

**Fundamentals of Aerospace Propulsion**  
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**Lecture - 17**

In the last lecture, we basically discussed about the combustion, which is very important, because for any propulsive device, the energy conversion will be taking place in the combustor itself, that is why I call it is the heart of any engine. That means, combustor is the heart of any engine and we need to understand the processes involved in combustion, which is quit complex in nature, as I had repeated through a pictures by saying that, it involves several other disciplines as well.

So, what we will do, we will also now look at thermodynamics of combustion, which you might have learn. But, for the sake of, what you call repetition or completeness sake and also to help you to recapitulate, what you have already learned and we will now indulge in it.

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**Chemical Reaction**

$\text{CH}_4 + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \Delta H^\circ_{\text{RT}}$

**Is it balanced ?**

**No !**

**The balanced equation would be**

$\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + \Delta H^\circ_{\text{RT}}$

**16 gm + 64 gm = 36 gm + 44 gm**

**No mass is created or destroyed in a chemical reaction, only changes in their forms take place.**

**Mostly air is used as an oxidizer.**

$\text{CH}_4 + 2(\text{O}_2 + 79/21 \text{N}_2) \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + 7.52 \text{N}_2$

If you look at like combustion always involve chemical reactions, chemical reaction what we will be considering basically a methane. That means, 1 mole of methane is reacting with the 1 mole of oxidizer and it is going to what, like it is going to the water and carbon dioxide and certain amount of heat being released that is, the amount of heat which is being released. Now, question arises, is this reaction really balanced, number 1

and why we need to look at really, whether it is balanced or not and what is the meaning of a reaction being balanced.

If you just look at this reaction, what I have written down here is it balanced, what is the meaning of balance. Balance means, if I look at in the left hand side that is, methane reacting with oxygen, I need to look at, whether the elements... for example, in methane, the elements will be one carbon, other is hydrogen, whether it is same as that of whatever is there in the right hand side that, either in the carbon dioxide or in the water, that is the meaning of balance.

In this case, it is very clearly being you can see that, it is not balanced and if you want to balance what you will have to do, you will have to basically take elements and balance it. And the balance equation would be 1 mole of methane is reacting with 2 moles of oxidizer going to the 2 moles of water and 1 moles of carbon dioxide, of course certain amount of heat being released. This kind of equation you might have being taught from your high school, one question I would like to ask, whether this reaction really take place in nature or not, can anybody tell me, whether similarly it is occurring or not.

Student: ((Refer Time: 03:49))

It cannot be really occur in nature, we will see little later on when we are talking about chemical kinetics. So, what is the meaning of this reaction, what we are saying this reaction is balanced that is, 1 mole of methane is reacting 2 moles of oxidizer and going to the product as 2 moles of water and 1 moles of carbon dioxide. That means, what you are saying, you are saying that, in the left hand side there are 3 moles are there, on the right hand side this is 3 moles, can I call it as a balance.

That means, in other words, if the number of moles of the participating spaces is same as that of the right hand side, can I call it as a balance, yes or no. But, in this case, it is looks to be like that, which is the right, actually if you look at I mean, we will be looking at whether the moles is balanced, number of moles in the left hand side of the various participating spaces and the product number of moles or we will have to look at mass.

So, let us consider that, what happens to the mass, mass if you look at, the 16 grams of methane is reacting with 64 grams of oxygen is going to the product 36 grams of water and 44 grams of carbon dioxide. What it indicates, in the left hand side it is how many

grams, it is something 80 grams on the left hand side if you look at, this is something 80 grams and this side is also 80 grams. That means, what it indicates, it indicates that mass is conserved.

That means, no mass is created or destroyed in a chemical reaction, only the change in their forms takes place. In other words, mass is conserved, is it really true, because it says I mean, we have done that that means, definitely it will be true. But, is it not that contradicting, what Einstein told energy can be converted into the mass and mass can be converted into energy, but here there is a amount of heat energy is there.

So, naturally this is violating that means, this is not right or what Einstein had told is not right. Can anybody tell me, how come it is not satisfying the concept as given by the novel or it Einstein what might be the reason.

Student: Mass change is very negligible.

Yes that means, in this case the mass change will be negligibly small such that, you cannot really measure. And if you want to look at that, some example is given in my thermodynamics book, you can look at it, because the amount of heat released is very very small to have any tangible change in the mass. So therefore, both are valid and generally, we use air as an oxidizer, most of the combustions. Of course, in the recent times, there are some combustions people are talking about in order to avoid NOX and other things that, oxygen combustion kind of thing.

But however, we will be using mostly the air as an oxidizer, so if you look at this, reaction can be written as the 1 mole of methane is reacting with the 2 moles of air. And keep in mind that, we are considering only the air means, nitrogen and oxygen, others are negligible. And it is going to the 1 mole of carbon dioxide and 2 moles of a water and large amount of seven point five two 7.52 moles of nitrogen.

So, what I would like to suggest that, although we have seen in this equations and also in this equation that, number of mole in the left hand side of the participating spaces is equal to the number of moles of the product in case of methane. But, it need not to be true for other hydro carbon, it is just a coincidence. That means, if equation is balanced, need not to be that, one can assume that, the number of moles in the left hand side is same as the number of moles in the product, that you should keep in the mind.

(Refer Slide Time 09:02)

**What is Stoichiometry?**  
 It is known as the ratio of oxidizer to fuel which is sufficient to burn fuel leading to the formation of complete products of combustion.

$C_xH_y + a(O_2 + 3.76 N_2) \rightarrow x CO_2 + (y/2) H_2O + 3.76 a N_2$   
 Where  $(a = x + y/4)$ . For  $CH_4$ ,  $a = 1 + \frac{4}{4} = 2$   
 Molecule weight of air

$(A/F)_{stoic} = (m_{ox}/m_{fuel}) = 4.76 a (MW_{air} / MW_{fuel})$   
 $(A/F)_{stoic} = 17.11$  for Methane-air mixture  
 $(A/F)_{stoic} \sim 15$  for other Hydrocarbon-air

Equivalence Ratio  $= \phi = \frac{(A/F)_{stoic}}{(A/F)} = \frac{(F/A)}{(F/A)_{stoic}}$   
 $\phi < 1$  Fuel Lean mixture  
 $\phi = 1$  Stoichiometric mixture  
 $\phi > 1$  Fuel Rich mixture

% stoichiometric air  $= \frac{100\%}{\phi}$

So, now question arises what is stoichiometry, because we have talked about balance equation that means, it will be related to the balance equation. What is the meaning of that, that meaning is that, the ratio of the oxidizer to fuel, which is sufficient to burn certain amount of fuel leading to the complete formation of products of combustion. That means, if I am taking like 1 mole of the methane, it is reacting with the 2 moles of oxidizer that means, it will be going to the product, that is what carbon dioxide and water.

For example, if I take a C x H y if you look at, it is the generic name, generic formula for a hydrocarbon that means, if I take x is equal to 1 and y will be what, 4 then, it became CH<sub>4</sub>. If I take x is equal to 2 and H is 6, that will be ethane, methane like x is 3 and H is 8, that will become propane. So, I mean, if I take a mole of generic hydrocarbons and reacting with a moles of air and it is going to the x moles of carbon dioxide and y by 2 moles of water and 3.76 a into a of course, nitrogen, this is generic I have written.

That means, if you look at the fuel oxidizer ratio, which will give the product like that means, complete conversion of fuel into their respective product. Like in case of hydrocarbon, all the carbon in the fuel will be converted into carbon dioxide and all the hydrogen will be converted into water, Of course oxygen will be there. Then, we call it as a complete combustion product, there might be cases where the product will be

containing excess oxygen. It might be containing certain amount of carbon monoxide, can you call it as a complete, reaction is complete, certainly no.

So that means, what is the ratio of oxidizer to fuel or in other words, fuel to oxidizer, which is sufficient to burn a 1 kg of fuel leading to the formation of the complete products of combustion, we call it as stoichiometry. So, in this balanced equation, where a is equal to x plus y by 4, of course if I take a methane what will happen to the a, if I take x as 1 and y is basically 4, that becomes a becomes for methane this 4, a will be what you call, 1 plus what you call a 4, by 4 is equal to 2.

We have seen in the last slide that, a turns out to be 2 for methane, so air by fuel stoichiometry what do we call, mass of oxidizer divided by mass of fuel and which happens to be 4.76 a molecular weight of air, this is molecular weight MW of air. And similarly, MW fuel is the molecular weight of fuel and for methane air mixture, the a by fuel stoichiometry happens to be 17.11. Whereas for others hydrocarbons, it will be around 15, do not think that, it will be exactly 15, in some cases it will be 14.9 or in some cases, it may be 15.2.

Most of the hydrocarbons will be around 15, expect methane therefore, this number is a ball park number what we keep in mind, but exceptional cases methane. Now, when you talk about this air fuel ratio, it is basically non dimensional number Kg of fuel by Kg of oxidizer, if it is fuel to air. If it is other way around, this will be Kg of oxidizer divided by Kg of fuel, if it is air fuel ratio. Now, but sometimes, we need to know, how far this air fuel ratio from the stoichiometry.

In real situation, you need not to really operate at stoichiometry, rather we always try to operate at the lean condition so that, enough oxygen will be there so that, complete combustion can take place. Ideally, at stoichiometric, all the fuel will be converted into their respective product, but in real situation, it would not occur. And sometimes we need to also go for a less amount of air or the oxidizer as compared to the stoichiometry requirement.

Particularly, when we will be trying to get some pyrolysis product or a gasify for example, I want to gasify a solid fuel or some liquid fuel then, naturally I will have to use less amount of oxidizer like we do that, like we will be starving. Starving in the sense, suppose somebody ask me a question, I do not give the answer, I will just give the

hint so that, you will think and get the answer. So that, he will develop his mind, instead of just remembering, listening to my answer and remembering, that is the way we should teach, not that give the answer.

So, similarly if I want to convert certain liquid fuel into a certain gaseous fuel or a product better one, I need to be throttling, choking, but in a controlled manner, this is very important. Generally, people always happy who ever will give you answer, but I say that, those teacher who give answer to the student directly, they spoil the students. So, the similarly in this way, like you need to have a lower air fuel ratio or depending on situations to have a conversion product.

So now, we need to define, how far this air fuel ratio is differing from the stoichiometry, because stoichiometry is the ideal or the theoretical air fuel ratio, which is required for complete combustion. So therefore, I need to define an equivalence ratio that is, basically a ratio of air by fuel stoichiometry divided by air by fuel. In other words, fuel by air divided by fuel by air stoichiometry, it can be lean mixtures, it can be rich mixtures. If I say,  $\phi$  is less than 1 I call it as a lean mixture, what kind of lean it is, it will be fuel lean.

If  $\phi$  is equal to 1 that is stoichiometry mixture, if  $\phi$  is greater than 1 that is, what you call fuel rich mixture, which we will be using it. So, you should keep in mind, if  $\phi$  is greater than 1 what is the meaning and  $\phi$  is equal to 1 is basically stoichiometry. And beside this, sometimes we will be using that, what is the percentage of stoichiometric air that is, 100 percent divide by  $\phi$  will give me, whether it is higher amount of oxidizer or less amount of oxidizer as compare to stoichiometric.

So, is that clear what I am talking about, fuel lean, fuel rich and stoichiometric like, depending upon whether  $\phi$  is less than 1 or  $\phi$  is greater than 1.

(Refer Slide Time 18:10)

**Example:** The gasoline (Octane =  $C_8H_{18}$ ) is burnt with dry air. The volumetric analysis of products on dry basis is  $CO_2 = 10.02\%$ ,  $O_2 = 5.62\%$ ,  $CO = 0.88\%$  &  $N_2 = 83.48\%$ . Determine (a) A/F ratio (b) equivalence ratio, and (c) % stoichiometric air used.

**Solution:**

$$x C_8H_{18} + a(O_2 + 3.76 N_2) \rightarrow 10.02 CO_2 + 0.88 CO + 5.62 O_2 + 83.48 N_2 + b H_2O$$

By mass balance;

N:  $3.76 \times 2 a = 83.48 \times 2$ ;  $a = 22.2$

C:  $8x = 10.02 + 0.88$ ;  $x = 1.36$

H:  $18x = 2b$ ;  $b = 12.24$

O:  $2a = 10.02 \times 2 + 0.88 \times 2 + 5.62 + b$   
 $44.4 = 44.4$  (checked)

Then the above balance equation becomes

$$1.36 C_8H_{18} + 22.2(O_2 + 3.76 N_2) \rightarrow 10.02 CO_2 + 0.88 CO + 5.62 O_2 + 83.48 N_2 + 12.24 H_2O$$

Recasting the above reaction in terms of 1 mole of fuel as given below;

$$C_8H_{18} + 16.32(O_2 + 3.76 N_2) \rightarrow 7.37 CO_2 + 0.65 CO + 4.31 O_2 + 61.38 N_2 + 9 H_2O$$

Then the air fuel ratio by mass becomes;

$$(A/F)_{actual} = \frac{m_{Air}}{m_{Fuel}} = \frac{16.32(32 + 3.76 \times 29)}{(12 \times 8 + 18)} = 20.19$$

The stoic fuel-air ratio can be found out by considering a balance equation;

$$C_8H_{18} + 12.5(O_2 + 3.76 N_2) \rightarrow 8 CO_2 + 9 H_2O + 47 N_2$$

So now, we will take an example that is, the gasoline what is being model as a octane  $C_8H_{18}$  is burnt with dry air, keep in mind that gasoline is what, what we use as a petrol in our petrol engines. And the volumetric analysis of the product on dry basis, one can obtain  $CO_2$  10.02 percent, oxygen is 5.6 percent and carbon dioxide is 0.88 percent, nitrogen is 83.48 percent. But, how you will get this thing, you need to measure this values by using gas analyzers, earlier days or set up it has being used, you might be aware or set up by chemicals means, weight chemicals means.

And nowadays of course, very good sensors are available, you can measure it and suppose these are given, now we need to determine from this product, what is this air fuel ratio and equivalence ratio and percent of stoichiometric air being used. Let us look at, how we will go about it, what we will do, we will have to basically look at a equation what we started with. That is, x moles of the octane is reacting a moles of air and these are the product like carbon dioxide which is given, CO and oxygen is given and nitrogen is given, but water is not given.

Water will definitely come, because it is hydrocarbon, hydrogen is there, so product must be having hydrogen. So, that is amount is not given, we will say let it be b then, what I will do, I will have to basically balance, can I just look at do it, of course some of you can do it, if you are having good concentration and mind power, you can do that, but you may sometimes make some mistake. So therefore, we need to do in a very systematic

manner, the one which I am going to illustrate is basically we will be doing a mass balance.

That means, what I will do, I will look at each element for example, nitrogen is here, I will look at nitrogen  $3.76 \times 2$ , because  $N_2$  and  $a$  is coefficient. I can say on the left hand side, right hand side will be what, right hand side will be  $83.48 \times 2$ . So, if I just take this balance,  $a$  happens to be,  $a$  is equal to  $22.2$  and similarly, for carbon if you look at, we are having  $8x$  in the left hand side is equal to  $10.02$  plus, because  $CO_2$  and for carbon monoxide, it is  $0.88$ , I can get  $x$  is equal to  $1.36$ .

And similarly, for hydrogen in the left hand side is  $18x$ , of course in this place, it is not there and water will be there, that is  $2H_2O$ , this will be  $2b$  from the water, so  $b$  will be  $12.24$  if you get that and oxygen you can look at, because oxygen is there  $2a$ . And then, in this case, from the carbon dioxide, it will be  $10.02 \times 2$  plus  $0.88$  from the carbon monoxide. And of course, from extra oxygen is there here, here it is not a stoichiometry mixture, because carbon monoxide is there and also the extra oxygen is there.

So, that will be  $2 \times 5.6$  plus  $b$  of course, in water there is  $a$   $b$  moles will be there, so then after that, you will of course get some values that is,  $b$   $12.24$ . And then, you have already know these things and you can cross check like, whether the left hand side is same as that of the right hand side for the  $O$ . If it is then, you can say it is basically, it is just to cross check, you may avoid it sometimes, but how you will cross check, that is given here.

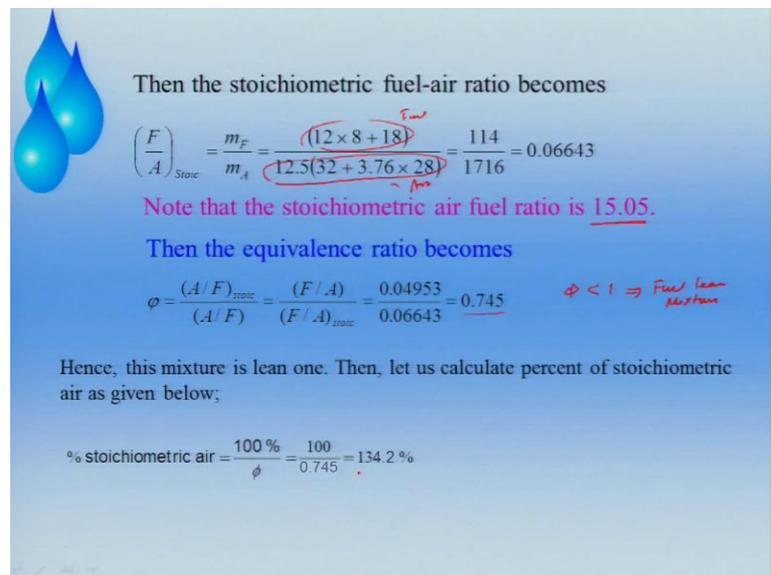
So, if you cross check that and then, you know sure that, it is well balanced, the above balance equation will be like this that is,  $1.36$  we have already seen  $x$  and of course,  $22.2$  that is our  $a$  and then, like  $b$  is  $22.24$ . That means, I can rewrite this equation in terms of 1 mole, what I have done, I have just divided by  $1.36$  and all those things I have divide by  $1.36$ . And then, I written down like this, so then air fuel ratio by mass becomes what, from the actual, because this is actual, this is not stoichiometry.

So, that will be mass of air divide by mass of fuel you will find that, it is something  $20.19$ , because all those things we are doing, all values we know we can just put it, because this is the air. If you look at, this is air and this is nothing but fuel, so I will get  $20.19$ . Now, I need to because, air fuel ratio  $a$  we have found out, we need to find out

equivalence ratio. For that, what we will have to do, we need to know what is the stoichiometric air by fuel.

Like stoichiometric, air fuel can be found out by considering a balanced equation that is,  $C_8H_{18} + 12.5 O_2 + 3.76 N_2$ , it is going to product carbon dioxide, water and of course, 47 nitrogen. You keep in mind that, there is no carbon dioxide in the product, there is no extra oxygen in the product. That means, all is converted into carbon dioxide, all the fuel is converted into carbon dioxide and of course, the water, so this is our stoichiometric reaction.

(Refer Slide Time 24:39)



Then the stoichiometric fuel-air ratio becomes

$$\left(\frac{F}{A}\right)_{Stoic} = \frac{m_F}{m_A} = \frac{(12 \times 8 + 18)}{12.5(32 + 3.76 \times 28)} = \frac{114}{1716} = 0.06643$$

Note that the stoichiometric air fuel ratio is 15.05.

Then the equivalence ratio becomes

$$\phi = \frac{(A/F)_{mixture}}{(A/F)_{Stoic}} = \frac{(F/A)}{(F/A)_{Stoic}} = \frac{0.04953}{0.06643} = 0.745 \quad \phi < 1 \Rightarrow \text{Fuel lean mixture}$$

Hence, this mixture is lean one. Then, let us calculate percent of stoichiometric air as given below;

$$\% \text{ stoichiometric air} = \frac{100\%}{\phi} = \frac{100}{0.745} = 134.2\%$$

So, the stoichiometric fuel air ratio if you look at,  $m_F$  by  $m_A$  and this is nothing but, your fuel and this is your air and you will get 0.06643. Keep in mind that, do not remove that decimal point, because it will incur some error. And if you look at, what is this air fuel by stoichiometric just to have a feel, it happens to be 15.05. As I told you, it will be around 15, sometimes in the exam or somewhere, you are landing some other number, please check whether it is around 15 or not that is, except methane, air or methane oxygen.

So, the equivalence ratio becomes what is that, a by fuel stoichiometry divide by air by fuel and you will find that, it amounts be 0.745, what is this, whether it is a fuel lean or fuel rich. Here, phi is less than 1, so therefore, it is fuel lean mixture, if it is phi is greater than 1 then, it is fuel rich mixture, it is because less amount of, what you call fuel as

compare to the stoichiometric oxidizer. So therefore, it is the fuel lean mixtures and hence, so let us calculate the percentage of stoichiometric that is, 100 divide by phi that happens to be 134.2 percentage.

So now, if you look at like in the combustion, we have seen that, we will be dealing with various mixtures of gases. That means, we have seen that, carbon dioxide, water, what you call fuel hydro carbons, oxygen, carbon monoxide, lot of gases will be there, both on the reactant and the product, some times in mixtures. Now, how we will deal with, whether we can consider this to be ideal gas or not and if we will consider it is a ideal gas, how to handle.

If it is real, how we will handle, the mixture of gases, that is a very important concept, which we must be knowing all those things what I am going to talk about it, because we need to handle this mixture of gases.

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**Mixture of Ideal Gases**

**What are the methods used to specify the composition of a mixture ?**

**Two methods : (i) mass analysis and (ii) molar analysis**

**Mass analysis of mixture of ideal gases**

**The total mass of the mixture  $m_m$  is equal to sum of the masses of the constituent gases which can be expressed as**

$$m_m = m_A + m_B + m_C + \dots + m_N = \sum_{i=1}^N m_i$$

$$1 = \frac{m_A}{m_m} + \frac{m_B}{m_m} + \frac{m_C}{m_m} + \dots + \frac{m_N}{m_m} = \sum_{i=1}^N \left( \frac{m_i}{m_m} \right) \Rightarrow \text{mass fraction} = x_i = \frac{m_i}{m_m}$$

$$\Rightarrow 1 = x_A + x_B + x_C + \dots + x_N = \sum_{i=1}^N x_i$$

So, question arises, what are the methods to be used to specify composition of a mixture, what are the ways, there are two ways of specifying a mixture composition, one is based on mass, that is mass analysis, other is molar analysis or number of moles. So, mass analysis of mixture of gases, one can think of as like, let us consider a container, which contains certain amount of gases. For example, carbon dioxide, methane, oxygen and other things or let us consider a container, which will be containing air, what you call certain a kg of gas A and then, may be another gas B and C, like that.

So, I can find out the total mass of the mixture is equal to sum of the masses of the constituent gases, which can be expressed as that,  $m_m$  is equal to  $m_A$  plus  $m_B$  plus  $m_C$  and there are  $n$  number of gases, so I can write down  $m_N$ . And I can write this in a compact form that is, summation of  $m_i$ , where  $i$  is equal to 1 to  $N$ , it can be anything. For example, if it contains carbon dioxide, water and carbon monoxide and nitrogen four gases, here it will be  $i$  is equal to 1 to 4.

And if I divide this equation by mass of mixture, similarly here mass of mixture what will happen, this will equal to 1 and  $m_A$  by  $m_m$  plus  $m_B$  by  $m_m$  plus  $m_C$  by  $m_m$  upto the  $m_N$  by  $m_m$ . And I can write down that is in a compact form,  $m_i$  divided by  $m_m$  and what is this term, this is nothing but, your mass fraction. So, I can write down mass fraction of  $i$  th species is equal to I mean, we can use a symbol  $x_i$  is equal to  $m_i$  divided  $m_m$ .

Now, if I use this symbol and write down in this expression what I will get is, 1 is equal to  $x_A$  plus  $x_B$  plus  $x_C$  upto the  $x_N$  summation of  $x_i$ . What it is saying that, mass fraction of all the participating species or all the species in a mixture is equal to 1, this is a very important concept, which you will be using several times and this you should keep in mind.

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**Mole/Mass Analysis**

Similarly total number of moles in the mixture  $n_m$  is equal to the sum of the number of moles of each constituent of the mixture that can be expressed as:

$$n_m = (n_A + n_B + n_C + \dots + n_N) = \sum_{i=1}^N n_i$$

$$1 = \frac{n_A}{n_m} + \frac{n_B}{n_m} + \frac{n_C}{n_m} + \dots + \frac{n_N}{n_m} = \sum_{i=1}^N \frac{n_i}{n_m} \Rightarrow \text{mole fraction} = y_i = \frac{n_i}{n_m}$$

$$1 = y_A + y_B + y_C + \dots + y_N = \sum_{i=1}^N y_i$$

But mass,  $m$ , can be related to  $n_i$  with  $MW_i$  as:  $m_i = n_i MW_i$

$$m_m = \sum m_i = (n_A MW_A + n_B MW_B + \dots + n_N MW_N) = \sum_{i=1}^N n_i MW_i$$

$$\frac{m_m}{n_m} = \frac{n_A}{n_m} MW_A + \frac{n_B}{n_m} MW_B + \dots + \frac{n_N}{n_m} MW_N = \sum_{i=1}^N \frac{n_i}{n_m} MW_i = \sum_{i=1}^N y_i MW_i$$

$$MW_m = y_A MW_A + y_B MW_B + \dots + y_N MW_N = \sum_{i=1}^N y_i MW_i$$

But,  $x_i = \frac{m_i}{m_m} = \frac{n_i MW_i}{n_m MW_m} \Rightarrow x_i = y_i \frac{MW_i}{MW_m}$

So, similarly we will be looking at mole also, like let us consider the a container, which contains certain amount of a mixtures gases. And let us say  $n_A$  moles,  $n_B$  moles and  $n$

C moles like that then, we can look at the total number of moles in a mixture that is,  $n_m$  is equal to sum of number of moles of each constituent of the mixture that can be expressed mathematically as  $n_m = n_A + n_B + n_C + \dots + n_N$ .

And I can write down summation of  $n_i$ , where  $i$  is equal to 1 to  $N$ , if I divide this by  $n_m$  here and similar way, I can write down this expression as  $\frac{n_A}{n_m} + \frac{n_B}{n_m} + \dots + \frac{n_N}{n_m}$  and keep in mind that, this can be written that summation of  $n_i$  by  $n_m$ . And if I can define this as a mole fraction of  $i$ th mixture is equal to  $y_i$  is nothing but,  $n_i$  by  $n_m$ . So, we can write down that in a similar expression that is,  $y_A + y_B + y_C + \dots + y_N = 1$  and summation of  $y_i$ .

What it indicates that, mole fraction of a mixture, sum of mole fraction of all the constituents in a mixture is equal to 1, but the mass  $m_i$  can be related to mole. Of course, with the help of molecular weight  $MW_i$  and because we know that,  $m_i = n_i MW_i$ ,  $i$  is the  $i$ th species, it can be carbon monoxide, it can be oxygen, it can be any other species,  $i$  means any species. So then, I can write down  $m_m = \sum n_i MW_i$  and is equal to, because I will just use in this expression  $n_A MW_A + n_B MW_B + \dots + n_N MW_N$ .

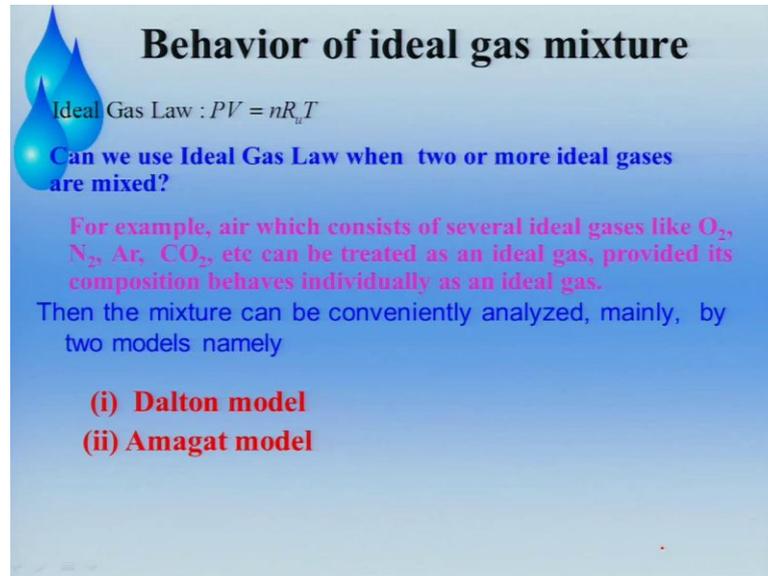
In a compact form I can write  $n_i MW_i$ , if you look at  $i$  is equal to 1 to  $N$  and if I divide this by the  $n_m$  like this expression  $\frac{n_i MW_i}{n_m}$ , similarly all this expression by  $n_m$ . If you look at I can write down in this way that is, summation of  $\frac{n_i MW_i}{n_m}$  and what is this term, this term by definition it is  $y_i$ . So, I can write down and what is this term, this term is basically the  $MW_m$  that is, molecular weight of the mixture is, basically sum of the product of mole fraction of gases like  $A$  into molecular weight of gas  $A$ .

That means, respective molecular weight and sum over that will give me the molecular weight of the mixture, this is very important statements, which you should keep in mind. Suppose, there are several gases, individual molecular weight I know then, I need to use this mole fraction to find out, what will be the total molecular weight of the mixture other. So, but  $x_i$  we know by definition,  $m_i$  by  $m_m$  and we know that,  $m_i$  is nothing but, your  $n_i$  and  $MW_i$  I can write down and this is nothing but, your  $y_i$ .

So, I can write down that,  $x_i$  is equal to  $y_i MW_i$  divided by  $MW_m$  that means, if I know the mole fraction, I can find out mass fraction, provided I know the molecular

weight of particular spaces and also the molecular weight of the mixture. That means, this can be related to one another following expression, this is a very important expression you should keep in mind.

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**Behavior of ideal gas mixture**

Ideal Gas Law :  $PV = nR_u T$

Can we use Ideal Gas Law when two or more ideal gases are mixed?

For example, air which consists of several ideal gases like  $O_2$ ,  $N_2$ , Ar,  $CO_2$ , etc can be treated as an ideal gas, provided its composition behaves individually as an ideal gas.

Then the mixture can be conveniently analyzed, mainly, by two models namely

- (i) Dalton model
- (ii) Amagat model

So now, we need to look at behavior of ideal gas, whether we can consider ideal gas or we need to consider this combustion products and then, mixtures kind of things as a real gas, is it possible we can assume to be ideal gas. Most of the case times, we use ideal gas why, because the temperature will be very high, of course the pressure also in case of rocket engine particularly will be high.

So, as the temperature is quite high and pressure also is equally high, we consider not really incurring too much of an error particularly in rocket engine for the simply say, but in other cases you can happily use ideal gas engines. Now, question arises, if I take this air and what will be the pressure and at which, we can consider the gas as an ideal. If I take a air simply, let us take air what will be the pressure, at which we can consider to be gas as a non ideal or I cannot apply, you know this thing.

For that, you need to recall or relearn about the compressibility chart, I will just give you the hints that, around 100 atmospheric pressure at ambient temperature, I can happily consider it to be ideal gas without really incurring too much of error. So, 100 atmospheric pressure is a quite big, most of the your gas turbine engines, we do not go to

that high pressure and temperature is high, therefore we can haply use for combustion processes ideal gas and use it.

So therefore, we need to know that and for ideal gas, we know  $P V$  is equal to  $n R u T$ ,  $R$  is the universal gas constant and can we use ideal gas law when two or more ideal gas are mixed, this is a very important question. Because, if in a mixture carbon monoxide is there and nitrogen is there or carbon dioxide is there as well, so whether each individual can be considered an ideal gas, but can I consider as an ideal gas total mixture, that is important.

So, it can be done only when that each individual composition behave as an ideal gas for example, like air which consist of several ideal gases like oxygen, nitrogen, argon, carbon dioxide and extra, can be treated as an ideal gas, provided the composition behaves individually as an ideal gas, that is very important. So then, under this condition, we can use the mixture to an ideal gas and then, the mixture can be conveniently analyzed mainly by two models, namely one is Dalton model and other is Amagat model.

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**Dalton's law of additive pressure**

*“The pressure of an ideal gas mixture is equal to the sum of the pressure, its individual components would exert if each existed alone at the same volume and temperature of the mixture”.*

$$P_m = \frac{n_m R_u T_m}{V_m} = \frac{(n_A + n_B + \dots + n_N) R_u T_m}{V_m} = \frac{n_A R_u T_m}{V_m} + \frac{n_B R_u T_m}{V_m} + \dots + \frac{n_N R_u T_m}{V_m}$$

$$\Rightarrow P_m = p_A(n_A, V_m, T_m) + p_B(n_B, V_m, T_m) + \dots + p_N(n_N, V_m, T_m)$$

$$\Rightarrow P_m = \sum_{i=1}^N p_i(n_i, V_m, T_m) \quad P_{air} = \sum_{i=1}^{N=3} p_i = p_{N_2} + p_{O_2} + p_{Ar}$$

So, the pressure of an ideal gas mixture is equal to sum of the pressure, it is individual components would exert if each existed alone at the same volume and temperature of the mixture. This is nothing but, your Dalton's law of additive pressure, which you have learned from the school days as well. Let us look at pictorial I have shown here, what it

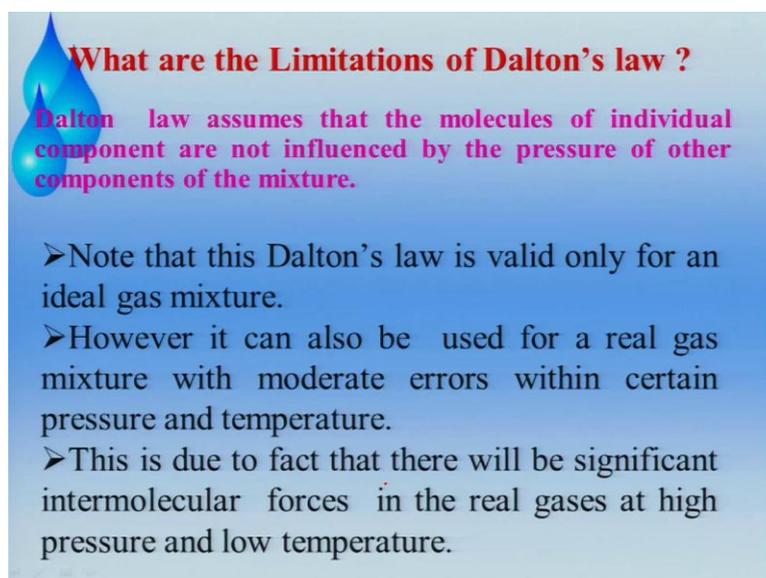
is saying the air, air contains nitrogen, oxygen and argon, it is having the same volume and same temperature  $T$ .

But whereas, the pressure will be different and these pressures of individual gases exerted if each alone at the same volume and the same temperature of the mixture then, we call it as a partial pressure. So, if you look at, if I take this pressure mixture by using a ideal gas law, we know  $n R T$  divided by  $V$ , all these symbol  $V$  is the volume,  $T$  is the temperature,  $n$  is the number of moles of the mixture.

Then, I can write down we have we know that,  $n$  is equal to  $n_A$  plus  $n_B$  plus upto the  $n_N$  then, I can regroup this and write down  $n_A R T$  divided by  $V$  and this is and similarly,  $n_B R T$  by  $V$  and all those thing. If you look at, this is nothing but what, that is  $P_A$ , similarly this will be  $P_B$  that is, a partial pressure of that, I can write out  $P_A$  total pressure experienced by the mixture will be sum of the partial pressure.

And for this example, what I have taken a, it will be  $P_A$  the partial pressure of nitrogen plus partial pressure of oxygen and argon, that is basically Dalton's law of additive pressure what we will be considering.

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**What are the Limitations of Dalton's law ?**

Dalton law assumes that the molecules of individual component are not influenced by the pressure of other components of the mixture.

- Note that this Dalton's law is valid only for an ideal gas mixture.
- However it can also be used for a real gas mixture with moderate errors within certain pressure and temperature.
- This is due to fact that there will be significant intermolecular forces in the real gases at high pressure and low temperature.

And now, let us move at, what is the limitation of this Dalton's law of partial pressure, so if you look at Dalton law assume that, molecules of individual component are not influenced by the pressure of other components of the mixture, this were assumptions. So

therefore, in real situation, this assumption may not be true, because and other one is the Dalton's law is valid only for an ideal gas mixture. Of course, you can apply this for a real gas with a moderate errors within certain pressure and temperature range, because if it is a very high pressure and low temperature then, actually this would not be valid.

And we would not be getting into that regime and this is due to the fact that, there will be significant intermolecular forces in the real gases at high pressure and low temperature, what is which are being neglected in case of an ideal gas hypothesis.

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**Amagat's law of additive volume**

*Amagat's law of additive volume states that "the volume of an ideal gas mixture is equal to the sum of the volume of each individual component gas that would occupy if each gas existed alone at the mixture temperature and pressure".*

$$V_m = \frac{n_m R_u T_m}{P_m} = \left( \frac{n_A + n_B + \dots + n_N}{P_m} \right) R_u T_m = \frac{n_A R_u T_m}{P_m} + \frac{n_B R_u T_m}{P_m} + \dots + \frac{n_N R_u T_m}{P_m}$$

$$\Rightarrow V_m = \sum_{i=1}^N V_i(N_i, P_m, T_m) \quad V_m = \sum_{i=1}^N V_i = V_{N_2} + V_{O_2} + V_{Ar}$$

So, and we need to look at this Amagat's law of additive volumes, which state that, that volume of an ideal gas mixture is equal to the sum of the volume of each individual component gas that would occupy, if each gas existed alone at the mixture temperature and pressure. In case of your Dalton's law of partial pressure what we are considering, we are considering that temperature and volume to be same for both mixture in each component.

In this case, the temperature and pressure to be same that means, volume will be changing. For example, if I consider the total volume of the air, which will be remaining same as the mixture temperature and same as the pressure will be equal to the volume of the nitrogen gas and oxygen gas and argon gas at the same mixture temperature and pressure keep in mind, that is very important point. So, if you look at mathematically

what is that,  $V_m$  is equal to again using ideal gas law that is,  $n_m R_u T_m$  by  $P_m$  and  $n_m$  in place of that, I can write down  $n_A$  plus  $n_B$  plus upto the  $n_N$ .

And if I take separate out if you look at, this is nothing but, your  $V$  what you call  $A$ , similarly this will be  $V_B$ , like that it goes on  $V_N$ . So, we can write down that,  $V_m$ 's of the mixture will be summation of individual mixture of the gases like or volume occupied by each gases in the mixture. So, if you look at,  $V_A$  is basically summation of the what you call  $V_i$ , where three gases are there nitrogen, oxygen and argon of the volume. These things will be using basically to look at various other properties like enthalpy, entropy and other internal energy kind of things.

(Refer Slide Time 44:18)

**Relations**

$$\frac{V_A(n_A, T_m, P_m)}{V_m} = \frac{n_A R_u T_m}{P_m} \cdot \left( \frac{P_m}{n_m R_u T_m} \right) = \frac{n_A}{n_m} = y_A \quad \Rightarrow V_A = y_A V_m$$

$$\frac{p_A}{P_m} = \frac{n_A R_u T_m}{V_m} \cdot \frac{V_m}{n_m R_u T_m} = \frac{n_A}{n_m} = y_A = \frac{V_A}{V_m}$$

Pressure fraction = Mole Fraction = Volume Fraction only for ideal gas

For mixture of three ideal gases namely A, B and C,

$$m_m = m_A + m_B + m_C; n_m = n_A + n_B + n_C \quad \Rightarrow P_m = p_A + p_B + p_C$$

$$V_m(P_m, T_m) = V_A(P_m, T_m) + V_B(P_m, T_m) + V_C(P_m, T_m)$$

$$U_m = U_A(n_A, T_m) + U_B(n_B, T_m) + U_C(n_C, T_m) = \sum_{i=1}^{N=3} U_i(n_i, T_m)$$

$$u_m = \sum_{i=1}^N y_i u_i(n_i, T_m) \quad h_m = \sum_{i=1}^{N=3} y_i h_i(n_i, T_m)$$

$$S_m = S_A(T_m, p_A) + S_B(T_m, p_B) + S_C(T_m, p_C) = \sum_{i=1}^{N=3} S_i(T_m, p_i); \quad s_m = \sum_{i=1}^N y_i s_i(T_m, p_i)$$

So, let us look at the relate these things and if you look at the volume  $V_A$  by  $V_m$ , if I look at in place of  $V$  using ideal gas law, I can write down  $n_A R_u T_m$  divided by  $P_m$  and  $V_m$  I can write down. Like that, if this will be cancelling out if you look at, this will be canceling what is that,  $n_A$  by  $n_m$  is nothing but, your mole fraction of the spaces  $A$ . And similarly, we can look at partial pressure  $P_A$  by  $P_m$  and if I look at that, we can write down  $P_A$  as  $n_A R_u T_m$  divided by  $V_m$  into  $V_m$  divided by  $n_m R_u T_m$ .

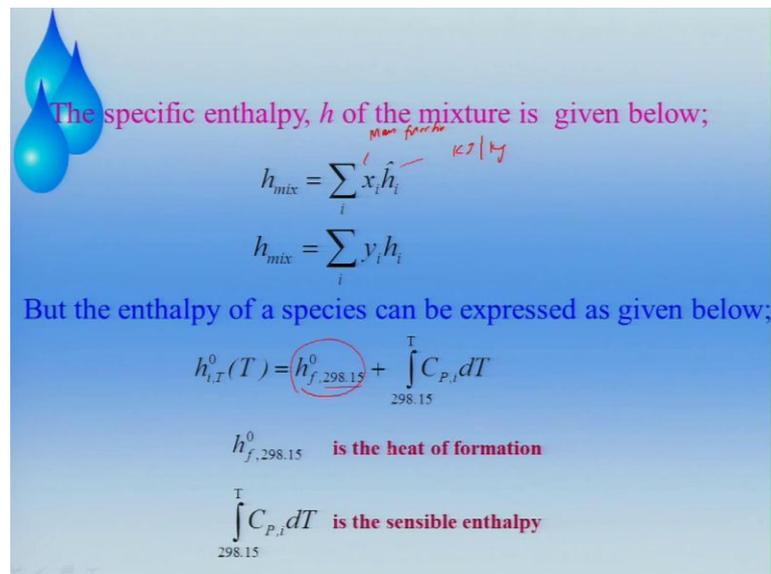
So, this will cancel it out what is that, this will cancel it out, here similarly we cancel it, you will get  $n_A$  by  $n_m$ , which is nothing but, your mole fraction of  $A$  and which is equal to  $V_A$  by  $v_m$ . What it indicates, it indicates that, the pressure ratio or pressure fraction is equal to the mole fraction, is equal to the volume fraction, of course only for

an ideal gas, this is a very important concept, which you must keep in mind. Now, for mixture of three ideal gases namely A B C, we can write down  $m_{mix}$  is equal to  $m_A$  plus  $m_B$  plus  $m_C$ .

Similarly,  $n_{mix}$  in terms of number of moles,  $n_{mix}$  is equal to  $n_A$  plus  $n_B$  plus  $n_C$  and I can write down basically  $P_{mix}$  is equal to  $P_A$  plus  $P_B$  plus  $P_C$ , this is from the Dalton's law partial pressure. So, from the Amagat's law, I can write down  $V_{mix}$  is equal to  $V_A$  plus  $V_B$  plus  $V_C$ , I can use that and we can write down this internal energy  $U_{mix}$  is basically  $U_A$  plus  $U_B$  plus  $U_C$  and summation of that in the three spaces. And if I look at the specific internal energy, it can be either for the like  $U_{mix}$  is summation of  $y_i u_i$  and  $i$  of course, the function of this.

And similarly, I can write down for enthalpy, which is summation of mole fraction and  $h_i$  that means, by using this concept, I can estimate what will be the entropy of the mixtures. And also the specific entropy in terms of mole fraction of the  $i$ th spaces, rather it can be summation over to 1 to  $n$ , for three spaces you can write down A B C like that. And now, let us look at about enthalpy, because we will be dealing with enthalpy, let us look at enthalpies kind of thing.

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The specific enthalpy,  $h$  of the mixture is given below;

$$h_{mix} = \sum_i x_i \hat{h}_i$$

*Handwritten note: Main factor is  $KJ/Kg$*

$$h_{mix} = \sum_i y_i h_i$$

But the enthalpy of a species can be expressed as given below;

$$h_{i,T}^0(T) = h_{f,298.15}^0 + \int_{298.15}^T C_{p,i} dT$$

$h_{f,298.15}^0$  is the heat of formation

$\int_{298.15}^T C_{p,i} dT$  is the sensible enthalpy

So, specific enthalpy of the mixture is given as a mixture, I am just writing to specify  $x_i h_i$  cap. Keep in mind that, this is enthalpy per Kg of fuel there. That means, enthalpy is a kilo Joule per Kg, this unit will be kilo Joule per K with a cap and without cap that is,

kilo Joule per kilo mole kind of thing. Similarly, and for this case, you will have to use the mass fraction and  $h$  mixture you will use the mole fraction and  $h_i$ , where this enthalpy of species can be expressed as  $h_i(T)$  is equal to  $h_f^\circ$  with respect to the standard that is 298.15 and the atmospheric pressure that is, 0 plus  $C_p \Delta T$ .

What you call this term, this term is nothing but, your heat of formation  $h_f^\circ$ , this is nothing heat of formation and  $C_p \Delta T$ , which will be integrated 298.15 to the particular temperature will be basically sensible enthalpy. So, this heat of formation you can get from a tables, of course it has been made from using the concept of reactions.

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**Heats of Reaction and Formation**

1 kmol CH<sub>4</sub>  
2 kmol O<sub>2</sub>  
25 °C, 0.1MPa

CO<sub>2</sub> + H<sub>2</sub>O  
25 °C, 0.1MPa

$Q = dH = H_P - H_R = \sum_P n_p h_p - \sum_R n_r h_r = \Delta H_{R,298}^\circ$

$H_R$  = total enthalpy of reactants,  $H_P$  = total enthalpy of products,  
 $n_{iR}$  = number of moles of  $i^{\text{th}}$  reactant,  $n_{iP}$  = number of moles of  $i^{\text{th}}$  product

$h_{iR}$  = Enthalpy of formation per unit mole of  $i^{\text{th}}$  reactant,  
 $h_{iP}$  = Enthalpy of formation per unit mole of  $i^{\text{th}}$  product

$\Delta H_{R,298}^\circ$  = Heat of reaction at standard states.

*Handwritten notes:*  $\Delta KE = 0$ ,  $\Delta PE = 0$ ,  $W_{sh} = 0$ , Heat of Reaction

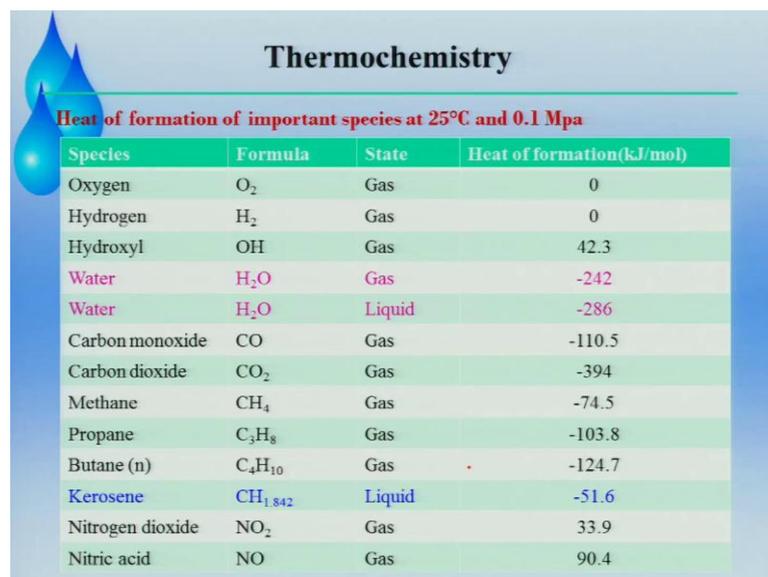
So, which I would not be getting into, but we can look at like, how to calculate this heat of reaction and formations. And we let us consider that, 1 mole of methane is reacting about 2 moles of oxygen going to the product CO<sub>2</sub> and water at 25 degree Celsius and 0.1 mega Pascal, keep in mind that this is also there. That means, both the reactant and product, there is the same temperature although there some heat being will be released in that, that is the assumptions.

So, if I use this and also make some assumption that, steady flow process, keep in mind this is the process and this is your CV and steady flow process, no shaft work like change in kinetic energy is 0, change in potential energy is 0 and there is no shaft work. And you will find that,  $Q$  is nothing but, your  $H_P$  minus  $H_R$  and where  $H_P$  summation of  $n_i P h$

$\sum \nu_i P_i$  is the basically product and  $\nu_i$  will be any number of spaces and similarly, minus  $\sum \nu_i R_i$ ,  $R_i$  is the reactant.

And keep in mind that, this portion is known as the heat of reaction at standard state, what is the standard state that is, 298.15, this we call as heat of reaction. And this heat of formation like per unit mole of  $i$  th reactant of any spaces you can use for the table.

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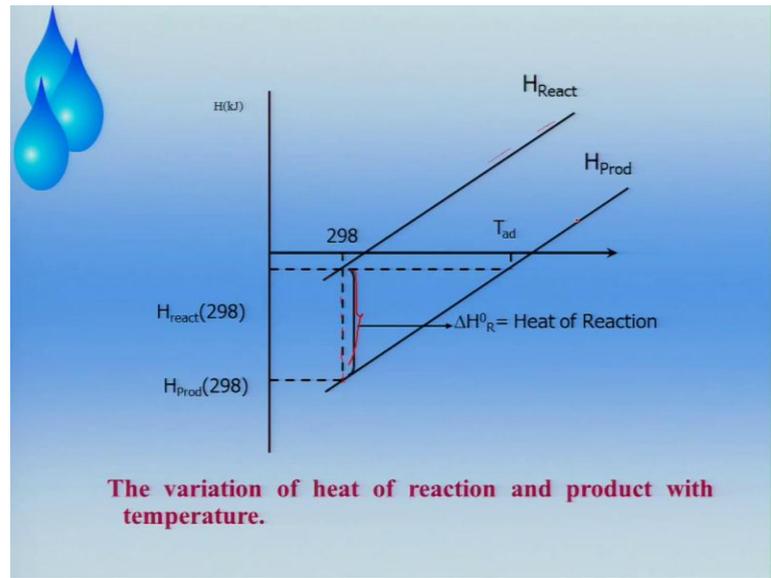
**Thermochemistry**

**Heat of formation of important species at 25°C and 0.1 Mpa**

Species	Formula	State	Heat of formation(kJ/mol)
Oxygen	O <sub>2</sub>	Gas	0
Hydrogen	H <sub>2</sub>	Gas	0
Hydroxyl	OH	Gas	42.3
Water	H <sub>2</sub> O	Gas	-242
Water	H <sub>2</sub> O	Liquid	-286
Carbon monoxide	CO	Gas	-110.5
Carbon dioxide	CO <sub>2</sub>	Gas	-394
Methane	CH <sub>4</sub>	Gas	-74.5
Propane	C <sub>3</sub> H <sub>8</sub>	Gas	-103.8
Butane (n)	C <sub>4</sub> H <sub>10</sub>	Gas	-124.7
Kerosene	CH <sub>1.842</sub>	Liquid	-51.6
Nitrogen dioxide	NO <sub>2</sub>	Gas	33.9
Nitric acid	NO	Gas	90.4

I will just show you that, various tables will be available you can see that oxygen heat of formation is 0, oxygen will be 0 and nitrogen will be 0 and water if you look at gas, it is minus 242 kilo Joule per mole. Whereas, for the liquid, it is 286 kilo Joule per mole, what I was talking about low heating value and high heating value in the last lecture. Similarly, kerosene it can be 51.6 and which is in liquid state, so you can use this table to estimate the...

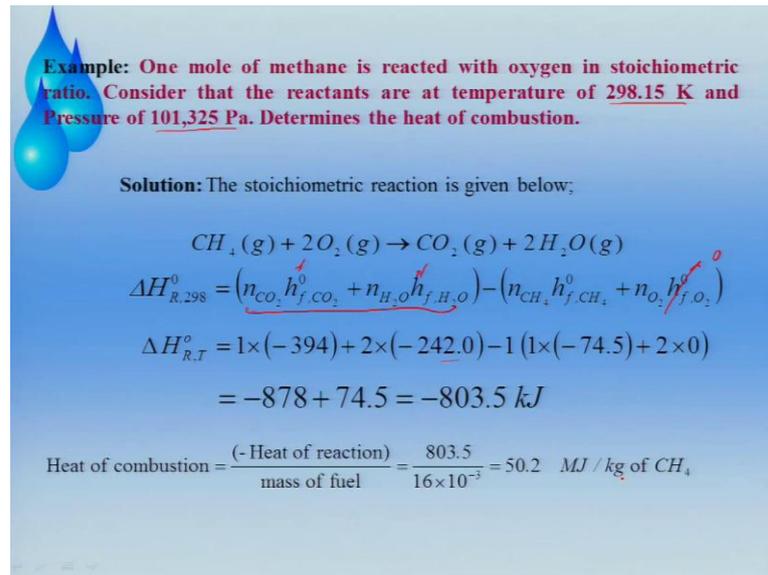
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And what is the meaning of this heat of reaction, basically if you look at, the reactant will be at here in this zone. This is keep in mind that, enthalpy versus temperature is being plotted like at various temperature it is changing, which indicates that, the heat of formation will be changing with the temperature as well. Similarly the product and this difference is nothing but, your heat of reaction, because you are considering at this point of the standard temperatures and variation of heat of reaction and product with temperature, which I have already told.

And although it is being drawn parallel, but in real situation, it would not be parallel keep in mind, it will be different. Because, the  $C_p$  is a function of temperature, that you should keep in mind.

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**Example:** One mole of methane is reacted with oxygen in stoichiometric ratio. Consider that the reactants are at temperature of 298.15 K and Pressure of 101,325 Pa. Determines the heat of combustion.

**Solution:** The stoichiometric reaction is given below;

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$
$$\Delta H_{R,298}^0 = (n_{CO_2} h_{f,CO_2}^0 + n_{H_2O} h_{f,H_2O}^0) - (n_{CH_4} h_{f,CH_4}^0 + n_{O_2} h_{f,O_2}^0)$$
$$\Delta H_{R,T}^0 = 1 \times (-394) + 2 \times (-242.0) - 1 \times (-74.5) + 2 \times 0$$
$$= -878 + 74.5 = -803.5 \text{ kJ}$$
$$\text{Heat of combustion} = \frac{(-\text{Heat of reaction})}{\text{mass of fuel}} = \frac{803.5}{16 \times 10^{-3}} = 50.2 \text{ MJ/kg of } CH_4$$

So, let us take an example like 1 mole of methane is reacted to oxygen is stoichiometric ratio, consider the heat of reactant at temperature 298 Kelvin and pressure of course, this is a standard pressure, determine the heat of combustion. How we will determine the heat of combustion, we will have to basically look at heat of the reactions and then, heat of reaction will be negative, because it is the exothermic reaction. So then, we will divide the mass of the fuel kind of thing, we will get the heat of reaction.

So, stoichiometric reaction is given below that is, methane reacting with 2 oxygen going to carbon dioxide and water. So, from this heat of reaction, I can get, I can write down here, this I can get from the table, write it a formation and similarly, oxygen of course, this will be 0, this will be zero heat of formation of oxygen. And if I will substitute these values from the table, like for heat of formation for carbon dioxide, for water and then, you need to use this heat of formation, whether it is a gas or a liquid, that is very important.

And similarly, for the methane, you have put substitute these values, when you put this thing, you will get minus 803.5 kilo Joule, keep in mind that. And heat of combustion will be heat of reaction, of course the minus sign of that, that became positive divide by mass of fuel. In this case, 1 mole you can put into molecular weight and you will get 50.2 mega Joule of heat being generated when you burn 1 Kg of fuel. With this, I will stop over, do you have any question to be asked, any doubt. Thank you.