t w_i)_{in}$$

W_s - shaft work, P_t total pressure

w_i - specific volume species 'i'

n - num of species

Now, this term w dot can be understood in some ways by looking at a term called flow work; what is flow work? Flow work is the work that is required to get material in a doubt of a system in the absence of friction; something, that has to be understood by actually making a calculation of the term F i P t omega i. Now, F i P t omega i in the absence of chemical reaction does not change. But P t omega i can change depending upon the condition and which your system is working; high pressure, low pressure whatever. So, in a sense P t, F i P t omega i which has units of joules per second or watts this really depend upon the reacting system.

Therefore, this difference between F i P t omega i out minus the F i P t omega i in this can be positive, it can be negative. If it is negative it means what? This amount of work has been put into the system so that the material can be put in and taken out. So, energy there is required to put material in and out of the system is what is flow work in the absence of friction. So, we can understand of the total amount of work that come out of the system W in terms of shaft to work; which we can measure, shaft work we can measure by measuring the amount of generator output in so on. While, flow work we cannot measure; but we can calculate, because F i P t omega i is a known quantity you can measure. And, therefore these two terms can be; this can be calculated, this can be measured. And, therefore you can calculate w dot.

So, keeping this in mind what we are saying is that if you look at an example; we, make a calculation of how much is the flow work required to put materials in and out through the sulfur dioxide plant. For example, say 3000 tons per d sulfur dioxide plant; what is the flow work we talking about? So, we can calculate is sigma F i P t omega i out, F i P t omega i in. Because we know what is P t typically 1 atmospheres; omega i we can calculate or we can simply say F i omega i is simply volumetric flow.

So, we know how much is the change in volumetric flow at the inlet to the out let why does it change; because temperature is changed. So, we can actually calculate their whole term and estimate of this is what have got here. The flow work for a plant of this size terms what to you about 125 kilowatt; it is a minus sign indicating that you have to put that amount of work so that the material can be put into out. But we have done calculation in earlier class as to the amount of energy there is required in terms of pressure drop; we have calculated that for 3000 tons per day plant and we found they out this close to about 2.5 mega watts.

So, what we saying here is that even in the absence of friction you would have to spend 125. And, in other words the minimum energy there is required put material in and out is not 0; this is the point where we have to appreciate when you have to deal with all these numbers.

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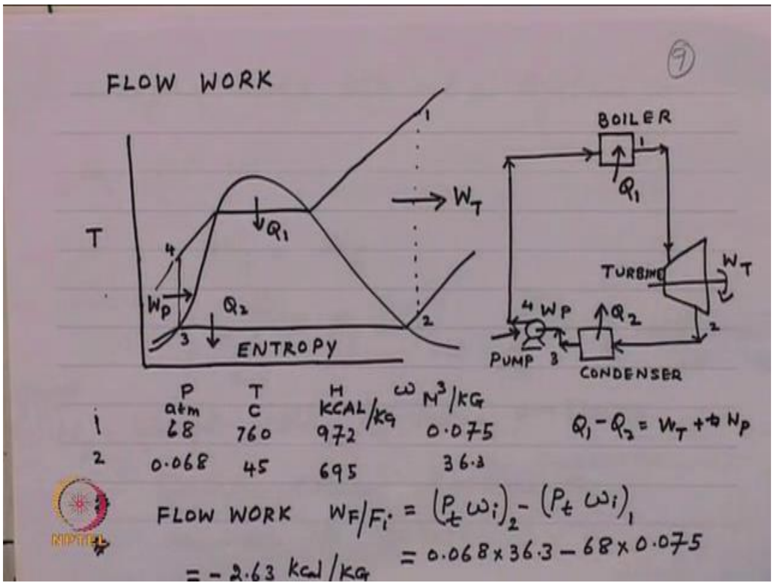

FLOW WORK

	P atm	T C	H KCAL/KG	ω M^3/KG
1	68	760	972	0.075
2	0.068	45	695	36.3

$Q_1 - Q_2 = W_T + W_P$

FLOW WORK $W_F/F_i = (P_t\,\omega_i)_2 - (P_t\,\omega_i)_1$

$= 0.068 \times 36.3 - 68 \times 0.075$

$= -2.63$ kcal/KG

We, can also calculate what is the energy that made and associated with expansion of steam through a turbine going from point 1 to point 2; this is stream turbine cycle producing part, this is the producing part what is it do? We have the boiler which provides energy into stream. And, then we have the condenser the Q 1 minus Q 2 is the amount of work that would come out of the system first law is the energy balance. And, that comes out partly through this, partly it used up here the network is W T plus W P this is what comes out; you Q 1 minus out of Q 2 this we know.

But what is the interest here is to find out what is the flow work from 1 to 2? So, I have got here what is the pressure? What is the temperature? What is the specific volume? So, we can calculate P t omega i 2 minus the P t omega i 1. So, this if we put all the numbers down you will find there is about minus 2.63 kilo calories per k g; showing that there is small amount of work that we have to do, to be able to put material in and out he will for the stream turbine.

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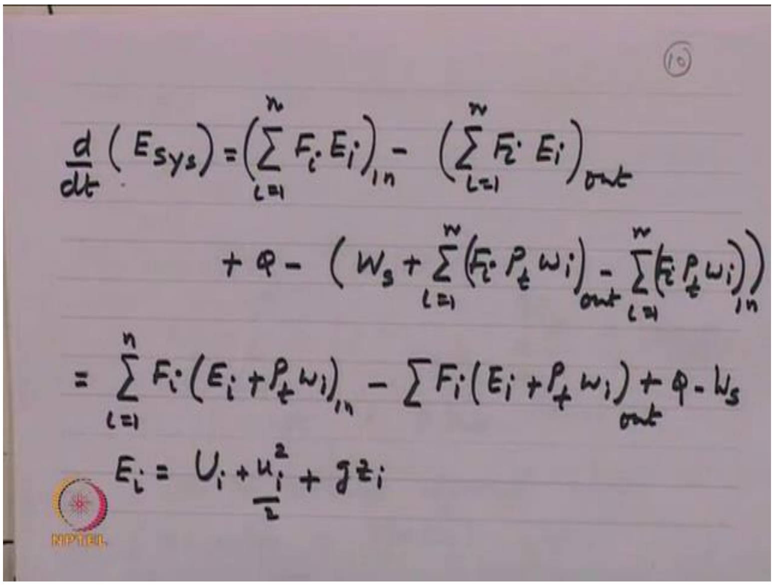

⑩

$$\frac{d}{dt}(E_{sys}) = \left(\sum_{i=1}^{n} F_i \cdot E_i\right)_{in} - \left(\sum_{i=1}^{n} F_i \cdot E_i\right)_{out}$$

$$+ Q - \left(W_s + \sum_{i=1}^{n}(F_i \cdot P_t \omega_i)_{out} - \sum_{i=1}^{n}(F_i P_t \omega_i)_{in}\right)$$

$$= \sum_{i=1}^{n} F_i \cdot (E_i + P_t \omega_i)_{in} - \sum F_i (E_i + P_t \omega_i)_{out} + Q - W_s$$

$$E_i = U_i + \frac{u_i^2}{2} + g z_i$$

So, what we saying that our statement of energy balance which is d by d t of the energy system which is energy in minus the energy out; plus Q is heat input. And, this work as separated the works in terms of shaft work and flow work; this terms F i P t omega i out and F i P t omega in can be appropriate club with the functions in and out. So, when you do that this equation something like this; where, E i plus P t omega i in and then E i P t omega i out multiplies the appropriate terms. So, E i consist of which is called as internal energy, kinetic energy and potential energy.

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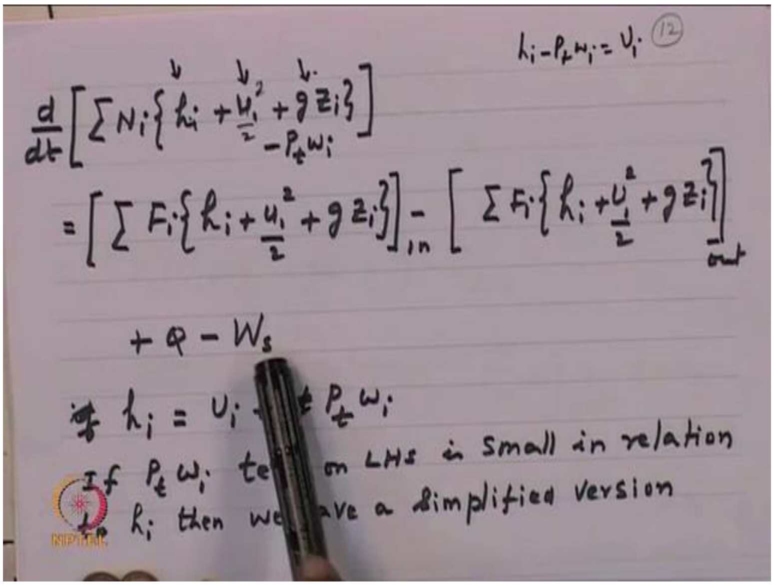

$h_i - P_t \omega_i = U_i$ ⑫

$$\frac{d}{dt}\left[\sum N_i \left\{ \overset{\downarrow}{h_i} + \overset{\downarrow}{\frac{u_i^2}{2}} + \overset{\downarrow}{g} z_i - P_t \omega_i \right\}\right]$$

$$= \left[\sum F_i \left\{ h_i + \frac{u_i^2}{2} + g z_i \right\}\right]_{in} - \left[\sum F_i \left\{ h_i + \frac{u_i^2}{2} + g z_i \right\}\right]_{out}$$

$$+ Q - W_s$$

$h_i = U_i + P_t \omega_i$

If $P_t \omega_i$ te on LHS is small in relation to h_i then we ave a simplified version

So, this E i is substitute here the whole term look something like this that the total amount of energy which is in the system which is E system. For example, consist of N i moles i put N i here multiplied by what is the energy? Energy is U i which is internal energy, kinetic energy, potential energy. You notice that here P t omega i occurs only in the flow term and not in the accumulation term; therefore, the term is not included their. So, this i clubbed U i plus P t omega i can be club, we recognized that P t omega i is P V U plus P V is h; so, it becomes enthalpy plus the kinetic energy and the potential energy.

So, the energy balance term when you club all this terms together it look something like this d by d t of Ni; the number of moles in the system multiplied by h i U i squared g z i minus P t omega i; I put it like that. That means, the put it the term h i even on the left hand side even though h i U i was there i called U i is h i minus the P t omega I; the right hand side term or club U i P t omega is the h i in, h i out. So, leaving these two terms which is kinetic energy and potential energy plus Q minus W s.

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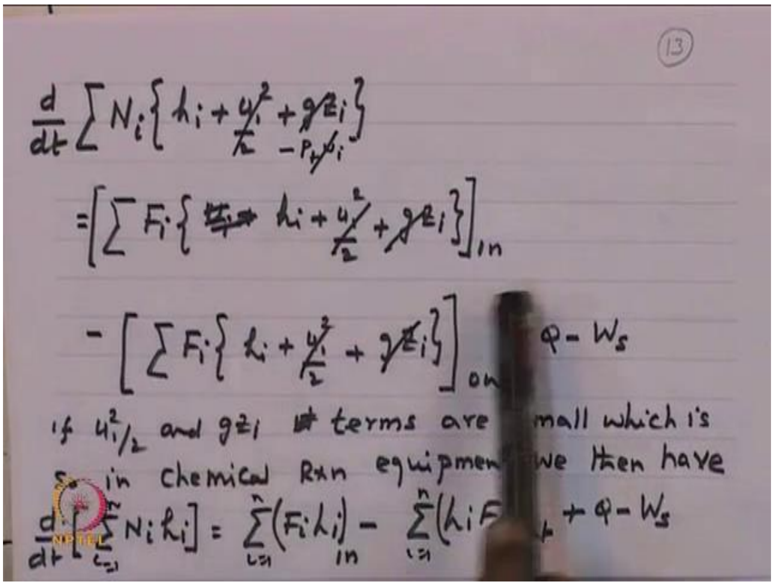

⑬

$$\frac{d}{dt}\sum N_i\left\{h_i + \cancel{\frac{u_i^2}{2}} + \cancel{g z_i} - \cancel{P_t \omega_i}\right\}$$

$$= \left[\sum F_i\left\{h_i + \cancel{\frac{u_i^2}{2}} + \cancel{g z_i}\right\}\right]_{in}$$

$$- \left[\sum F_i\left\{h_i + \cancel{\frac{u_i^2}{2}} + \cancel{g z_i}\right\}\right]_{o} \quad Q - W_s$$

if $u_i^2/2$ and $g z_i$ terms are mall which is in chemical Rxn equipmen we then have

$$\frac{d}{dt}\left[\sum_{i=1}^{n} N_i h_i\right] = \sum_{i=1}^{n}(F_i h_i)_{in} - \sum_{i=1}^{n}(h_i F \quad + Q - W_s$$

So, what seen to happen in reacting systems is that these terms are not very important; generally, these terms are not very important on other words by a large we are dealing with the enthalpy of the materials which we are dealing with. So, a simplify it form with the energy balance can be can be looked up like this. You have d by d t of N i h i and then you F i h i in, F i h i out plus Q minus W s. So, these something we could have written even without having go through all this; something that we know for the long time. But the point have writing this is to draw your attention and into important features when we write d by d t of N i h i; we are actually neglecting the effect of P t omega i, we are neglecting the effect of U i squared and g z i.

So, this is important to recognize; because there could be instances while these not negligible. So, you must recognize that these assumptions are involved in the simplified representations of the energy balance that is return here. So, that means on the left hand side N i h i is actually that h i was not there, U i was there; we replaced it by h i when can be do this? We can do this if U i and h i are not very different; which is not often the case as for as reacting systems of concerned in or domain of interest. But it may not be always; so, we have we have simplified on the left hand side here. On the right hand side we have neglected kinetic and potential terms which may not by and law they be the write in most cases; but there are situations where they may not be correct.

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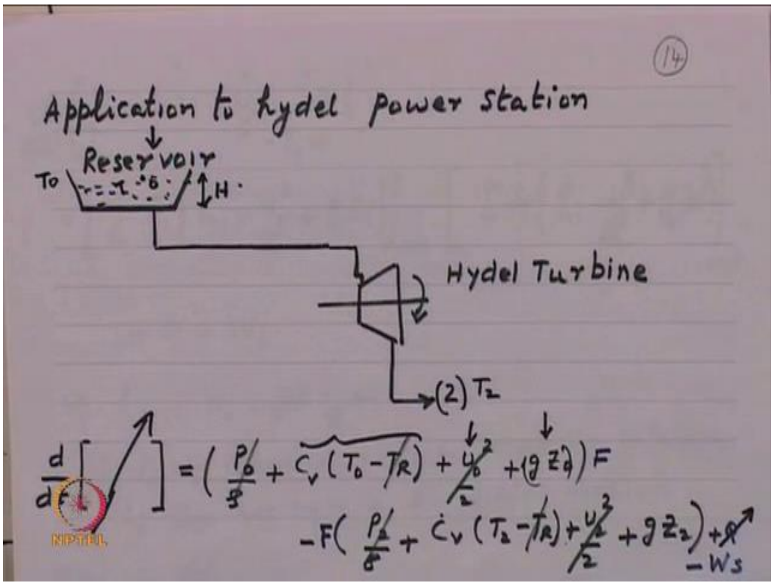

$$\frac{d}{dt}\left[\ \cancel{\ }\ \right] = \left(\frac{P_0}{\rho} + \overbrace{C_v(T_0 - \cancel{T_R})} + \cancel{\frac{u_0^2}{2}} + g z_0\right)F - F\left(\frac{P_2}{\rho} + \dot{C}_v(T_2 - \cancel{T_R}) + \cancel{\frac{u_2^2}{2}} + g z_2\right) + \cancel{Q} - W_s$$

So, just to summarize; what we are saying is that they simplified representation which involves in N i h i on the left hand side and F i h i in the right hand side is a very simplified representations which will apply for most cases; but may not before all cases. Just to understand this let as just look at Hydel turbine; so, what is the hydel turbine? You have a reservoir which has water, a huge quantity of water it is available at a certain height H; so, that you can use the potential energy to run a turbine.

How to apply an energy balance? What is your energy balance d by d t of system? So, what we trying to say here is that when the huge amount of energy here and we are drawing a small amount on a daily bases or hourly basis; the rate at which the energy of the system changes we can neglected under the quasis studies the appropriation. That means; if the time scale for which we are observing the system is small in relation to the time scale over which the reservoir gets consume the left hand side we can be seen as quasis studies; therefore, can be deleted.

On the right hand side what is this term? What is the right hand side term? We, said if you look at here the right hand side terms are h i U i squared by 2 g z i and P t omega i we have neglected. Here, h i by g z I; but in the hydel prostration this term is important, in the hydel prostration this term is important. Therefore, this term is should take into account that is why I said; whenever we deleted term we should be very careful. So, what have done is that I have again looking that this put all this terms that are appropriate to hydel prostration. So, what is it look? What is the h i U i squared by 2? And, then g z i all that I putting here; so, it look like this.

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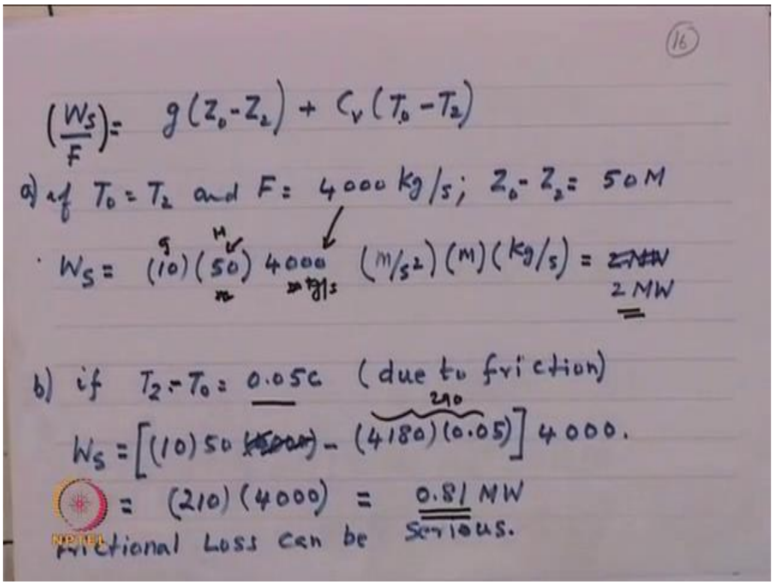

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$$\left(\frac{W_s}{F}\right) = g(Z_0 - Z_2) + C_v(T_0 - T_2)$$

a) if $T_0 = T_2$ and $F = 4000$ kg/s; $Z_0 - Z_2 = 50$ M

$$W_s = \overset{g}{(10)}\,\overset{M}{(50)}\,\underset{kg/s}{4000}\,(m/s^2)(m)(kg/s) = \underline{\underline{2\ MW}}$$

b) if $T_2 - T_0 = \underline{0.05C}$ (due to friction)

$$W_s = \left[(10)50 - \overbrace{(4180)(0.05)}^{209}\right] 4000.$$

$$= (210)(4000) = \underline{\underline{0.81\ MW}}$$

Frictional Loss can be Serious.

So, you have the effect the left hand side is 0, the right hand side has the effect of pressure. And, at position 0 and position 2 both are opened to atmosphere; I have taken it has to P 0. Both P 2 and P 0 as it is the same pressure; so, I am knocked it out. And, to do my energy balance between position 0 and position 2. And, what is the h i? I taking it as

C v t naught minus of t r; I could put C v or C P, both are not very different. And, then you have neglected this term U naught term is not a very important; therefore, the g z naught has the term here and similarly, you have g z 2 at this here.

So, what we done; we have retain the energy balance was the left hand side is 0, we knocked out the pressure terms, we simply have what is called as a simplified form of the energy balance which look like this; which means the amount of energy that we produce per unit mass of flow is g z, is g terms z naught minus it 2 and C v times T naught minus of T 2. Now, if T naught is equal to T 2; then, this term goes away then the amount of part that produce. If w, if I take it is 4002 mega watts is that clear. So, if I taking C v multiple this term is 0. Suppose, we find this is the small increasing temperature small; I taken as a 0.005 or point 005 it is really depends upon how will you design the conduit leading from the reservoir to the hydel term.

So, you notice here the if you a long in increase of 0.05 you have lost more than 50 percent of the power; this is want I want to appreciate how the flew mechanics which designs this conduit from the reservoir to the to the hydel turbine which made by several kilometer away ok; it may not be nearby. And, the velocity is far part of the reason; why have reason I knocked out this term U naught; because velocity would not same in both the place that is where the knocked it out ok.

So, the point remember here is that we can loss a large amount of energy; but not taking care of the design of the conduits that flew mechanics is an important part of design see we all thing that mechanical energy can be transmitted without loss of efficiency. We always think inefficiency; but thinking is an instance of mechanical inefficiency which is as I say 50 percent; so, this care we should take in the design.

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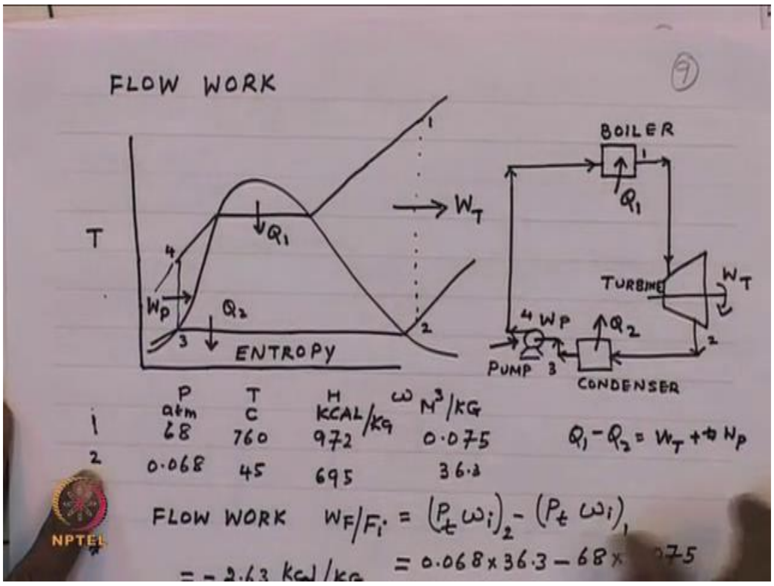

FLOW WORK

	P atm	T C	H KCAL/KG	ω M³/KG
1	68	760	972	0.075
2	0.068	45	695	36.3

$Q_1 - Q_2 = W_T + W_P$

FLOW WORK $W_F/F_i = (P_t\omega_i)_2 - (P_t\omega_i)_1$

$= 0.068 \times 36.3 - 68 \times 0.075$

$= -2.63$ kcal/kg

So, let us see what happens in a stream turbine? Stream turbine we have done in a way we have already calculated the stream turbine; we have calculated here. If we do this same calculation for this stream turbine is about the minus 0.2.63. So, we can calculate the flow work required for a stream turbine or for a sulfur dioxide.

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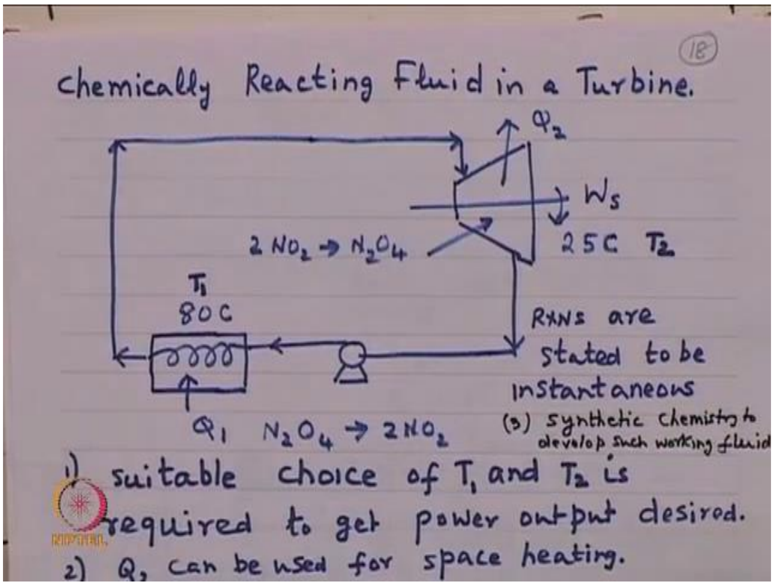

Chemically Reacting Fluid in a Turbine.

$2NO_2 \rightarrow N_2O_4$

$N_2O_4 \rightarrow 2NO_2$

RXNS are stated to be instantaneous

(3) synthetic chemistry to develop such working fluid

1) suitable choice of T_1 and T_2 is required to get power output desired.

2) Q_2 can be used for space heating.

Now, we also said that this is not common; but this something that we would like to do that we can apply as energy balance also to run; what we call as a reacting system which will produce power. How do you make a reactive system produce power? That means a reaction like this 2 N O 2 times N 2 O 4 this reaction; of course, reaction known to be instantaneous. Therefore, depending upon the free energy change of this reaction there are 2 reactions; one is N 2 O 4 going to N O 2 or N O 2 going to N 2 O 4.

So, you can here this picks up energy and then delivers energy, picks up energy delivers energy. So, here it picks up energy at Q 1 may be at 80 degree centigrade and there in Q2 it may be at 25 degree centigrade it delivers. So, it is Q1 minus Q 2 is the work produce; if you can make the produce work. So, in some cases we are not able to produce work or we able to use it for a space heating applications .So, has the lot of the low temperature heat is available in many places; we can pick it up using a chemical reaction and delivers it to for space heating.

The important point is here there is tremendous scope for designing working fluids which is able to pick up heat at low temperature for space heating application. Otherwise, you have to we use more expensive material here is an instance was so much of heat is available at this low temperature which is required for a space heating applications.

So, reacting fluids and our energy balance is able to make use of all these; because the energy balance is return keeping in mind that the energy what is our energy balance? Our energy balance only saying that d by d t of N i h i is F i h i and F i h i out, F i h i in. Basically, it saying how much energy is coming in? How much energy is going out? How much heat you put in? How much work into take out?

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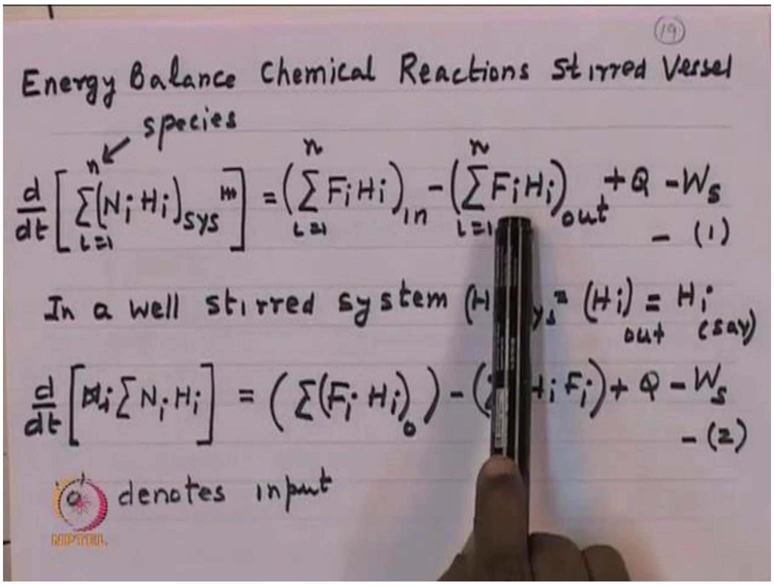

(19)

Energy Balance Chemical Reactions Stirred Vessel

species

$$\frac{d}{dt}\left[\sum_{i=1}^{n}(N_i H_i)_{sys}\right] = \left(\sum_{i=1}^{n} F_i H_i\right)_{in} - \left(\sum_{i=1}^{n} F_i H_i\right)_{out} + Q - W_s \qquad -(1)$$

In a well stirred system $(H$ [illegible] $)_{sys} = (H_i)_{out} = H_i^{\circ}$ (say)

$$\frac{d}{dt}\left[\cancel{M_i}\sum N_i H_i\right] = \left(\sum (F_i H_i)_0\right) - \left(\text{[illegible]} H_i F_i\right) + Q - W_s \qquad -(2)$$

0 denotes input

So, reacting fluids and our energy balance is able to make use of all these; because the energy balance is return keeping in mind that the energy what is our energy balance? Our energy balance only saying that d by d t of N i h i is F i h i and F i h i out, F i h i in. Basically, it saying how much energy is coming in? How much energy is going out? How much heat you put in? How much work into take out? So, just to summarize it that we are saying is that you have a energy balance with system has some amount of energy equal to amount of energy coming in, amount of energy going out plus Q minus W s. Just you put it in the context of the stirred vessel; what we have stirred is that h i system therefore, is also equal to the h i out. On nomenclature is that the intensive properties of the system is also equal to the intensive property of the excite stream.

Therefore, I denoted the h i and then I put is 0 to take care of input streams. So, in this equations I written it slightly differently taking into account the factor h i in the system is same as h i in the excite stream; while h i and F i in the inlet stream as got as 0 here to indicate there it is the input stream ok. So, this the statement of the energy balance d by d t of N i h i some do overall the species equal to some do overall species; F i h i at inlet minus sigma F i h i at the outlet knows subscript, plus Q minus W s.

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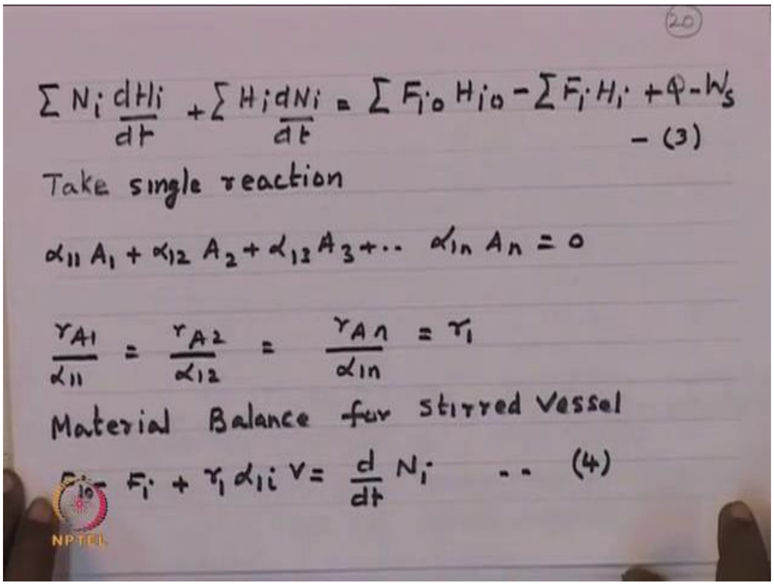

⑳

$$\sum N_i \frac{dH_i}{dt} + \sum H_i \frac{dN_i}{dt} = \sum F_{io} H_{io} - \sum F_i H_i + q - W_s \quad - (3)$$

Take single reaction

$$\alpha_{11} A_1 + \alpha_{12} A_2 + \alpha_{13} A_3 + \ldots \alpha_{1n} A_n = 0$$

$$\frac{r_{A1}}{\alpha_{11}} = \frac{r_{A2}}{\alpha_{12}} = \frac{r_{An}}{\alpha_{1n}} = r_1$$

Material Balance for stirred Vessel

$$F - F_i + r_1 \alpha_{1i} V = \frac{d}{dt} N_i \quad \ldots (4)$$

Now, our interest is to be able to put this whole equation in to a form that we can use for our reactive systems. Let us see how to do this? To do this what we have done here is that this term the sigma N i h i d by d t; and, this separating it as 2 terms N i d h i at h i d N i d t. The first term here N i d h i d by d t is return as 2 terms. Now, the advantage of doing this is that when you look at the single reaction alpha 11 A 1 plus alpha 12 is equal to alpha 1n A n is equal to 0. We recognize that they rated which species A 1 reacts divided by the strike to metric co efficient equal to rated which species n reacts divided by strike to metric coefficient.

So, all these equality equal to r 1; which we denote as the intensive rate of that reaction. So, if I ask you what is rated? Which component A 1 is getting form you will say that it is r 1 multiplied by alpha 11 what is the rated which component A n is reacting? You will say it is r 1 multiplied by alpha 1 n; so that is the nomenclature which will be. Therefore, our material balance in the stirred vessel for component you will look as input, output, generation. What is the generation it term for component? You will say r 1 times alpha 1; because multiplied equal to d by d t of N i ok.

So, our statement of material balance for component i. Now, our interest is what our interest is to see whether we can generate this term h i d N i by d t. Because you can generated from this by multiplying by h i and summing over all species; what is meant by multiplying by h i summing over all species? what is meant is; we write 1 equation F

1 0 f one minus F 1 r 1 alpha 11; v equal to d N 1 by d t. There in 1 equation similarly, there are N equations. So, each of the equations you multiplied by the appropriate species enthalpy and some over all species.

So, that is what when you multiplied throughout and some over all species; what you find is let if we use the multiply throughout the h i and some over all species what you get is sigma h i F i 0. Please note here and this multiplying the h i and summing over all species correct. Multiplying the h i summing the overall species; then, what I will get some will get h i F i and then the last term. So, what I have done here is I multiplied this by h I; therefore, it becomes h i F i 0, h i F i. And, then multiply this term by h i and sum do overall species; therefore, I get r 1 alpha 1 i h 1 V is equal to h i d N i by d t sum do over all species.

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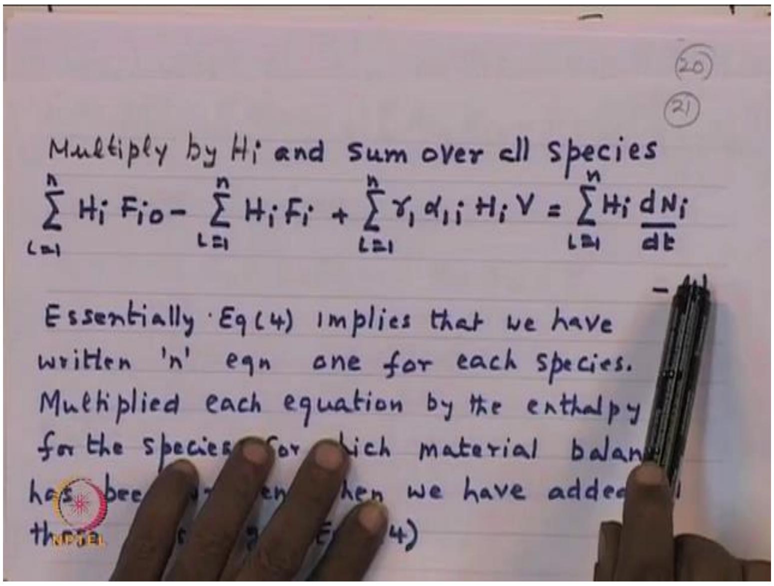

(20)

(21)

Multiply by H_i and sum over all species

$$\sum_{i=1}^{n} H_i F_{io} - \sum_{i=1}^{n} H_i F_i + \sum_{i=1}^{n} r_1 \alpha_{1i} H_i V = \sum_{i=1}^{n} H_i \frac{dN_i}{dt}$$

Essentially Eq (4) implies that we have written 'n' eqn one for each species. Multiplied each equation by the enthalpy for the species for [illegible]ich material balan[illegible] has bee[illegible] [illegible]en [illegible]hen we have adde[illegible] th[illegible] [illegible] 4)

So whatever we have done now; we can simplify what we do now. Now, we have the equation here; so, we have this equation where h i d N i by d t they are generated using material balance. So, I am substitute for the term from this equation 4 is at clear. So, we are generated this h i d N i by d t by looking at the material balance; therefore, in this equation 3 you can replace h i d N i by d t by the left hand side of this equation.

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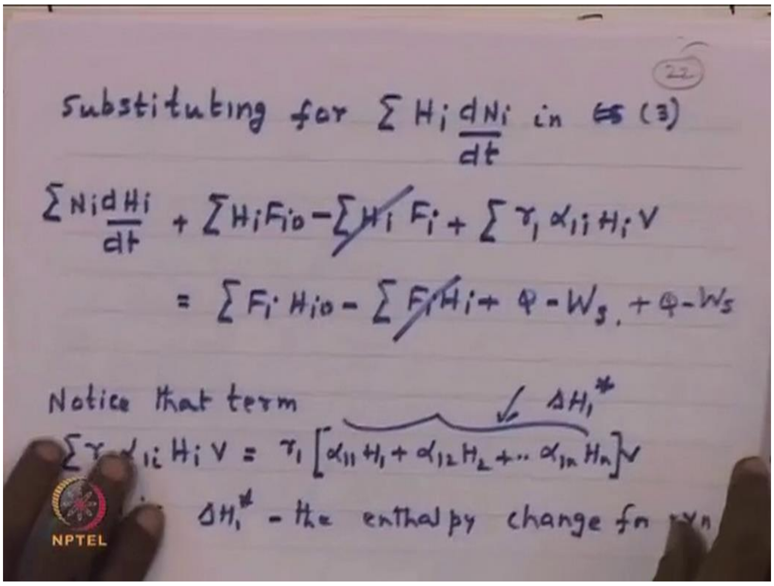

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Substituting for $\sum H_i \frac{dN_i}{dt}$ in Eq (3)

$$\sum N_i \frac{dH_i}{dt} + \sum H_i F_{i0} - \cancel{\sum H_i F_i} + \sum r_1 \alpha_{1i} H_i V$$

$$= \sum F_i H_{i0} - \cancel{\sum F_i H_i} + Q - W_s + Q - W_s$$

Notice that term

$$\sum r_1 \alpha_{1i} H_i V = r_1 [\overbrace{\alpha_{11} H_1 + \alpha_{12} H_2 + \dots \alpha_{1n} H_n}^{\Delta H_1^*}] V$$

ΔH_1^* - the enthalpy change for rxn

So, when you do that what you find is this; so, I put in all the terms at return you find left hand side, right hand side all that terms you find it short of some terms knock of out. And, we recognize that this term r 1 alpha 1 i h i V is essentially r 1 times alpha 11 h 1 alpha 12 times h 2 times alpha 1 N h N. Which means, what this is an enthalpy change for reaction 1; so, this term becomes enthalpy change the reaction 1? Therefore, this whole term becomes N 1; so, how the energy balance looks like.

Now, it is N i d h i by d t is the first term. And, second term h 1 F i 0 h 1 F i 0 is the h i is naught F I; so, you can combine these two terms you get h i so what I get here is you can see here. The common thing here is what have a missed term here; F i 0 should be F i naught sorry. So, it simplifier as it is simplifies as N i d h i by d t and F i naught from here can see both h i minus h i naught. And, this term becomes r 1 times delta h 1 star which is the enthalpy changes for reaction plus Q minus W s.

Now, it is in the form which is a little easier for as to make use of even; for example, suppose the reactor many extremes are entry, many streams and entry. And, all those streams made the entering different temperature, different quantities; all those affect can be appropriately account to it; because each stream coming a different temperatures, coming a different enthalpies. So, the form in which equation is return helps you to manage various input into a reactor, various temperature into all those kinds of things can be handled; for a special cases we can do lot of simpler things.

So, this term r 1 time d h i star this is what; this is for the single reaction. You can write this r 1 in terms of what is called as r 1 time alpha 1 k and divide by this alpha 1 k what is that means; this is the formation of component k multiplied by the enthalpy change expressed with respective component k; this how data is often available. So, what is important is to recognize this term and put it into the forms at even one can understand r 1 time alpha 1 k refers to rate of formulation component k; this often readily available.

Because we measure in our experiment, we will measure this term. So then in that case which multiplied by rate of the heat of formation; sorry, enthalpy change to the reaction expressed with respective that component that is important than it will be consistent. So, in this form the way in which equation is return it is probably the most general form in which you can write a chemical reactive energy balance. It takes in to account all sorts of variations that might occur.

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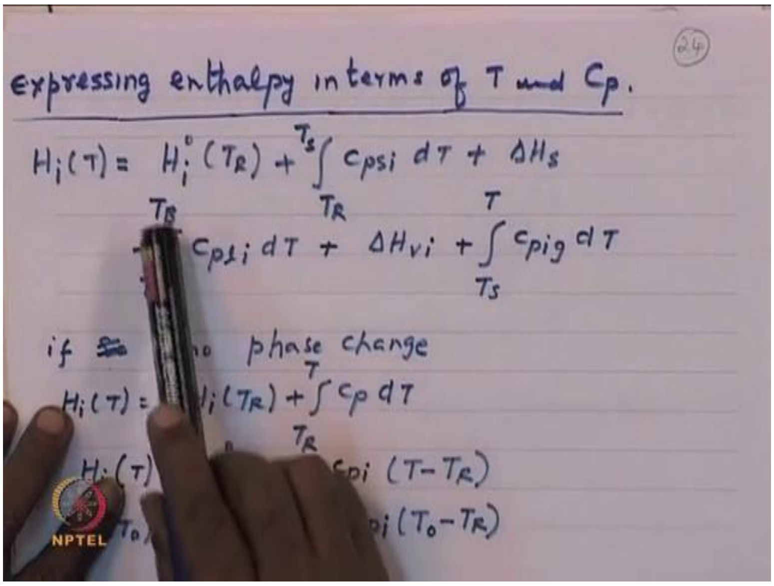

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expressing enthalpy in terms of T and Cp.

$$H_i(T) = H_i^0(T_R) + \int_{T_R}^{T_s} c_{psi}\,dT + \Delta H_s$$

$$+ \int^{T_B} c_{pli}\,dT + \Delta H_{vi} + \int_{T_s}^{T} c_{pig}\,dT$$

if ~~so~~ no phase change

$$H_i(T) = \quad {}_i(T_R) + \int_{T_R}^{T} c_p\,dT$$

$$H_i(T) \quad c_{pi}(T - T_R)$$

$$T_0 \quad {}_{pi}(T_0 - T_R)$$

How we said that we recognize that this term H i can be put in terms of temperature; because the enthalpies are available to 2 as in terms of a standard heat of formation plus various C p delta T; which takes into account the effect of the specific heats. So, what we have said is that if there is no phase change; then, clearly we do not the account for phase change solid to liquid, liquid to gas all those things. This is not required we simply can look at enthalpy at temperature T is standard heat of formation plus an integral which goes; which is the average specific heat in that interval T and T R.

So, we can express H i at T like this H i T 0 also like this. So, this is an assumption what is the C P? The C P is the average in this range this is the average; so, every time we will look at this, we look at the average specific heat in the range T to T R in T to T naught.

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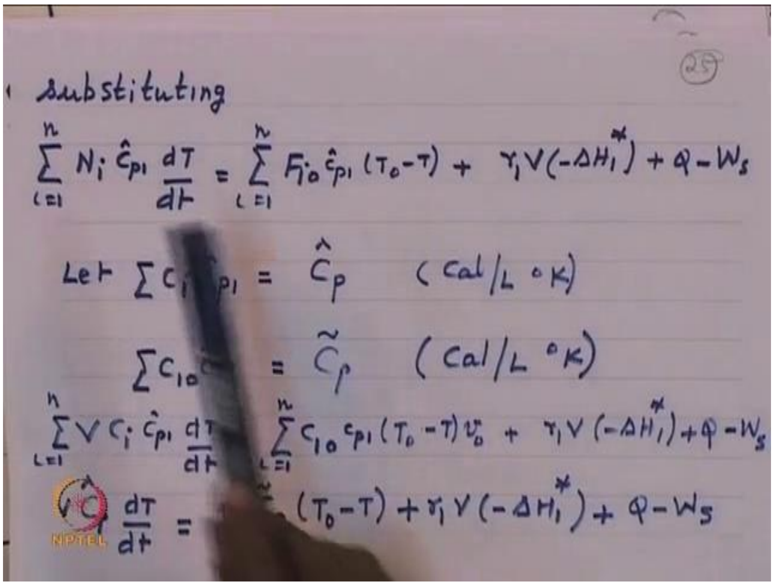

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substituting

$$\sum_{i=1}^{n} N_i \hat{c}_{p1} \frac{dT}{dt} = \sum_{i=1}^{n} F_{i0} \hat{c}_{p1} (T_0 - T) + r_1 V(-\Delta H_1^*) + Q - W_s$$

Let $\sum C_i$ [illegible] $_{p1} = \hat{C}_p$ (cal/L °K)

$\sum C_{10}$ [illegible] $= \tilde{C}_p$ (cal/L °K)

$$\sum_{i=1}^{n} V C_i \hat{c}_{p1} \frac{dT}{dt} \text{ [illegible] } \sum_{i=1}^{n} C_{10} c_{p1} (T_0 - T) v_0 + r_1 V(-\Delta H_1^*) + Q - W_s$$

$\frac{dT}{dt} =$ [illegible] $(T_0 - T) + r_1 V(-\Delta H_1^*) + Q - W_s$

So, expressing our looking; but are equation here where is the equation. So, this are the equation N i d h i. Now, I can replace the h i in terms of temperature and specific heat; therefore, the whole equation N i d h i by d t simplifies as something like this. So, first term is N i d h; by this what we have written here go through it is this is N i which is return as this is V i sorry; this is V i ok. So N i is V i times C p i correct is this clear. Please understand N i d h i by d t, N i is what? V i terms C i; specific i will written it here I will written it properly here.

So the first term; let we say like that is N i let no harm in that N i C p i this is return in this for V times C p i; c p means specific d t. Similarly, the right hand side; so what we have done now? So, we have what we have done is that this each of this terms h i naught and h I; we are put in terms of specific heats. Therefore, the right hand side now looks in terms of V i C p i. This terms C i C p i the only term that has to be summed over all the species is V i C p I; on the right hand side the only term your do some is C i 0 C p i. On the other words what we have done is that by expressing the enthalpy in the terms of specific heat even toughs.

If we look at this H i naught and H i naught is known H i changes; depending upon the extend of reaction. Similarly, H i changes; because the extend of reaction. But by this formulation of writing in terms of volumetric specific heat; what we have done is at C i C P I, C i changes. But C i C P i for a mixture does not change very much ok. On other words if draw the difficult problem we have converted into the simpler problem by combining C i C P i. So that the left hand side now simply looks like a volumetric specific heat multiplied by the reacted volume d T d t. Why is this possible? Because we have written this sigma C i C P i as a volumetric specific heat which does not change during this reaction this is the assumption. And, this is not the bad assumption; you can do calculation for several system you will find that sigma C i C P i for all the species taken together for the reaction may not of changed very much.

Similarly, sigma C i 0 C P i summed over all species also not a change very much. So, it is simplifies; otherwise it massy kind of system the whole equation looks in this form V C P d T d t is V naught C P t naught minus of T. The assumption here is that all that feeds stream is coming at T naught; see in this formulation is not useful when a many stream is coming in different temperature. But this formulation is very useful; so what is important for you is to recognize that we must use the appropriate formulation for our application ok.

So, we have this statement for a single reaction saying that r 1 v this is heat generation. If it is exothermic reaction or heat absorption; if it the endothermic reaction heat added the output. Typically, this may not be important in many case; because we are not trying to a in a most cases. But it may be important in some and appropriately you have the deleted terms that are the relevant your application ok.

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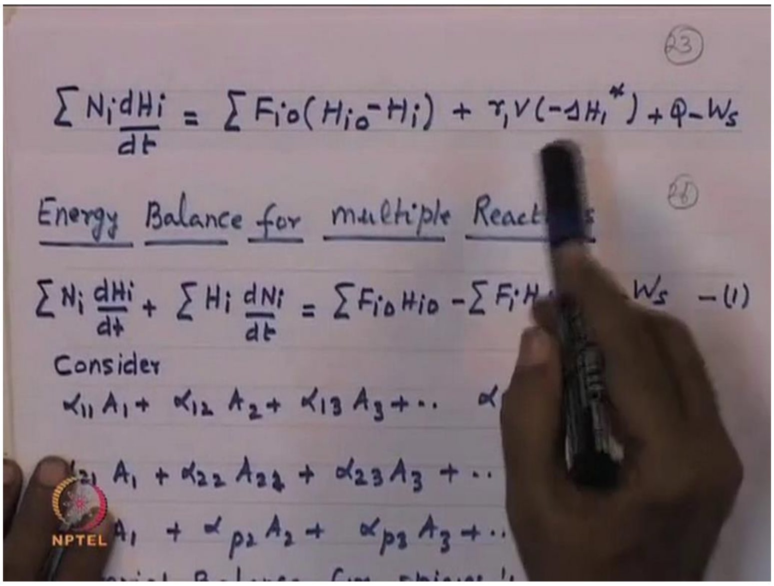

(23)

$$\sum N_i \frac{dH_i}{dt} = \sum F_{io}(H_{io} - H_i) + r_1 V(-\Delta H_1^*) + Q - W_s$$

(24)

Energy Balance for multiple React

$$\sum N_i \frac{dH_i}{dt} + \sum H_i \frac{dN_i}{dt} = \sum F_{io} H_{io} - \sum F_i H \quad W_s \quad -(1)$$

Consider

$\alpha_{11} A_1 + \alpha_{12} A_2 + \alpha_{13} A_3 + \cdots \alpha$

$_{21} A_1 + \alpha_{22} A_{22} + \alpha_{23} A_3 + \cdots$

$A_1 + \alpha_{p2} A_2 + \alpha_{p3} A_3 + \cdots$

Now, if we go from a single reaction to a multiple reaction; so what we you do? We had only one reaction here correct. Now, we have many reactions and other word how do you go from a single reaction to multiple reactions? So, what we have done for that case is that the left hand side; we have only one term of the left hand side is sigma Ni d H i by d t H i N i by d t which we did some the manipulation; we can do this same here. How do you do the same here; we recognize that we have N, we have p the reaction alpha 11 A 1 to alpha 1 n A 1.

Similarly, alpha p 1 A 1 to alpha p 2; they are p such reactions which are taking place in our is to stirred vessels. So, what we want do is that we want to generate; what is this term Hi d N i by d t for the case of multiple reactions. So, how do you do that? We do that by writing the energy, the material balance for the i it is species input, output the generation is because of r 1 alpha 1 i, r 2 alpha 2 i, r p alpha p i. Notice that all the rate processes appear in the generation term multiplied by V equal to 0. So, this is the statement of energy of bio material balance and we want this term H i d N i by d t; which means what we are to multiply this by H i and summed over all the species.

So, let me say it one second; what we have saying here is that when we have a multiple reaction this term H i N i by d t; we want to replace from energy material balance. And, we do that by writing the strike to metric, writing the energy material balance was species i; which is what F i naught minus the F i plus the generation of all the piece species r 1 alpha 1 i, r 2 alpha 2 i, r p alpha p i. So, now we can multiply by H i and some over all species; ones you do that being generate this term that is what. So, when you do that and it is lot of simplifies nicely.

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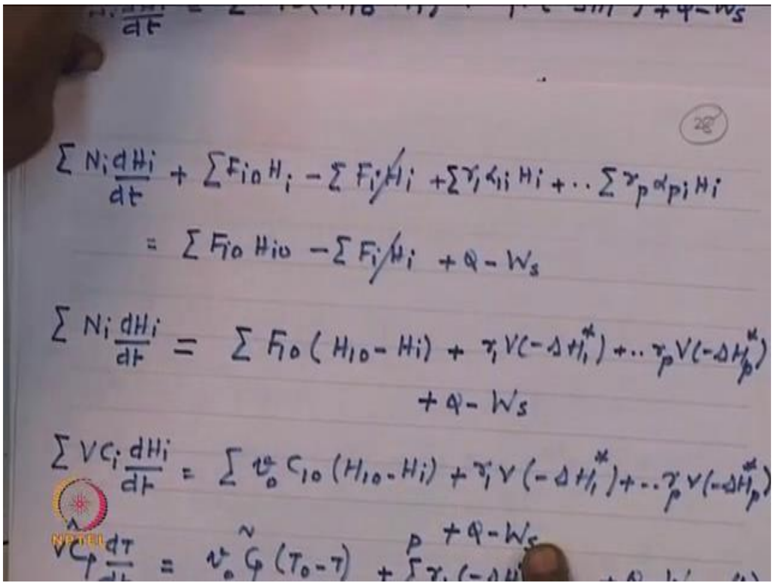

28

$$\sum N_i \frac{dH_i}{dt} + \sum F_{io} H_i - \sum \cancel{F_i H_i} + \sum r_1 \alpha_{1i} H_i + \cdots \sum r_p \alpha_{pi} H_i = \sum F_{io} H_{io} - \sum \cancel{F_i H_i} + Q - W_s$$

$$\sum N_i \frac{dH_i}{dt} = \sum F_{io} (H_{io} - H_i) + r_1 V(-\Delta H_1^*) + \cdots r_p V(-\Delta H_p^*) + Q - W_s$$

$$\sum V C_i \frac{dH_i}{dt} = \sum v_o C_{io} (H_{io} - H_i) + r_1 V(-\Delta H_1^*) + \cdots r_p V(-\Delta H_p^*) + Q - W_s$$

$$V C_p \frac{dT}{dt} = v_o \tilde{C}_p (T_o - T) + \sum^{p} r_j (-\Delta H$$

So, we not go through this when you do that whole things it simplifies like this equation; that means that which means this terms for a multiple reaction; when a substitute it is look like this. What we have done is that the second term H i d N i by d t; which is substituted from material balance and then the whole equation look something like this. So, only change that taken place is that wherever the reaction term occurs in the reaction term previous with the one reaction; now there are p reactions.

So, this term now becomes j equal to one to p r j delta j star V. So, this term the heat generation and the heat absorption previously it was because the only one reaction; we are only one reaction correct. And, now we have p reactions; therefore, this term becomes r j alpha j that is what it becomes? So, it becomes r j multiplied by the heat of enthalpy formulation, enthalpy change for the formation of j i th reactions, j going from 1 to p. So, if the energy balances for a single reaction of the multiple reactions it does not really matter; because the form is identical ok.

So, now we can replace the everything in terms of temperature; when you do that if all the freed stream is the T naught this is how the equation looks like. Why the summation is are i equal to 1 to N? This, is here; now this term alpha 1one i H i we have replaced it as delta H i star with 1 star. So, this is for the single reaction this term is the important thing is that; this term is actually delta H 1 star for single reaction. Now, when there are many reactions; then, it will become for j reactions it will become delta H j star r j is here the intensive rate of formation, intensive rate of that reaction j. So, r j it j is a going from 1to p there are p processes is that clear.

So, all the feed is coming it is same temperature this is the assumption; but in this form it is not so bad. Because that effect is there; so, we here at in this form you can deal with different component coming at different temperature. But from this point to this point all the components are coming at same temperature. So, which level you whether use this or use this it depends upon what is the application you are looking at; that you should take care whether it is single reaction or multiple reactions; when there is 1 reaction then you j going to 1 to 1.

So, this form equation 4 is the very general statement of energy balance for the stirred vessel; where V C P which volumetric specific heat rate of change of temperature of the system equal to V naught C P T naught minus of T it is the flow term is the reaction term heat addition and work this is how it looks. If I ask you for example, suppose we have instance of a multiple reaction taking place in a let us say a stirred vessel; why the temperature are is maintain constant. It is still it is in the sense what I am saying in that there is instance.

Let us say you have an equipment which is into which fills is coming, but nothing is going out what are we saying V naught is finite; but there is nothing going out. Now, this the way this equation is return the v naught is finite; but nothing is going out. So, people tend return to think to you knows this second term should not be there. But second term is coming; because of H i what is h i? It is an enthalpy of the stream in the equipment you understand. So, we have the typically we think the second term should be removed. But no this is the important point and see in many instances where people knock out the second term.

This is within the H i is what? H i is the enthalpy of stream in the equipment. So, it is multiplied the V naught; V naught is input not output is at clear. So, you should be a very careful in a given exercise; the equation how they play out in your application you have to be very careful. Otherwise, you my knock out terms which are actually not a appropriate to be knock to out. And, I thought we did some exercises where I pointed out this out to you also. In one exercise some of you said that no, no we should knock it out; and then we look by the equation realize is that no we cannot knock it out. It is in semi batch you will find these kinds of problems.

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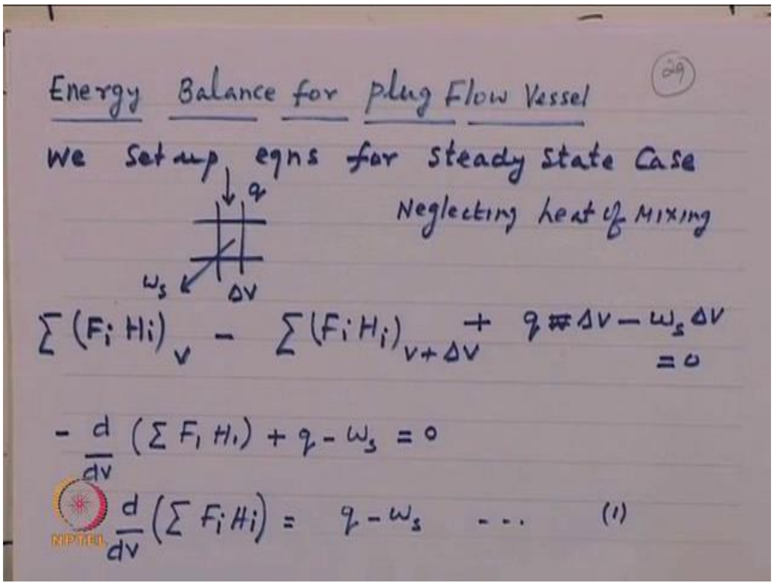

Energy Balance for plug Flow Vessel

(29)

We Set up eqns for steady state Case

Neglecting heat of Mixing

$$\sum (F_i H_i)_V - \sum (F_i H_i)_{V+\Delta V} + q\Delta V - w_s \Delta V = 0$$

$$-\frac{d}{dV}(\sum F_i H_i) + q - w_s = 0$$

$$\frac{d}{dV}(\sum F_i H_i) = q - w_s \quad \ldots \quad (1)$$

Now, let us look at the same problem; therefore, the case of we looked at stirred vessel we look at plug flow vessel what is the plug flow vessel? A plug flow vessel is one in which there is no mechanical starring. So, we have here a vessel through into which flew it is coming in flew, it is going out; and out material balance is for this differential element. So, what is the statement of the energy balance input of energy minus output energy plus q which is the heat input per unit volume? Therefore, i multiplies it is small q by delta v; and then w s times is the heat work output per unit volume.

So, input, output, generation there is no generation; this is heat input work output equal to 0 for the studied state. We are writing the material balance for studied state; we have not had to time to look at the unstudied state yet put. So, in the limit as delta v times to 0; the general material by energy balance for a plug flow vessel look like this. This is so d by d v of F i H i becomes q minus w s. Now, d by d v of H i F i is what we have the deal with and put it in appropriate forms so that we can see what happens should temperature of the equipments. For that what we have done; we know that we can expand this is F i d H i d v and H i d F i d v. And, the material balance equation tells us what is d F i d v.

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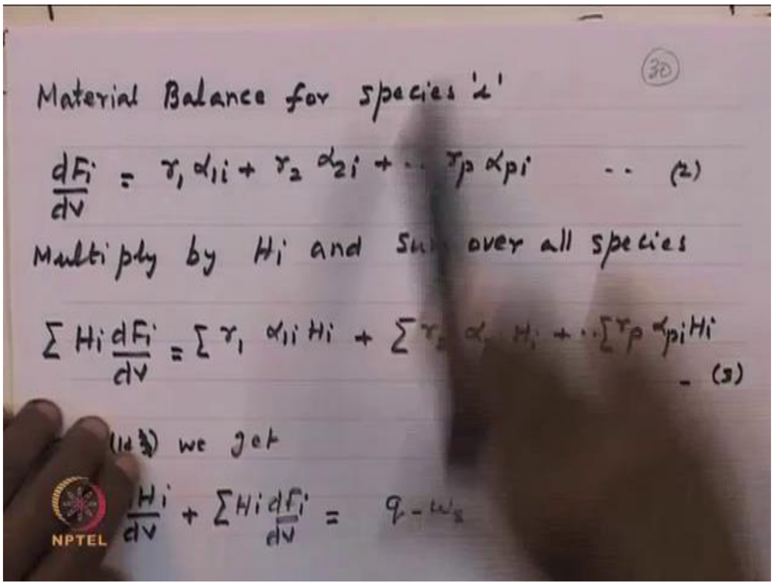

Material Balance for species 'i'

$$\frac{dF_i}{dV} = r_1 \alpha_{1i} + r_2 \alpha_{2i} + \cdots r_p \alpha_{pi} \quad \text{-- (2)}$$

Multiply by H_i and Su over all species

$$\sum H_i \frac{dF_i}{dV} = \sum r_1 \alpha_{1i} H_i + \sum r_2 \alpha_{2i} H_i + \cdots \sum r_p \alpha_{pi} H_i \quad \text{- (3)}$$

(1 & 3) we get

$$\frac{H_i}{dV} + \sum H_i \frac{dF_i}{dV} = q - w_s$$

So, if you look at d F i d v how does the look d F i d v due to a is equal to rate of generation of component i; what is the rate of generation of component i? r 1 alpha 1 i up to r p alpha p i. So, d F i d v in terms of all that species; therefore, when you multiply by H i and some over all species H i d F i d v becomes sigma r 1 alpha 1 i H i what is this? we know this is heat of enthalpy change for the reaction 1; alpha 1 i H I, alpha 2 i H i is change for reaction 2 r alpha p i H i n p i th enthalpy to change for reaction p.

Therefore, this term this whole term H i d F i by d v is what we have done is that if we recalled here this is F i d H i d v H i d F i d v. Therefore, the term H i d F i d v you can now replace from here correct. So, what I have done is so this equation here this equation have I written it as F i d H i d v plus H i d F i by d v this what I have written; I am written it again here. So, our equation 1 I have written it by expanding the term F i d H i d v. So, I put written it in this form 2 terms are appearing this H i d F i d v can be substituted from here. Which is what? r 1 delta H 1 star, r 2 delta H 1 star, r p delta H p star; therefore, this term it becomes r 1 delta H 1 star, r 2 delta H 2 star.

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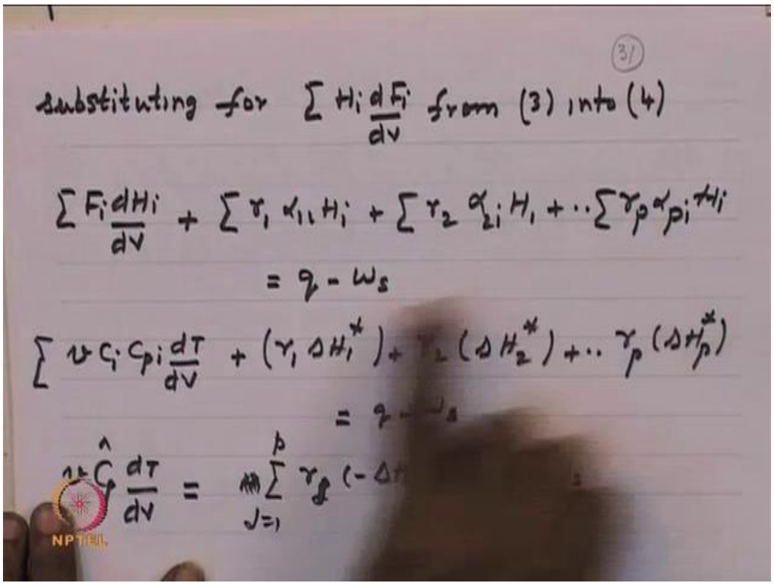

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substituting for $\sum H_i \frac{dF_i}{dV}$ from (3) into (4)

$$\sum F_i \frac{dH_i}{dV} + \sum r_1 \alpha_{11} H_i + \sum r_2 \alpha_{2i} H_1 + \cdots \sum r_p \alpha_{pi} H_i$$
$$= q - w_s$$

$$\sum v C_i C_{pi} \frac{dT}{dV} + (r_1 \Delta H_1^*) + r_2 (\Delta H_2^*) + \cdots r_p (\Delta H_p^*)$$
$$= q - w_s$$

$$v \hat{C} \frac{dT}{dV} = \sum_{j=1}^{p} r_j (-\Delta$$

Similarly, up to r p delta H p star; therefore, our energy balance now becomes F i d H i d v plus all these r 1 delta H 1 r 2 up to r p equal to q minus w s. So, this if we take in to the other side it becomes this the F i d H i d v putting in terms of a volumetric specific heat becomes volumetric flow time, volumetric specific heat that sigma C i C p d t d v this terms is simply summation over j equal to 1 to p; there are p rate processes here plus. So, I have taken it to other sign; therefore, they put in a negative sign this I taken to the other side of the negative sign plus q minus w s.

So, for a plug flow vessel where there is no starring; we find that v C p d t d v which is the accumulation per unit, volume this is v c p d t d v within the rate of the changes of temperature of equipment. And, this is the rate of the heat generation if it is an exothermic reaction this is heat input this work output. The only thing the different between the stirred vessel and plug flow vessel here q is heat input per unit volume; it is per unit per volume that is the difference it is not heat input per unit time in the previous case it was heat input per unit time ok. So, that is the difference that we should take care all right.

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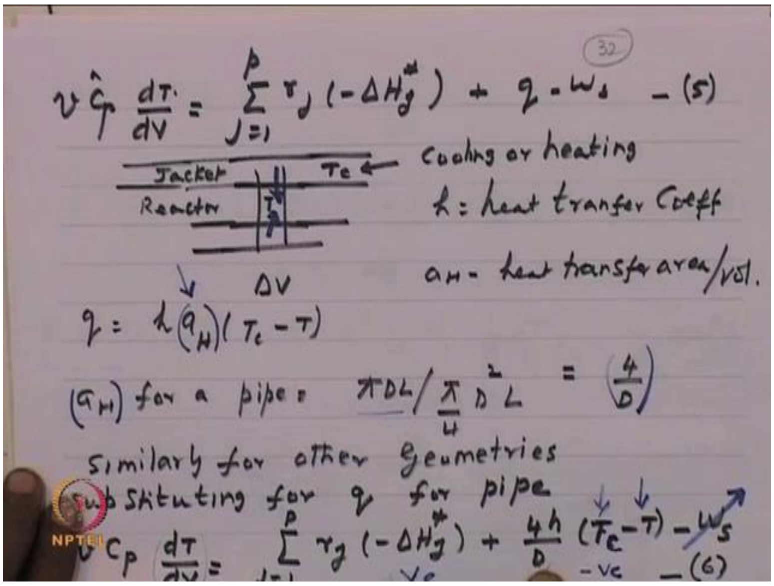

32

$$v \hat{C}_p \frac{dT}{dV} = \sum_{j=1}^{p} r_j (-\Delta H_j^{*}) + q - W_s \quad - (5)$$

← Cooling or heating

h : heat tranfer Coeff

a_H - heat transfer area/vol.

$$q = h (a_H) (T_c - T)$$

$$(a_H) \text{ for a pipe } = \pi D L / \frac{\pi}{4} D^2 L = \left(\frac{4}{D}\right)$$

similarly for other geometries

substituting for q for pipe

$$v C_p \frac{dT}{dV} = \sum_{j=1}^{p} \underset{\text{ve}}{r_j (-\Delta H_j^{*})} + \frac{4h}{D} \underset{-\text{ve}}{(T_c - T)} - W_s \quad - (6)$$

Now, let us see what is simplifications we can do this term q heat input per unit volume; assuming that our equipment is that pipe or it tube. So, tube surface area is see the volume of a adjust calculated here our heat transfer is h heat transfer surface area multiplied by the driving force. Therefore, if you have the unit volume here; suppose this how the heat is coming in like this. This, heat per unit volume have written into where the a H is a is a heat transfer; so surface per unit volume what is the a H? It is the heat transfer surface per unit heat volume; for a pipe what is that equal to surface area divided by the volume of the pipe which is 4 by d.

On other words this a H for a pipe is 4 by d; therefore, the small q for a pipe is actually 4 H by d t C minus of C understand. Therefore, the energy balance for a pipe looks v C p d t d v summation overall p rate processes plus 4H by d times minus w s. These by turn out to be typically 0 it may not be I say see it may turn out be and it may not be. But what are we saying now; see we are saying that in a plug flow vessel the rate of change of temperature with volume is heat if it is the exothermic if it is the heat generation and this is per unit volume and per unit time; we can see this unit per volume per unit time plus what is the heat that is removed by? What is this T C? T C minus of T this is the heat that is added to this system ok.

Typically, we will find this term is negative; because you will remove heat therefore, the T C minus T would be negative. So, you will find this is the positive. So, this is the positive term typically form exothermic reactions ok. This is terms out to be a negative term; therefore, this positive and this negative when they balance each other then it at with the hot spot or the point of maxima in the profile temperature. The point of maxima in the temperature profile occurs at a point where the heat removal becomes equal to the heat generation; then this becomes 0 this is negative, this is positive. Therefore, the becomes 0.

So, point at which it becomes 0 is the point of maximum. Now, the interesting thing that is for as an relevant to as is generally we like to see that temperature at which the maxima occurs is within the allowable limits of the material of constructions. In more importantly allowable the limits of the catalyst that you may be using most as the cases it is that catalyst which is crustal to ensuring that this temperature never goes beyond what is permissible. So, what you would do is that is you would like see there when it is goes to 0 what is the temperature at which is equality takes place and what is the temperature for a given choice of pipe size.

For the given choice of pipe size you will see what is the this temperature whether that temperature is good enough for the catalyst to be acceptable. Now, what you will do is that frequently when the pipe is large we will find the this temperature becomes the un acceptable. So, you will find that the choice at pipe size or the size that you will choose will be determined by the hot spot temperature your system will permit. So, this calculation you will do to find are what is the best temperature, what is the best choice of pipe size it can use when you use the small pipe.

Because it occurs in the nominate heat transfer is very large. So it stabled to dissipate the heat is very fast when you uses for small pipe; when use the large pipe it is not gabled to dissipate heat very fast and therefore, the hot spot temperature goes up you understand. So in this many so all this equation this are the point that is greatly important to us what is the choice of d; so that this temperature is what you would like to see. On other word as when you do a numerical calculation; what you will do you will choose the different pipe sizes and you will generate this hot spot profile and see what is the profile that is acceptable to you. And, you will choose that profile which is the acceptable to you or that pipe size which is acceptable to you is at clear. So, this the most important point as far as the design of the reactants of the constant.

You will find in the many cases we would like to operated adiabatically; that means this q is 0. There are many instances particularly we go to an ammonia plant and sulfur di oxide plant it is an adiabatic operation; why is adiabatic operation? That means we said this equal to 0 that means this allow the temperature to you are rise we allow the temperature to rise; but you do not allow it rise beyond the point. On the other words you have very short bed; the bed is very short allow the temperature to rise and you cool you understand. So that is the idea of you allow the temperature to rise, you allow cool, allow the temperature to rise you cool, you allow the temperature to rise cool; so that your able to reach the k the extent which you want to reach you ok.

So, all those strategies are built in to this equation now; because you will write this equation for every reactor. There are 7 reactors means write in from the every reactor; so all those are integrated into this statement of energy balance. Now, there are people who talk about what is called as radial flow reactors; what is radial flow? You can a flow out wards or in wards. Now, you will find the way this is formulated; you can talk into account radial flow quite comfortably. But here you should change this because this is for a pipe this way return for the pipe. So, for a radial flow reactor you will change; this a H you will change for a radial flow ok.

So, what I am trying to point cruces that see whatever simplification that we make it is under the assumption that we are using the pipe. But moment it is not a pipe than that left hand side is formulated properly; but the right hand side is not satisfactory. So, you should formulate this 4 H by d which is for a pipe, for a radial flow reactor; then it becomes the appropriate for the radial flow reactor. So, what in other words what you trying to point out to here is that the equations are written in a fairly general form; so that you can use it for the design that is appropriate your application. What is important is to replace those terms which are not appropriate; so that it applies to your situation appropriately is that clear what we say.

So, you whether in the stirred vessel we had in stirred vessel, we had a generation of energy term, we had heat transfer term we had work term ok. And, there we did not have of this kind of problems. But here in tubular reactor; because there it is no mixing we have this new feature for which you have to appropriate choice of pipe sizes are required. And, much of tubular reactor design that you will see in the processes industry; a great deal of a effort is in a spent in time to make a good choice of size of the pipe it is important. I will stop here.