Fundamentals of Combustion

Prof. V. Raghavan

Department of Mechanical Engineering

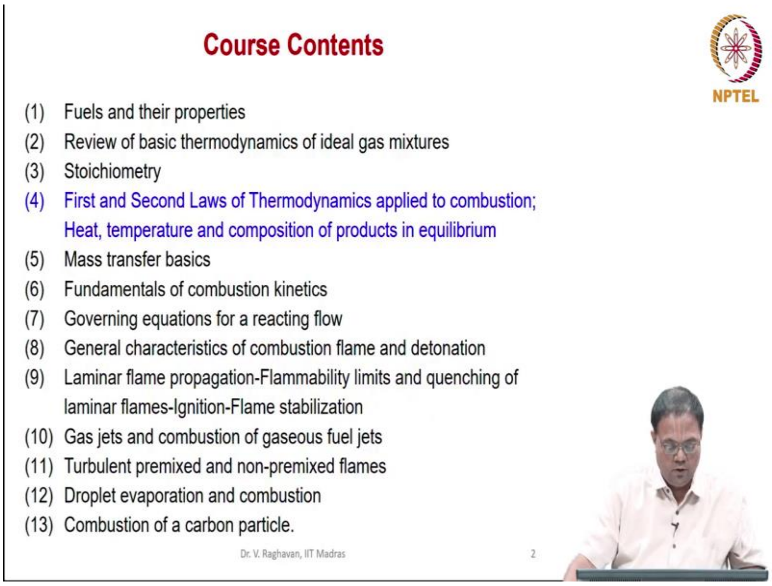
Indian Institute of Technology, Madras

Lecture – 9

First Law and Second Law of Thermodynamics Applied to Combustion - Part 01

Heat Calculation

(Refer Slide Time: 00:19)



Course Contents

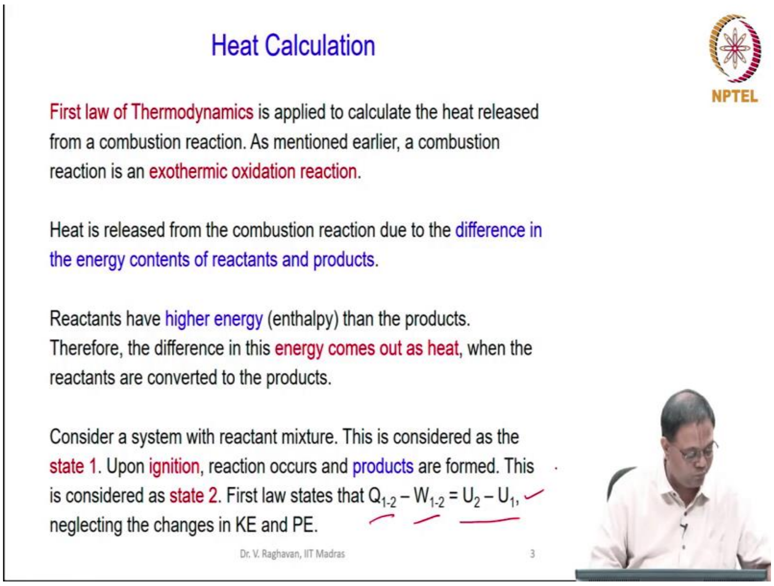
(1) Fuels and their properties
(2) Review of basic thermodynamics of ideal gas mixtures
(3) Stoichiometry
(4) First and Second Laws of Thermodynamics applied to combustion; Heat, temperature and composition of products in equilibrium
(5) Mass transfer basics
(6) Fundamentals of combustion kinetics
(7) Governing equations for a reacting flow
(8) General characteristics of combustion flame and detonation
(9) Laminar flame propagation-Flammability limits and quenching of laminar flames-Ignition-Flame stabilization
(10) Gas jets and combustion of gaseous fuel jets
(11) Turbulent premixed and non-premixed flames
(12) Droplet evaporation and combustion
(13) Combustion of a carbon particle.

Dr. V. Raghavan, IIT Madras

2

Here, we will try to calculate the heat released by the combustion process, then the temperature attained by the combustion chamber, and the composition of the products in equilibrium based upon a given temperature and pressure.

(Refer Slide Time: 00:43)



Heat Calculation

First law of Thermodynamics is applied to calculate the heat released from a combustion reaction. As mentioned earlier, a combustion reaction is an exothermic oxidation reaction.

Heat is released from the combustion reaction due to the difference in the energy contents of reactants and products.

Reactants have higher energy (enthalpy) than the products. Therefore, the difference in this energy comes out as heat, when the reactants are converted to the products.

Consider a system with reactant mixture. This is considered as the state 1. Upon ignition, reaction occurs and products are formed. This is considered as state 2. First law states that $Q_{1-2} - W_{1-2} = U_2 - U_1$, neglecting the changes in KE and PE.

So, first law of thermodynamics is applied to calculate the heat released from a combustion reaction. Combustion is an oxidation reaction which is exothermic in nature

Heat is generated and transferred to the surroundings and first law is used based upon what is the problem in hand. Heat is released from the combustion reaction due to differences in the energy levels of the reactants and the products. You can say energy or enthalpy of the reactants and the products. So, heat is released because the reactants are at higher energy level than the products. The difference in the energy comes out as heat.

Let us consider a system. System is a space under consideration in which there will be energy transfers like work transfer and heat transfer etcetera, but there is no mass transfer which is taking place. So, initially you fill up the reactants in that and upon ignition products are formed. No other mass transfer is allowed. We can say it is a closed system and this system initially has reactants. The reactant state is defined as state 1. Once ignition is accomplished then chemical reaction occurs and products are formed. So, that the products when completely formed that state is called state 2. Now, the first law can be applied to this state. We have already seen that this is a highly irreversible process.

Once the reactants are converted into products as the reverse reaction is not possible and you give sufficient time for the reaction to occur as we do in thermodynamics after the completion of reaction you get the state 2 where only products are present.

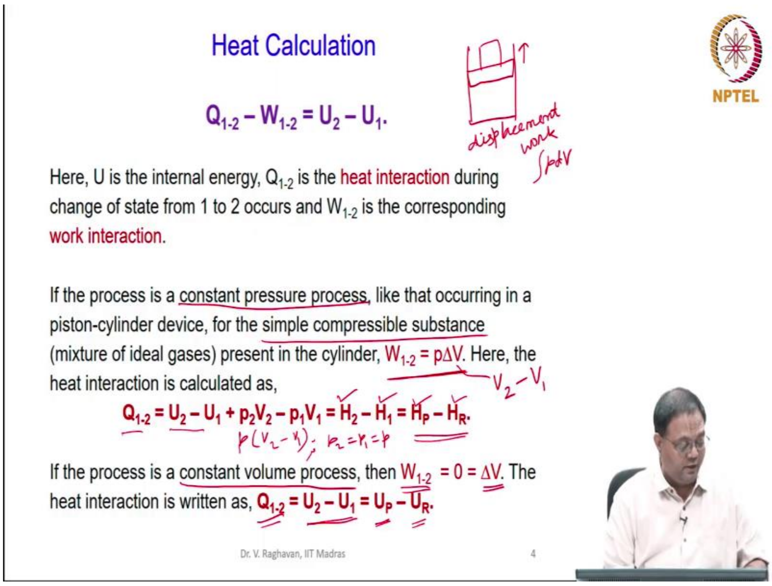
What is the combination of product formed etcetera we will see based upon what is the temperature prevailing in the combustion chamber or the system, we will calculate it using these laws.

Now, if you apply the first law of thermodynamics between these two states; initial state is state 1 reactant state and final state 2 is the product state. During this process what is the heat interaction between the system and the surrounding that is labelled as Q_{1-2}. Q_{1-2} is the heat interaction between the system and the surrounding when this change of state from 1-2 occurs.

Similarly, there may be some work interaction that is defined as W_{1-2}. So, in the absence of changes in the kinetic energy and potential energies, the only energy change what we see is the change in the internal energy $U_2 - U_1$. So, the first law of thermodynamics for this system is written as the difference between the heat interaction and the work interaction is equal to the change in the internal energy of the system.

So, if there is a change in kinetic energy or potential energy that may also be added here. In many cases the changes in kinetic energy and potential energy are negligible. We neglect that so that we can write the first law as stated here.

(Refer Slide Time: 04:19)



Heat Calculation

$$Q_{1-2} - W_{1-2} = U_2 - U_1.$$

displacement work $\int p\,dV$

Here, U is the internal energy, Q_{1-2} is the heat interaction during change of state from 1 to 2 occurs and W_{1-2} is the corresponding work interaction.

If the process is a constant pressure process, like that occurring in a piston-cylinder device, for the simple compressible substance (mixture of ideal gases) present in the cylinder, $W_{1-2} = p\Delta V$. Here, the heat interaction is calculated as,

$V_2 - V_1$

$$Q_{1-2} = U_2 - U_1 + p_2V_2 - p_1V_1 = H_2 - H_1 = H_P - H_R.$$

$p(V_2 - V_1)$; $p_2 = p_1 = p$

If the process is a constant volume process, then $W_{1-2} = 0 = \Delta V$. The heat interaction is written as, $Q_{1-2} = U_2 - U_1 = U_P - U_R$.

Dr. V. Raghavan, IIT Madras

So, this is the first law of the system. Here U is the internal energy and Q_{1-2} is the heat interaction during the change of state and W_{1-2} is the corresponding work interaction when the change of state occurs.

Now, let us consider two cases: in one, the pressure of the system is held constant. So, if the pressure of the system is constant, it is called constant pressure process. For example, we consider a piston-cylinder arrangement in the cylinder there is a piston which is almost frictionless and free to move.

Based upon the pressure rise inside the system the piston can move up gradually. If you take this device the pressure is held constant because of the movement of the piston and you can operate this at any pressure based upon whatever external load you have.

So, let us keep the pressure constant say p and you have this ideal gas mixture which is going to be there. So, initially the reactants or ideal gas mixtures are present then products are formed adiabatically. They are simple compressible substances. So, mixture of ideal gases are simple compressible substances and they are present in the cylinder

This movement of the piston in the cylinder contributes to what is called the displacement work. Normally it is given by p times dV integral pdV.

Now, since pressure is constant, we can write the work interaction, the displacement work which is involved in the constant pressure process like a piston cylinder device as p × ΔV; ΔV is a change in the volume $V_2 - V_1$. The piston goes up from a volume of V_1 and the gas has now occupied a volume V_2 in the second state; pressure is constant. Now, incorporate this in the first law and write this. You can say that the heat interaction will be equal to the change in internal energy $U_2 – U_1 + p_2V_2 - p_1V_1$, but actually this is nothing, but $p \times (V_2 - V_1)$. So, in other words, $p_2 = p_1 = p$. In a constant pressure process, I can write this. Why I am doing this here because I am going to club $U_2 + p_2V_2$ and $U_1 + p_1V_1$ and as per the definition they are the enthalpies. So, $U_2 + p_2V_2 = h_2$ and $U_1 + p_1V_1 = H_1$.

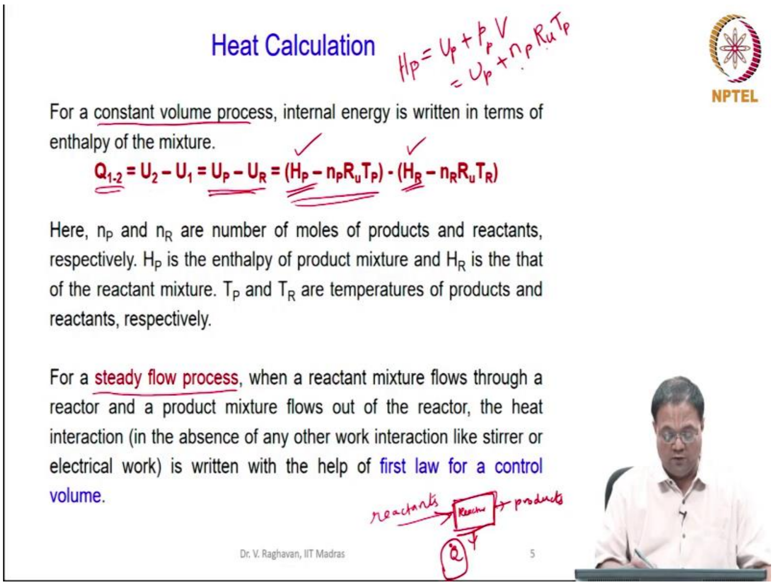
So, $H_2 - H_1$ that is a final state enthalpy minus initial state enthalpy which is nothing, but the enthalpy of the product mixture minus the enthalpy of the reactant mixture. So, that will be the heat interaction. The heat interaction in the system will be the enthalpy of the product mixture minus enthalpy of the reactant mixture, if the combustion occurs during a constant pressure process.

On the other hand, if the process is constant volume like in a bomb calorimeter, we have a constant volume rigid vessel and you allow the pressure to rise. Now, what happens is since the volume does not change $\Delta V = 0$; that means, the displacement work will be equal to 0.

W_{1-2} will be p × V. So, $\Delta V = 0$. The $dV = 0$. So, $W_{1-2} = 0$. So, in this scenario you get the heat interaction Q_{1-2} as the change in the internal energy U_2 the final state internal energy minus U_1 the initial state internal energy or the products internal energy minus the reactant internal energy.

For a system undergoing a constant pressure process the change in the enthalpy will be the heat interaction. So, Q_{1-2} will be equal to $H_P - H_R$, for the constant volume process the heat interaction will be the change in the internal energy. So, $Q_{1-2} = U_P - U_R$. This is the first law applied to a system.

.(Refer Slide Time: 09:18)



Heat Calculation

$$H_p = U_p + p_p V = U_p + n_p R_u T_p$$

For a constant volume process, internal energy is written in terms of enthalpy of the mixture.

$$\underline{Q_{1-2}} = U_2 - U_1 = \underline{U_P - U_R} = \overset{\checkmark}{(\underline{H_P - n_P R_u T_P})} - \overset{\checkmark}{(H_R - n_R R_u T_R)}$$

Here, n_P and n_R are number of moles of products and reactants, respectively. H_P is the enthalpy of product mixture and H_R is the that of the reactant mixture. T_P and T_R are temperatures of products and reactants, respectively.

For a steady flow process, when a reactant mixture flows through a reactor and a product mixture flows out of the reactor, the heat interaction (in the absence of any other work interaction like stirrer or electrical work) is written with the help of first law for a control volume.

Dr. V. Raghavan, IIT Madras

Now, let us expand this more. Consider a constant volume process. We have arrived that the in the heat interaction will be equal to U_2 - U_1 or U_P - U_R. Now, generally it is not easy to measure internal energies. So, when you want to measure it is easy to measure the enthalpy of the individual species.

Normally it is easy to calculate the enthalpy of the mixture, product mixture or reactant mixture. They are tabulated say in NIST website and so on. So, the enthalpy tables are available but internal energies are calculated based upon the definition of the enthalpy.

For example, H_P the products enthalpy can be written as U_P + pressure of the product × volume; volume is constant now this is constant volume process. So, based upon this we can also write U_p plus this pV can be written as nR_uT the equation of state for the ideal gas.

So, number of moles of the product mixture × universal gas constant R_u × T. Now, U_P can be calculated as H_P - n_PR_uT. So, in terms of enthalpy and using the equation of state we calculate the internal energy of the product mixture.

You have to first calculate the enthalpy of the product mixture, then use the equation of state to calculate n_PR_uT and subtract it from that so that you get the internal energy of the product mixture. Similarly, you do it for the reactants and this difference is the heat energy which is normally enthalpy. So, this means that the enthalpy is very important for us. Calculating the enthalpy of the mixture is very important.

So, how to calculate that, that is the important thing, we should see later. Now, here as I told you n_P and n_R are the number of moles of the products and reactants in kilomole and H_P is the enthalpy of the product mixture and H_R is that of the reactant mixture. T_P and T_R are the temperatures of the product and reactants. So, this is the way we write for the system.

Now, if you take several reactors, they are not system based, they are flow process. You inject the reactants and products come out. For example, I can inject the reactant in a furnace and the product comes out as the exhaust gas after going through the boilers.

This means that we have to consider a control volume. In this control volume mostly after the initial transient operation this process will be continuously in steady state. We continuously feed reactants and the products come out. The variations are not much with time. It is almost a steady state steady flow process.

Let us consider such a steady flow process, now we need a control volume for this. What happens here is the reactant mixture flows through the reactor which is a control volume. For example, I have a control volume like this and the reactant mixture flows through this, then combustion occurs in this reactor. This is a control volume.

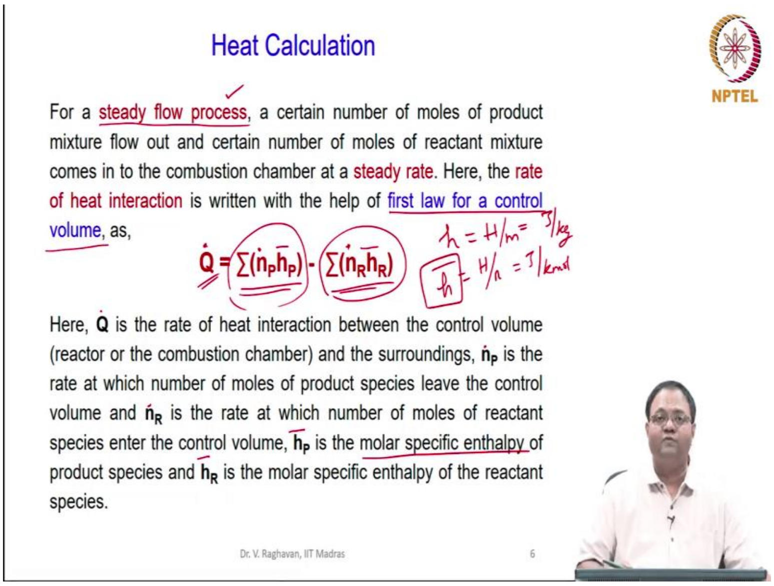
Reactant comes in and whatever heat is generated we can take it out. Heat interaction is allowed here. Similarly, products go out. Here you can see that heat interaction is allowed. Similarly, you can also have some work interaction like stirring work and so on. Normally we do not have stirrer in a combustion chamber, nobody stirs a combustion chamber. So, heat which is released during the chemical reaction will be absorbed by the surroundings.

So, heat is transferred to the surroundings; reactants enter reaction takes place and heat is transferred to the surrounding and the products leave. This is a control volume in which we are trying to apply the first law. So, this is the $\dot{Q}$ what we are trying to find now.

So, this is a steady process. Initially when you start the reactor it may be time dependent. For example, if the reactor is going to run for say some few months; initially for some few hours it may be time dependent in nature, after that slowly it will become steady. We will be able to supply that required fuel flow rate, air flow rate.

So, reactant is fed at a given velocities and mass flow rates, then products are formed. They come out with whatever temperature you want based upon the heat interaction what you do with the reactor. I am not considering any work interaction; I am considering heat interaction in the absence of any other work. There is no displacement work here since volume is constant. But we can have some other type of work such as stirring work, electrical work etcetera, but not suitable for this particular reactor. We do not normally use that. So, we have to use what is called the first law for control volume to determine $\dot{Q}$.

(Refer Slide Time: 15:02)



Heat Calculation

For a steady flow process, a certain number of moles of product mixture flow out and certain number of moles of reactant mixture comes in to the combustion chamber at a steady rate. Here, the rate of heat interaction is written with the help of first law for a control volume, as,

$$\dot{Q} = \sum(\dot{n}_P \bar{h}_P) - \sum(\dot{n}_R \bar{h}_R)$$

$h = H/m = J/kg$

$\boxed{\bar{h}} = H/n = J/kmol$

Here, $\dot{Q}$ is the rate of heat interaction between the control volume (reactor or the combustion chamber) and the surroundings, $\dot{n}_P$ is the rate at which number of moles of product species leave the control volume and $\dot{n}_R$ is the rate at which number of moles of reactant species enter the control volume, $\bar{h}_P$ is the molar specific enthalpy of product species and $\bar{h}_R$ is the molar specific enthalpy of the reactant species.

Dr. V. Raghavan, IIT Madras

Here, I have not put these dots for convenience. I have written the nomenclature below this equation. So, I have not put dots normally it is better to put dots here to represent the rate at which heat is released. When you want to say rate at which a particular quantity is transferred then it is customary to put a dot over this.

Here, you can see that a certain number of moles of products product mixture flow out at a given rate So, $\dot{n}_P$ is the number of moles of the product mixture. So, $\dot{n}_P$ dot means number of moles which is going out per unit time.

Similarly, $\dot{n}_R$ dot it is a number of moles of the reactants which are coming in at a particular time dependent rate. Actually, this is steady. Please understand that the rate at which number of moles of product leave the combustor is not equal to rate at which the number of moles of reactant enter, but mass is same.

The mass of the reactants entering the combustion chamber will be same as the mass of the product which are leaving. In fact, mass of the fuel plus mass of the oxidizer will be equal to mass of the product. So, mass is conserved, but the number of moles need not be conserved. We can see that the first law of control volume states that the rate at which heat interaction occur. So, I have written here Q I have not put dot, but anyway you can put dot also if you want. $\dot{Q}$ is the rate at which heat interaction occurs between the control volume and the surrounding. The control volume is reactor or the combustion chamber and $\dot{n}_p$ is the rate at which number of moles of the products species leave.

Similarly, $\dot{n}_R$ is the rate at which the number of moles of reactants species enter the control volume. Again, one more nomenclature is if you say see Turns books for molar specific quantities say molar specific enthalpy. So, $\bar{h}_p$ is the molar specific enthalpy of the product species.

When you put an overhead bar I emphasize the fact that it is a molar based quantity. So, if I say h this is H / m which is J/kg. When I say $\bar{h}$ bar this is H / n which is J/kmol.

So, $\bar{h}_p$ is the molar specific enthalpy of the product species and $\bar{h}_R$ is the molar specific enthalpy of the reactant species. For example, we will write the equation and we have already seen how to do this.

So, for example, if there is a 1 mole of methane and say 2 moles of oxygen, then reactant species is 1 × H_{CH_4} + 2 × H_{O_2}. So, that summation is done here to get the mixtures enthalpy.

Similarly, for product CO_2, H_2O and nitrogen may be present. So, based upon the number of moles of each species you have to multiply the number of moles times the enthalpy. So, number of moles of species should be multiplied to get the product enthalpy and reactant enthalpy. In summary this is nothing but product enthalpy minus reactant enthalpy because this flow process is normally a constant pressure process.

So, we have already seen here for a constant pressure process Q_{1-2} heat interaction in a system, Q_{1-2} is H_P - H_R, the change in the enthalpy of the system. That is, H_P the final state enthalpy - H_R the initial state enthalpy.

Similar to that for steady flow process you see that this is the product enthalpy and this is the reactant enthalpy.

So, the rate at which the heat is released from the combustion chamber or the reactor will be equal to the rate at which the enthalpy of the product leave and rate at which the enthalpy of the reactants enter. That is the difference here. But the point I want to emphasize here is the steady state, the steady flow process is also a constant pressure process.

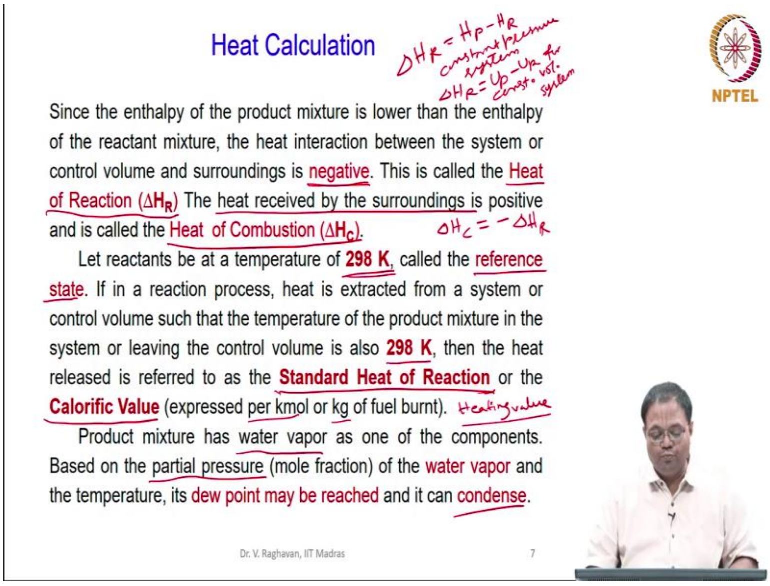
Pressure remains almost a constant not much variation will be fine. Any flow process will behave like a constant pressure process so pressure will not change much. So, this is the application of first law.

Just quickly recollect first law for a system. There is no mass transfer allowed here. It is written in simple terms the heat interaction will be equal to H_P - H_R if the process is constant pressure process or the heat interaction it is written as U_P - U_R, change in internal energy if this is a constant volume process.

You have to keep in mind that the internal energies are written in terms of enthalpy and the equation of state. For a steady flow process, the rate at which the reactant enter and rate at which the number of moles of products leave are taken into consideration. The rate at which heat transfer occurs is calculated using the simple equation.

So, for all this we require enthalpy values. Normally we go for molar specific enthalpy values H for each species and try to find the mixtures values.

(Refer Slide Time: 21:05)



Heat Calculation

$\Delta H_R = H_P - H_R$ constant pressure system

$\Delta H_R = U_P - U_R$ for const. vol. system

Since the enthalpy of the product mixture is lower than the enthalpy of the reactant mixture, the heat interaction between the system or control volume and surroundings is negative. This is called the Heat of Reaction (ΔH_R) The heat received by the surroundings is positive and is called the Heat of Combustion (ΔH_C). $\Delta H_C = -\Delta H_R$

Let reactants be at a temperature of **298 K**, called the reference state. If in a reaction process, heat is extracted from a system or control volume such that the temperature of the product mixture in the system or leaving the control volume is also **298 K**, then the heat released is referred to as the **Standard Heat of Reaction** or the **Calorific Value** (expressed per kmol or kg of fuel burnt). Heating value

Product mixture has water vapor as one of the components. Based on the partial pressure (mole fraction) of the water vapor and the temperature, its dew point may be reached and it can condense.

Dr. V. Raghavan, IIT Madras

Now, heat calculation. Since the enthalpy of the product mixture is lower than that of the reaction reactant mixture the heat interaction between the system or the control volume and the surroundings is negative. The heat interaction is negative means the heat is transferred out of the system or out of the control volume by the sign convention of heat; heat transfer to a system or heat transfer to a control volume is considered positive. On the other hand, if heat is rejected by a system or control volume it is taken as negative.

So, by this convention, it is called heat engine convention, for the heat engine the heat given to the heat engine is positive and heat rejected by the heat engine is negative. The difference between these two is the work.

So, by the heat engine convention we will see that the heat interaction in a system or control volume is actually negative because the heat is rejected by this reactor to the surroundings. This change is called heat of reaction and we represent that by ΔH_R. So, ΔH_R is a heat of reaction.

Now, we will say $\Delta H_R = H_P - H_R$ for constant pressure system. Similarly, I can write $\Delta H_R = U_P - U_R$ for constant volume system. Since H_P is lesser than H_R or U_P is lesser than U_R you get ΔH_R as a negative quantity implying that the heat is rejected from the system or control volume to the surroundings. So, the heat received by the surroundings that is for a surrounding, taking surrounding as a system now, you will see that the heat interaction is positive.

Surrounding can be taken as a control volume or system and that is positive now. This heat which is received by the surrounding is called heat of combustion. So, that is ΔH_C. Now, we can say that ΔH_C is equal to $-\Delta H_R$.

So, by applying the first law we will be able to calculate the heat of reaction. Heat of reaction is ΔH_R. Based upon the final state the product we will calculate the enthalpy or internal energy of the product mixture by can calculating the enthalpies of the individual species in the product. Applying chain rule or mixing rule what we say, we calculate the enthalpy of the product mixture. Similarly, calculate the enthalpy of the reactant mixture and calculate ΔH_R.

Normally you know the we have to have some reference state. Please understand that for all these properties we have to have some reference state. Actually, two properties are required to fix this - one is pressure another is temperature.

So, the temperature is taken as 25^oC. It is ambient temperature 298 K, 25^oC or 298 K that is taken as the reference temperature. Reference pressure is 1 atmosphere. But enthalpy or internal energy does not depend on the pressure. So, it is better to only refer the temperature here. Let the reactants be at a temperature of 298 Kelvin which is reference temperature reaction occurs and products are formed. Once the products are completely formed you try to extract heat so that the products cool. They also reach a temperature of 298 K. So, you cool the products until the products reach the temperature of 298 K. Reactants enter at 298 K and reaction occurs, then the heat is extracted such that the products are going to be cooled and products reach the reference state of 298 K.

In this scenario, the heat released or the heat of reaction is called standard heat of reaction because we are operating in the standard state initially reactants are at standard state and finally products are also in the standard state. So, you will be able to extract whatever heat is possible that heat of reaction is this.

So, please understand that the heat of reaction is not a constant because of the variation in temperature. For example, reactants can come in at any temperature I can preheat air and supply with fuel or for example, I can heat the liquid fuel to some temperature and supply the hot liquid fuel or vaporize that under hot condition and supply the vapours, hot vapours. Reactants may not enter at 298 K they can enter at any temperature. Similarly, I need not completely cool it. There is a danger of cooling it completely because the reaction may not fully complete. If I do that instead of coming out at 298 K the products can come out at say 500 K or something like that.

In such scenarios the heat of reaction can be varying because of the conditions. The enthalpy is calculated at a particular temperature for each species and the mixing rule is used to find the products reactant or product mixtures enthalpy and it is used in ΔH_R calculation. But when I say standard heat of reaction, I actually do the calculation. It may not be possible to do this.

We can actually extract data and get this based upon the property evaluation. I can calculate what is the amount of heat that can be extracted such that the reactants are at 298 K and products formed are also cooled to 298 K. That will give me the maximum heat which can be extracted.

Because the atmospheric condition is 298 K let us say, I cannot cool it beyond 298 K. It is not worth it to cool below the atmospheric temperature. So, what I emphasis here is the standard heat of reaction is the heat which is extracted until the products are cooled to 298 K which is the maximum value what we get. This standard heat of reaction is called the calorific value.

So, this is expressed in kmol/kg of fuel. You can see that this calorific value or heating value. Under a particular reference condition or a standard condition if this experiment is done and heat interaction is calculated then you get the calorific value or heating value which is called standard heat of reaction.

Basically, the calorific value or heating value are negative of standard heat of reaction. It is heat of combustion. So, you can say standard heat of combustion is called calorific value or heating value because that should be positive. If heat of reaction is negative standard heat of reaction is also negative.

Now, this is one definition what we want. This will be an important property for a particular fuel. What is the standard heat of reaction? Calorific value is very important property as we have already seen.

Now, the products when you have a hydrocarbon or hydrogen, you burn the hydrogen and water vapour is produced. So, based upon the temperature when you try to cool it for example, when you try to extract the heat the temperature is going to be reduced. So, when you go to say 298 K what happens is some of the water vapor in the products may condense to liquid. So, that means, that we have two scenarios now. If none of the water is going to be condensed or if all the water condenses what will be the standard heat of reaction. Again, I am trying to cool the products to 298 K, supplying reactants at 298 K. Now, what happens to the water vapor in the product mixture?

So, we know definitely that 100 is the boiling point of the water, but you have a partial pressure for water vapour. For example, water vapour is only having some mole fraction among the products with which it is existing.

So, based upon the partial pressure of the water vapour a dew point temperature may occur when you steadily cool it. After it reaches this dew point temperature the water condenses. So, the two scenarios you can see - one scenario we can assume all the water to be in vapour state or we can assume that all the water has condensed to a liquid state.