Basic Thermodynamics

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Lecture - 27

Thermodynamics of Reacting System-I

Good morning. Today we will start a new chapter thermodynamics of reacting systems. When reaction takes place, new species are formed. So far we have discussed in thermodynamics that the process takes place between difference species, where the species remain unchanged. There is no formation of a new species or depletion of original species.

When chemical reaction takes place, from some original species new species are formed. This is because of breaking inter automatic or internal molecular bounds and readjustments of the atoms, molecules or electrons we are not going that deep. The new species are formed from some old species. This is basically how we can define a chemical reaction classically. In this case, the new species that forms from the old species…. the analysis is almost the same, but with a little different approach.

Let us know the representation of reactions. Let us consider a reaction like with two species A and B. They react to form C and D.

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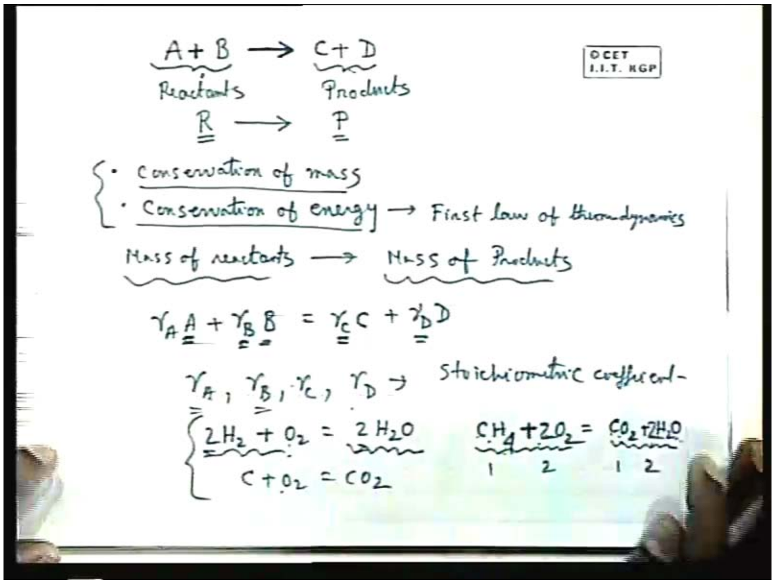

$$\underbrace{A+B}_{\text{Reactants}} \longrightarrow \underbrace{C+D}_{\text{Products}}$$

$$\underline{\underline{R}} \longrightarrow \underline{\underline{P}}$$

- Conservation of mass
- Conservation of energy → First law of thermodynamics

Mass of reactants → Mass of Products

$$\gamma_A \underline{\underline{A}} + \gamma_B \underline{\underline{B}} = \gamma_C \underline{\underline{C}} + \gamma_D \underline{\underline{D}}$$

$\gamma_A, \gamma_B, \gamma_C, \gamma_D$ → Stoichiometric coefficient

$2H_2 + O_2 = 2H_2O$ $\quad \underbrace{CH_4}_{1} + \underbrace{2O_2}_{2} = \underbrace{CO_2}_{1} + \underbrace{2H_2O}_{2}$

$C + O_2 = CO_2$

If a chemical reaction is expressed like this, that two species react with each other in an conducive environment when the reaction is possible and produces C and D. In that case there are certain terminologies, this A and B, the original species are known as reactants and the species which are formed out of the reactants are known as products. Therefore, we write a reaction symbolically as reactant to products. The reactants may constitute different species and products may constitute different species. As a whole these species which are being formed are known as products.

These species which react with the initial species to form the products are known as reactants so reactants to products. When this reaction takes place, the total mass of the reactants must be equal to the total mass of the products. For these reactions, the conservation principles of mass and energy has to be obeyed. They cannot violate the principle of conservation, mainly the conservation of mass and conservation of energy separately. Mass to energy and energy to mass is excluded. As we have done for other processes and reacting processes; for a chemical reaction also, conservation of mass and conservation of energy have to be obeyed separately.

The scope of the first law of thermodynamics deals with the conservation of energy. The second law of thermodynamics will be applied to find out the direction in which the reaction will take place. For any process the conservation of energy is the first law and deals with things that how much heat has to be removed or how much heat has to be added, how much work is done or how much work is added, for a process to change from one state to other state.

Whether a process will take place in a particular direction whether from one state another final state is achievable or not, if achievable what should be the directions in which it will be achievable? These are the information furnished by second law. We must know that, even if the conservation of energy is stated by the first law, it is a quantitative statement of the conservation of energy.

Second law is an independent law, which gives the feasibility of a process, the direction in which a process takes place. We have discussed in detail these things. Similarly, the second law tells us in the direction in which reaction takes place. For example, in this reaction, C+D may also react to give A+B. So, when C + D are formed, this will again react produce A+B.

Net reaction will go in which directions? Whether A+B will be depleted finally to give C+D or in the reverse direction? The direction in which the reaction will take place and also the equilibrium composition of reactant at the present moment looks like an information. These are being furnished by the second law of the thermodynamics.

First, we will discuss the conservation of mass and then conservation of energy. Conservation of mass is the reaction in which no mass can be destroyed. Therefore mass of reactants must be equal to mass of products. So, mass of reactants must be equal to mass of products.

We will write this chemical equation in a balanced form. Let A and B are the typical species, which may be element or compound, C and D are also like that. They have got some fixed number of moles to make the reaction complete. For example, we can write gamma_AA plus gamma_BB gives gamma_CC plus gamma_DD.

This is the basic chemistry. That gamma A number of moles of A can react with gamma B number of moles of B. These are the necessary and sufficient condition is gamma A is the necessary condition. You can tell gamma A number of moles of A can react with gamma B number of moles of B to produce gamma C number of moles of C and gamma D number of moles of D. These are the number of moles which are required to balance the equation. These gammas are known as gamma A, gamma B, gamma C, gamma D, stoichiometric coefficients.

For example, $2H_2 + O_2 = 2H_2O$. So stoichiometric coefficients are 2 gamma A, 2 gamma B 1 and gamma C gamma D. That means 2 moles of hydrogen react with 1 mole of oxygen to give 2 moles of water.

Similarly, $C + O_2 = CO_2$. Here all stoichiometric coefficients are 1, for reactants and products, which is 1 mole. This gives the mass balance, the mass for the reactants equals to the mass of the products.

Another example, if you consider a combustion reaction of fuel methane, which reacts with oxygen, CH_4 +2O2=CO + $2H_2O$. Therefore, gamma A is 1, gamma B is 2, gamma C is1, gamma D is 2, so these are the 1 2 1 2 are the stoichiometric coefficient means, 1 mole of methane requires 2 moles of oxygen to produce 1 mole of carbon dioxide and 2 moles of water vapor. For a complete conversion, these are the mole ratios.

If we have to multiply or take more moles, it means that, these moles are correspondingly multiplied with the stoichiometric coefficient. You can multiply 2, 3 by any integer in both the left hand and right hand side, but the mole ratios will be proportion way of this stoichiometric coefficient. Professor Das mentioned that, in all cases the total mass in of reactants must be equal to the total mass of the products. We shall first understand these things with a simple problem. Whatever we have discussed will be made clearer, if we go through the simple problem.

Let us see this problem... A fuel has a mass analysis by chemical element of 85 percent carbon,

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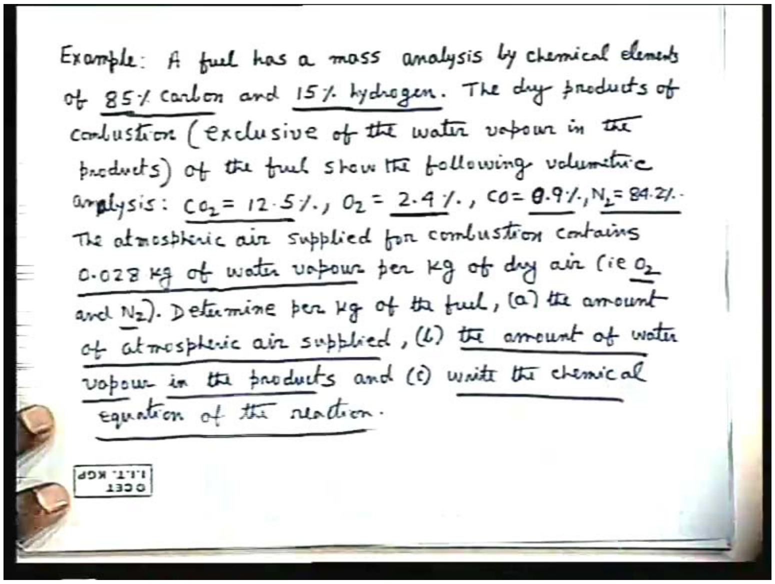

Example: A fuel has a mass analysis by chemical elements of 85% carbon and 15% hydrogen. The dry products of combustion (exclusive of the water vapour in the products) of the fuel show the following volumetric analysis: $CO_2 = 12.5\%$, $O_2 = 2.4\%$, $CO = 0.9\%$, $N_2 = 84.2\%$. The atmospheric air supplied for combustion contains 0.028 kg of water vapour per kg of dry air (ie O_2 and N_2). Determine per kg of the fuel, (a) the amount of atmospheric air supplied, (b) the amount of water vapour in the products and (c) write the chemical equation of the reaction.

85 percent carbon is mass analysis and 15 percent hydrogen. These are the pertinent data. The dry products of combustion, exclusive of the water vapor in the dry products that means without water vapor, dry products show the following volumetric analysis. CO_2= 12.5 percent, O_2=2.4 percent, CO=0.9 percent and N_2=84.2 percent. The atmospheric air supplied for combustion, this is the combustion reaction. The rapid exothermic oxidation of a hydrocarbon with oxygen is known combustion reaction. Combustion contains 0.028kg of water vapor per kg of dry air. Dry air means oxygen and nitrogen.

We have to determine per kg of the fuel, the analysis have to be made per kg of the fuel. The amount of atmospheric air supplied the amount of water vapor in the products and we have to write the chemical equation of the reaction.

The problem has got 85 percent carbon and 15 percent hydrogen by mass. The dry products show a composition by volume, carbon dioxide oxygen, carbon monoxide nitrogen. Nitrogen comes from air. These are the constituents of the products keep it in mind and the atmospheric air supplied for combustion contains this much kg that is 0.028kg of water vapor per kg of dry air. We have to find out the amount of atmospheric air supplied, the amount of water vapor in the products and we have to write the chemical equation. This type of problem is totally based on the analysis by mass.

First of all we have to find out the number of moles. We know that 85 percent Carbon and15 percent hydrogen.

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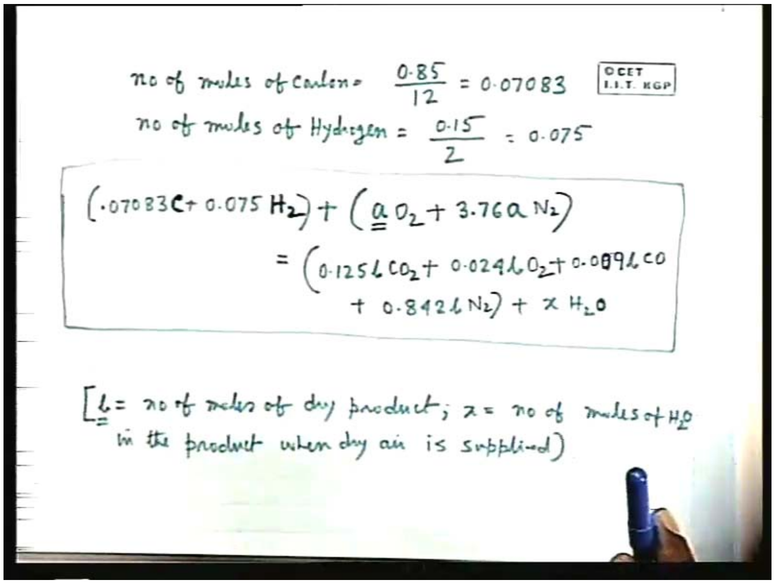

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no of moles of Carbon = $\frac{0.85}{12} = 0.07083$

no of moles of Hydrogen = $\frac{0.15}{2} = 0.075$

$$\boxed{\begin{aligned}&(.07083\,C + 0.075\,H_2) + (\underline{\underline{a}}\,O_2 + 3.76a\,N_2)\\ &\quad = (0.125b\,CO_2 + 0.024b\,O_2 + 0.009b\,CO + 0.842b\,N_2) + x\,H_2O\end{aligned}}$$

[$\underline{\underline{b}}$ = no of moles of dry product; x = no of moles of H_2O in the product when dry air is supplied)

Number of moles of carbon is per kg. We have to make the analysis per kg of fuel, so 1kg of fuel is 0.85 kg of carbon. Hence, the number of moles will be 0.85 by the molecular weight of carbon is 12. So, this gives the figure 0.07083. Similarly, the number of moles of hydrogen can be found. 0.15 kg, 15 percent by mass, that means per 1kg of fuel it will be 0.15kg and the molecular weight of hydrogen is 2. This will give the value 0.075, which is the number of moles of hydrogen.

We can start with this, fuel is expressed as (0.07083 C + 0.075 H_2), it is not known whether air is sufficient or more. We know stoichiometric chemical reaction that for 1mole of fuel…. For example, if we consider the burning reaction or combustion reaction this much mole of air is required but if you use more air or more oxygen is needed, this is known as excess air. This is usually expressed in terms of percentage over the theoretical air.

Theoretical air is the air or oxygen required just for a complete reaction of one mole of the fuel. We consider a as the number of moles of the air. We can write as, a O_2, there is no number of moles for O_2, this will be 3.76 a N_2. We assume ‘a’ as unknown number of moles of O_2 is being supplied and 3.76 numbers of moles of N_2 will be supplied because nitrogen to the oxygen volume ratio is 3.76. This has to be known and the ratio of volume is ratio of moles because mole represents the volume.

One mole of oxygen and one mole of nitrogen represent the same volume at the same pressure and temperature. Therefore, the mole fraction is equal to the volume fraction and is scaled by their molecular weight. The mass is scaled by their molecular weight to express the volume or the moles. The moles are representative of the volumes, so mole fraction is the volume fraction and volume fraction is the mole fraction, which are 3.76.

Let b is the number of moles of dry product per kg of fuel and x is the number of moles of H_2O in the product. When dry air is supplied; we will have to assume these two things, because these are not known priory. Therefore, we have to use the b as number of moles of dry air dry product and x is the number of moles of H_2O in the product when dry is supplied. H_2O is formed because of the reaction of hydrogen of the fuel with oxygen of the air.

If, b is the number of moles of dry product, we can find out the number of moles of the carbon dioxide oxygen and carbon monoxide, which are the constituents of the products. Since their volumetric composition given is 12.5 percent that means, I can write 0.125 b into CO_2. 2.4 percent by volume means, the number of moles of b is the total number of moles of dry product, which means it will be 0.024. 2.4 percent into b will be representing the mole of oxygen.

Carbon monoxide is 9 percent that means it will be 0.009CO. Nitrogen is 84.2 percent, which is plus 0.842 into b into nitrogen and we consider x as the number of moles of H_2O when dry air supplied. First, we will consider dry air because in wet air due to moisture it will be added both on the left and right hand side. This is what is found from the reaction: water vapor is generated in the product because of the reaction of hydrogen and oxygen xH_2O. If we can write this equation in molar form then, next is your application of the conservation equation means conservation of mass. Now you apply the conservation of mass and so first make the mass balance of C. If you make the C balance C is here.

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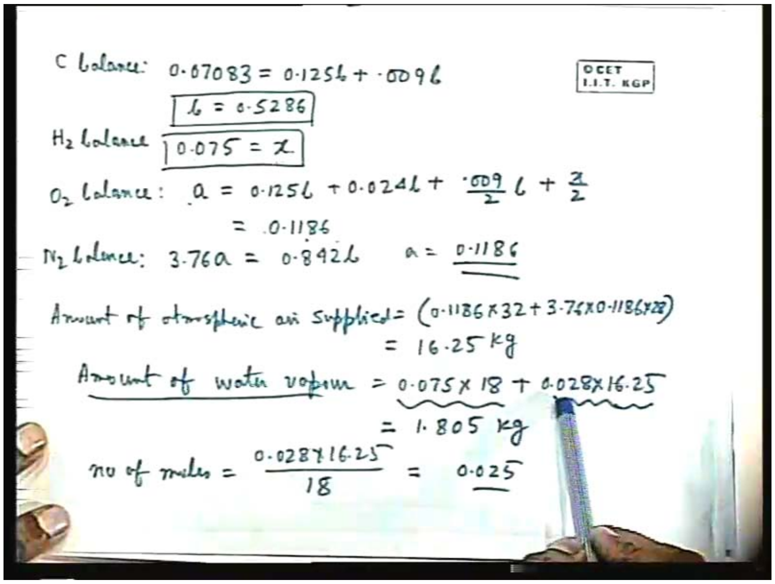

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C balance: $0.07083 = 0.125b + .009b$

$\boxed{b = 0.5286}$

H_2 balance $\boxed{0.075 = x}$

O_2 balance: $a = 0.125b + 0.024b + \frac{.009}{2} b + \frac{x}{2}$

$= 0.1186$

N_2 balance: $3.76a = 0.842b$ $\quad a = \underline{\underline{0.1186}}$

Amount of atmospheric air supplied $= (0.1186 \times 32 + 3.76 \times 0.1186 \times 28)$

$= 16.25$ kg

Amount of water vapour $= 0.075 \times 18 + 0.028 \times 16.25$

$= 1.805$ kg

no of moles $= \frac{0.028 \times 16.25}{18} = \underline{0.025}$

Therefore we can write 0.07083 = 0.125b + 0.009b. This is an explicit equation for b and it gives; b = 0.5286. We get kg mole of dry products per kg of fuel, as you know the nomenclature of D. H_2 balance is 0.075. These are all mass balance.

The total mass of reactant is equal to total mass of the products. Here, I am using a gross mass balance. You can track a particular element, which was combined in giving some product; which is going to other product. For example, hydrogen was there initially with carbon to define the compound hydrocarbon. Now it has gone with the water oxygen to define water vapor.

Therefore, a particular element or a single individual element mass is also conserved, because that element is not being destroyed, it is being recombined to give a different compound. That is the basic definition of reaction. If we track a particular element, this mass is being conserved before and after the reaction.

H2 is only here and straightway x is given so we get b. I get x explicitly from the two equations. Next, O_2 balance is, a equal to 0.125b in the reactants only, plus 0.024b plus 0.009 by 2b CO plus x by 2. Since, b and x are known beforehand, this gives explicitly a. If you put the value of b and x, then I get a value which equals to 0.1186. So, I get the value for b. This is value of x. You can trace that why cannot make nitrogen balance here. The problem should be well placed in such a way that even if you use the nitrogen balance you should not disturb the results because everything is found out.

If you make a nitrogen balance, we will get 3.76a. This will be redundant equation, in the sense that the balance is automatically maintained 3.76 a must be equal to…. We search for this thing where it is 0.842b. If you put the value of b, this also gives 0.186, but by calculation it comes to 0.84. However, it does not matter, that means we can tell that as a check. We can make the nitrogen balance is there or not with the values of abx. On the other hand, from the nitrogen balance we get explicitly a whether you get the same value of a or not.

Therefore everything is known, I can substitute a, b, c, so the entire equation is written as a chemical equation. We are in a position to find out all these things which have been asked. Per kg of fuel the amount of atmospheric air supplied. The amount of atmospheric air supplied will be 0.1186 O_2. Put the molecular weight; 32 + 3.76 × 0.1186 × 28 that means, this kg of dry air is supplied per kg of fuel. To find out the amount of water vapor in the products, you may tell that, I know this x H_2 and I know x, so the amount of water vapor is x × H_2.

Sometimes, this confusion is there, for hydrogen it is all light 1 2. But for oxygen, whether the atomic weight is 16 or the molecular weight is 16, it is 32. The key by which, I used to remember is the gravimetric composition of water is 1 each to 8. Remember the gravimetric composition that means the composition by weight of water vapor or H_2O compound is 1 each to 8. If this is so and hydrogen is 2, it has to be like that.

The amount of water vapor can be found out by: x × H_2O. So one can tell that you have got the value of x so it is as simple as this thing, 0.075 × 18, amount of vapor in the product; plus some amount is supplied with the air.

The atmospheric air supplied for combustion contains 0.02 kg of water vapor per kg of dry products, which means 0.028 × 16.25 kg. Therefore, this will be the total water vapor in the products and this value will be 1.805kg of water vapor per kg of fuel. I’ am not going to write the chemical equation, it is left to you as an exercise.

Chemical equation is very simple; we put the value of a, b and x, you get the chemical equation. When you write the chemical equation, do not forget to write the important thing here; some moles of the water vapor. How to find out the moles of water vapor? Because we have to write the chemical equation in terms of moles, so number of moles of water vapor which is carried with the air. I’ am not writing everything, this will be this part, that means 0.028 × 16.25 ÷ 18, gives a value 0.025,will be the number of moles of air.

When you write the equation, you will have to write 0.025 H_2O apart from x. This initially could not be written because, the value was not known. By putting the value of a, b and x as you have got a is 0.1186b, b is 0.5286 and x is 0.075, from which equation can be written. This gives you clear idea about the mass conservation. The chemical equation must be written in terms of moles.

Try to find out from that what are known and what are unknown? You have to assume some number of moles as unknown, which will automatically come out if you make the conservation of mass of a particular element taking part in the reactions. The mass balance will give the number of moles.

I will come to the conservation of energy or first law analysis.

It is kg and this one I have divided by 18. This is the kg, that is being generated from the reaction and this is by the problem 0.028kg of water vapor per kg of dry air, this is the kg of dry air and this is kg of water vapor which is carried by the dry air and is there before the reaction after the reaction. Thus, it gives equivalent moles. I will have to express in terms of mole. 18 is the molecular weight of water vapor.

Next is the important part which is the first law of conservation of energy. Before going into the analysis, I tell you certain things about conservation of energy of the first law.

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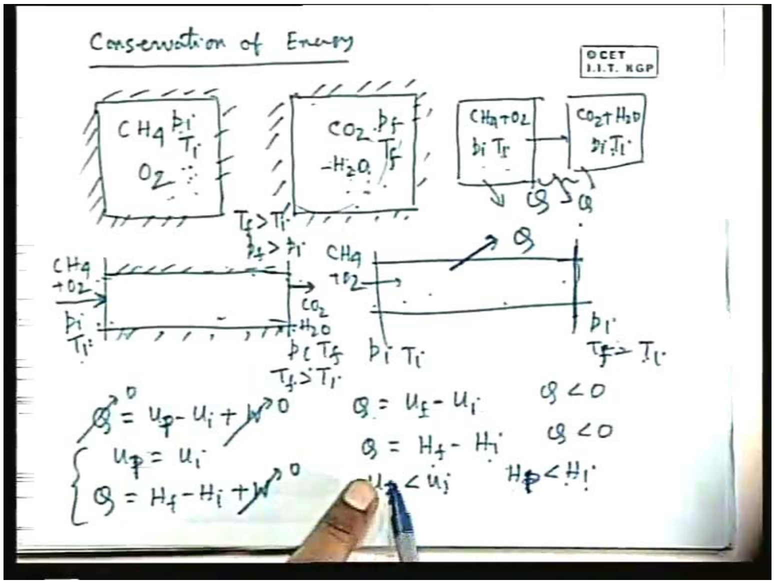

We will be restricting ourselves here for the combustion reaction, that is the burning or oxidation of hydrocarbon with oxygen. This is valid for all reactions to understand the physical thing. Let us consider that we have a closed insulated vessel and in the vessel we have methane and oxygen, which the environment is conducive for burning. Consider any pressure P_i and temperature T_i.

Initial pressure and temperature is in an equilibrium state initially, but this pressure and temperature are such that this is conducive for burning. I discussed about this in the problem, of how the burning takes place? For example, this is conducive for burning just at the outset of burning we consider this state. We see here, that the burning is completed.

Let us wait for sometime because burning will take sometime and the burning will complete. If we give sufficient time for burning to complete, then we have CO_2 and water vapor. Now, CH_4 will be left, because if we mix it with stoichiometric air or more than stoichiometric air all the CH_4 will be burnt and made insulated.

What did you observe practically? The pressure and temperature which will be generated will be higher than this. First, start with a common experience, because thermodynamic is based on the common experience. All the laws of thermodynamics are being determined and have been made from the day today experience from nature. Therefore, we see that T_f is greater than T_i and p_f is greater than p_i; that means temperatures are much more than the initial temperature.

Similarly, if we make an open system completely adiabatic and allow CH_4 and O_2 to enter through this section to this the steady process where the pressure and temperatures are p_i T_i will be conducive for burning. The burning is completed within this length and you come with CO_2 and H_2O which have a pressure.

In a steady flow process, pressure is constant until and unless we take care of the frication losses. We consider the pressure to be constant in ideal case, but T_f is greater than T_i; so temperature is increased. If, I write the first law of thermodynamics; we get Q is equal for both the cases U_f - U_i + W. There is no work transfer in this cases; W is 0 and there is no heat transfer in these two cases. Q is 0, means U_f has to be equal to $U_{i,}$ because of the first law the internal energy remains same, but the state point changes.

Here, the temperature and pressure is more; here the temperature is more even if the pressure is less. This is our common experience which tells that, probably the reactants and the products do not have the same internal energy at the same state. That means the internal energy of the products at this state is equal to the internal energy of the reactants at this state. These two states are different because this is P_i T_i P_f T_f. Here also the internal energy of the reactants at P_i T_i is equal to internal energy of the products at P_i T_f. Therefore we see the internal energy of the products and reactants are not same even the state is same.

Consider these two products and reactants as ideal gasses, that means two ideal gasses mixture of ideal gasses of different species and they do not reveal the same internal energy. We have to brush of our earlier knowledge to change this scale of internal energy something we have to do because we cannot hold that particular assumption. I go further step to strengthen this b.

Let us consider, that I want a reaction at isothermal condition, which means, I start with P_i T_i CH_4 + O_2 at P_i T_i and make the reaction isothermal, such that I end up with

CO_2+H_2O at P_i T_i. Our common experience tells; if I have to do this since with adiabatic condition the temperature suits up, that means to make an isothermal process of combustion, isothermal and isobaric, we have to continuously take heat so that heat has to come out. During the process, I have to continuously extract heat so that some amount of heat has to be taken out to make the process isothermal and that the initial pressure and temperature is isothermal.

I will also add pressure, such that initial temperature and final temperature will be equal; initial pressure and final pressure will be equal. Similar is the case here; if I have to make the process isothermal along with isobaric, that means T_i and T_f is equal to T_i. From our experience, as in adiabatic case, the temperature suits up, that means I will have to take out some heat out to make this condition same.

In that case, Q is not 0, but is equal to U_f - U_i. W is 0 in the both cases. If you write this for the stead flow process, this will be H_f - H_i + W, by a stead flow energy equation. That means W=0, I only told in terms of internal energy, when steady flow process is there, that means enthalpies are same even if the state or different.

At the same time, both internal energy and enthalpy has to be thought off. For this process Q is U_f - U_i and for this process Q is H_f - H_i. This process tells that though the state point is same, to make the state point same during reaction, I will have to take out some heat which is, here Q is less than 0 because this is the equation from first law where Q is the heat added, when we write the final minus initial internal energy or final minus initial enthalpy. When Q is less than 0, this tells that U_f is less than U_i or H_f is less than H_i, otherwise the first law of thermodynamics will not be valid. At the same state, the enthalpy of two or the internal energy of the two reactants and products are not same, rather in this case it is less.

The internal energy of the product is less that is U product final state is T_f, I write this as the product. Finally, I write the product and the initial state. You can write f also so the products of the final state which is less than that of the initial state. The enthalpy of the final state is less than that of initial state.

Therefore, from this we can find out one thing that in this case the reactants and products do not reveal the same internal energy or same enthalpy when the state is same, for this type of reaction where the temperature and pressure is increased, when it is made in an adiabatic system in a flows process and non-flow process.

Similarly, in a steady flow process where the temperature is increased, and is made in adiabatic condition or other way; you can tell to make it an isothermal condition. We have to take away heat. In this type of reaction, the internal energy of the products of the final state has to be less than the internal energy of the reactants at the same pressure and temperature, similar is for enthalpy. Therefore, we see that the internal energy or enthalpy is not same at the same state for products and reactants. With this in mind, let us draw a curve like this.

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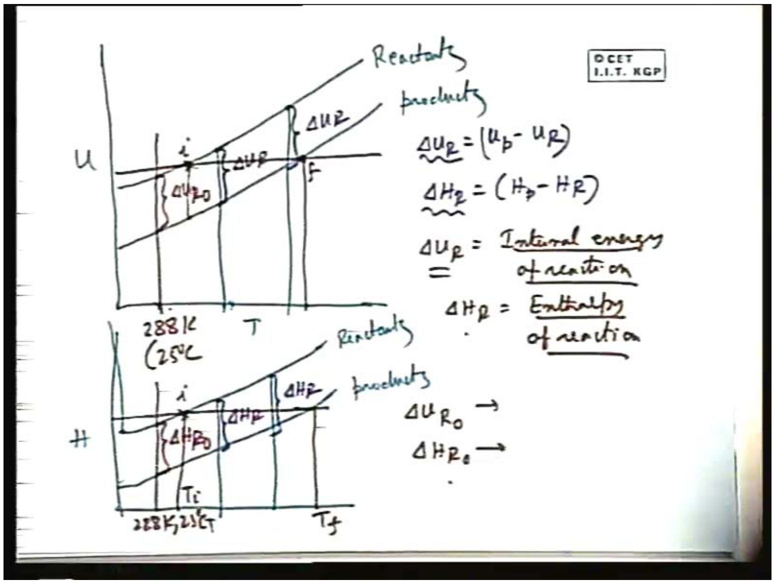

Consider the ideal gas reactions, where enthalpy and internal energy is expressed in terms of temperature and other property. For internal energy we usually recommend volume, because it pertains to a close system and for a steady flow process we recommend the pressure because it is done in a steady flow process in the constant pressure process. Therefore, T_p or T_v is the usual representation. But, if we consider an ideal gas reaction, we can substantially consider that internal energy and enthalpy functions the temperature only.

If, we draw a graph because a figure will give you things in a more clarified way that internal energy. For example, this is temperature and the curve goes like this. This is the reactants and this is products. Similar is the case for H and T. This is reactants and this is products.

Hence, at any temperature if you draw a vertical line at any temperature, the reactants and products do not reveal the internal energy. Internal energy of the reactant is more than the product and this intercept is the difference in the internal energy or difference in the enthalpy. The difference in internal energy or enthalpies is known as enthalpy internal energy of reaction.

We define this as delta U_R by magnitude and delta H_R. Delta U_R is defined as; U_P products minus U_R. So the magnitudes is this, but if it is defined like this; U_P is less, U_R is more, it is negative. Hence, the value is negative, therefore, it is defined in this way; U_P-U_R this is the internal energy of reaction at a given temperature, if it is an ideal gas at a given temperature. It will vary from temperature to temperature because the two curves may not be parallel. Similarly, delta H_R is given by H_P - H_R, this is definition and this is known as internal energy of reaction or enthalpy of reaction.

Delta U_R is the internal energy of reaction and delta H_R is enthalpy of reaction enthalpy of reaction. These are the definitions, usually this internal energy of reactions and enthalpy of reactions at the normal condition not standard condition rather you can tell 288K that means 25 degree Celsius.

Here 288K or 25 degree Celsius is given as delta U_{R0} and delta H_{R0}. They are referred to as internal energy of reaction at standard condition and enthalpy of reaction at standard condition and usually for all practical cases these values are referred as internal energy of reaction and enthalpy of reaction. If nothing is told or if it is told that internal energy of reaction is at this standard temperature that means it is the difference of internal energy or enthalpy of the products minus that of the reactants at 25 degree Celsius.

Henceforth, whenever we tell that internal energy of reaction or enthalpy of reaction we will mean this value, which is at standard condition. One very interesting thing is that, when the process was performed adiabatically, internal energy is constant in a closed system. I can show the process by a horizontal line, parallel to t, that means, if my initial point is this, though I draw a horizontal line these curves get the final point.

Automatically the final point gives a higher temperature. Physically it means this internal energy is fixed for the reactant. The same internal energy will be exhibited by the products, if it can attain this temperature, otherwise not. At the same temperature there will be a difference, and the internal energy of the product is less.

Similar is the case, if the initial point is this and the stead flow system the process is cost at adiabatic condition that means the enthalpy remain same, work transfer is not there change in kinetic potential energies are negligible stead flow energy equation tells H_f is H_i. The same H has to be exhibited by the products. It has to attain a temperature, which is higher than the initial temperature of reactants. We can write the equations when this is not adiabatic. Let us again draw the figure U versus T. again draw the reactants and the products.

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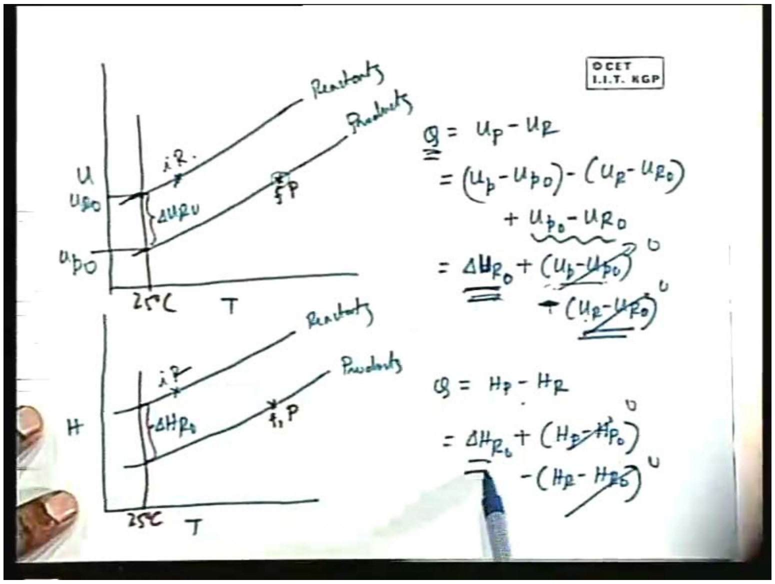

$$\underline{\underline{Q}} = U_P - U_R$$
$$= (U_P - U_{P0}) - (U_R - U_{R0}) + \underbrace{U_{P0} - U_{R0}}$$
$$= \underline{\underline{\Delta U_{R0}}} + \cancel{(U_P - U_{P0})}^{0} + \cancel{(U_R - U_{R0})}^{0}$$

$$Q = H_P - H_R$$
$$= \underline{\Delta H_{R0}} + \cancel{(H_P - H_{P0})}^{0} - \cancel{(H_R - H_{R0})}^{0}$$

It may not be an adiabatic process. Let us consider, i is the initial point, we can give a nomenclature R because, initial state is the state of the reactants and the final state is the state of the product. Let the final state here be the state of the product. Similar is the case here, some initial state arbitrarily, I fix some final state for the product if I fix. This is the final state product. How can I write the equation? Equation is very simple for a close system. Q is nothing but U_P, which means this point minus U_R whatever, is the internal energy here so this is the difference in the first law of thermodynamics.

Similarly, we can write $Q = H_P - H_R$. In this type of case our main objectives is find out the heat transfer, that means the problem is like, if our initial state of the reactants are told in a close system combustor. If my final state is known, I have to find out the heat transfer, whether heat is added or heat has been taken out and if it is so what is the amount? So, $Q = U_P – U_R$.

There is a convention to write this equation in little different form with some school level rearrangement of algebra. I can write this as $(u_p - u_{P0})- (u_R - u_{R0}) + (U_{P0} - U_{R0})$ that means, this becomes equal to delta U_{R0}, which is the internal energy of reaction and these are the given things. In a table, we get the internal energy of reaction. That is why I am rearranging this thing for easier calculations. Minus u_P minus u_{P0} plus u_R minus u_{R0}.

Similarly, we can write this as delta H_{R0} plus H_P minus H_{P0} minus H_P minus H_R. Here the most important thing is that, we have to add this with this that means 25 degree Celcius. Let this is the 25 degree Celsius line. Therefore delta U_{R0} is delta H_{R0}, this is only algebra nothing else, so your initial reactants may not be exactly at 25 degree Celsius. It is away from 25 degree Celsius. This will be reflected here, $U_R - U_{R0}$.

U_{R0} here means this value is U_{R0}. Similarly, U_{P0} is the value U_{P0}. The product finally is at the state which is departed from U_{P0}, which means the case which we discuss about an isothermal burning, where the temperature remains the same. This state remains the same that means this part and this part will be 0, in that case because the reactions starts with these, and if that is at the standard condition. For example, if a condition at 25degree Celsius and one atmospheric pressure,. I take the heat away so that in this type of reaction where the temperature suits up, I will have to take the heat away.

So, that will be automatically manifested in this equation. I will make the reaction in such way that it comes with the same temperature and pressure. It will be 0 in that case you see the heat transfer is responsible for this internal energy because of this we have defined it the other way. The heat transfer is given by the internal energy of reaction and enthalpy of reaction.

The type of reactions where the enthalpy of reactions or internal energy of reaction is negative, the reactants have got more internal energy or more enthalpy than that of the products; these terms are negative and heat is negative that means heat has to come out of the system. This type of reactions is known as exothermic reactions. Exothermic reaction is the reaction, which liberates heat. Heat is an energy that flows or energy in transit. So whenever there is a temperature difference, some kind of energy flows or some kind of energy place in transit which we call heat. Liberation of heat or storage of heat is not acceptable.

Exothermic reaction is reaction where an internal energy of reaction or enthalpy of reaction is negative, which means the reactions for which the internal energy of the reactants or enthalpy of the reactants is more than that of the products at the same state. If it is an ideal gas at the same temperature, reverse is there. If the reactants internal energy or enthalpy could have been lower than the products, you could have expected at an adiabatic process, the temperature should fall down just you reverse on or to make the temperature same, you have to give the heat.

Heat demanded from the surrounding for this type of reaction which is endothermic and heat is being liberated to the surrounding to make the process isothermal. Heat is being generated or heat is being absorbed. So, it is the internal energy of reaction or enthalpy of reaction whether positive or negative, whether reactants having more or the products having more quantity

We see that at the same temperature and pressure. For example, the standard state reactants and products are differing in internal energy, where from does it come? This is not the job of persons dealing with classical thermodynamics. This is the scale we fix, but

I can tell you from molecular theory, that this comes from inter atomic bond; the energy which we sometimes loosely call the chemical energy.

If I tell that, oxygen at one atmospheric pressure and at 30 degree Celsius or 25 degree Celsius and in one compartment methane is there, you will definitely tell the internal energy of the methane is more because chemical energy of the methane is more, but they do not use the chemical energy. From the view point of thermodynamics, apart from heat transfer all kind of energy transfer is work transfer, whether it is an electrical energy that is passing out correct across the voltage difference, whether it is a magnetic flux because of the difference in the magnetic intensity or any other type of work. An energy transfer comes under the category of work transfer.

We can give some adjective with electrical work transfer, magnetic work transfer, mechanical work transfer all these come into the category of work transfer. Ultimately in thermodynamics, there are two forms of energy from first law, again I recapitulate to give the two status of energy. One energy in transit that is heat and work transfer, other energy in storage is the internal energy.

Whatever is the internal energy, which means you, should not tell that methane at same temperature and pressure and oxygen and same temperature and pressure. Methane has more energy because its chemical energy is more. No, methane has got more internal energy, and that internal energy of methane is in the form of the atomic or molecular bond that is a sort of chemical energy though the pressure temperature based internal energy is the same.

Therefore, we have to add this chemical energy, if I tell the change of internal energy from this pressure and temperature to another pressure and temperature then that will follow the same rules cp delta you have understood. But, the base value is different because of inter atomic bond.

The difference in internal energy and enthalpy makes the reaction exothermic and endothermic whether the temperature is in this way, which heat has to be taken out to make the process isothermal

Next class, I will tell you the enthalpy of formation, how internal energy scales are fixed. The question comes; are internal energy we have understood at those same state internal energies of reactants and products are different? We do not identify which is reactant and which is product, so we have to make a uniform scale for elements and compounds to define the enthalpy, so that the enthalpy of reactions and internal energy of reaction are automatically taken care of, such that scale is define through the defining of enthalpy of formation or internal energy formation which I will discuss in the next class and will solve a problem.

Thank you