Fundamentals of Combustion

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Lecture - 14

First Law and Second Law of Thermodynamics Applied to Combustion - Part 06

Worked Examples

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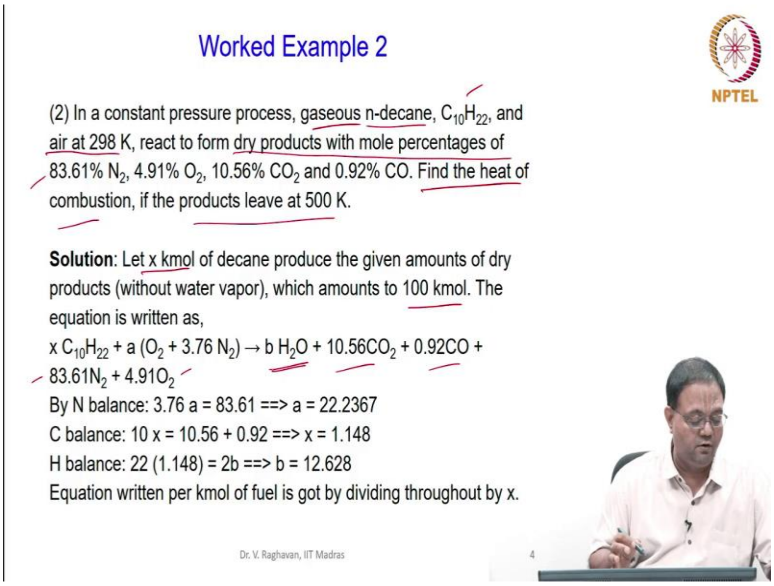

Worked Example 2

(2) In a constant pressure process, gaseous n-decane, $C_{10}H_{22}$, and air at 298 K, react to form dry products with mole percentages of 83.61% N_2, 4.91% O_2, 10.56% CO_2 and 0.92% CO. Find the heat of combustion, if the products leave at 500 K.

Solution: Let x kmol of decane produce the given amounts of dry products (without water vapor), which amounts to 100 kmol. The equation is written as,

$x\,C_{10}H_{22} + a\,(O_2 + 3.76\,N_2) \rightarrow b\,H_2O + 10.56CO_2 + 0.92CO + 83.61N_2 + 4.91O_2$

By N balance: 3.76 a = 83.61 ==> a = 22.2367

C balance: 10 x = 10.56 + 0.92 ==> x = 1.148

H balance: 22 (1.148) = 2b ==> b = 12.628

Equation written per kmol of fuel is got by dividing throughout by x.

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Second example, in a constant pressure process, gaseous n-decane, please understand that normally n-decane will be in liquid state at atmospheric conditions, but if you try to pre vaporize it by heating it or anything, you get gaseous n-decane that is fed to the combustion chamber.

So, this gaseous n-decane and air both at 298 K they react to form dry products. The composition is given here 83.61% N_2, 4.91% O_2, 10.56% CO_2, and 0.92% CO; H_2O is not there because it is removed after condensing. So, dry products, this means that in the reaction you should include H_2O.

Now, you have to find the heat of combustion given that the products leave the combustion chamber at 500 K, so it is not a standard heat of combustion here. Standard heat of combustion means you have to cool the products to 298 K, here since the product is not cooled to that level; it is leaving at 500 K, you have to calculate the enthalpy of the product mixture taking the absolute enthalpy of each product to be at 500 K.

So, as we know that when you have dry products composition known, then if we sum up it will be 100 kilomoles. So, to produce 100 kilomoles of dry products, let us assume that x kilomole of n-decane reacts with the air. So, reaction is given as x × $C_{10}H_{22}$ + a × O_2 + 3.76 N_2 giving products, we do not know the number of moles of H_2O.

$$x\,C_{10}H_{22} + a\,(O_2 + 3.76\,N_2) \rightarrow b\,H_2O + 10.56CO_2 + 0.92CO + 83.61N_2 + 4.91O_2$$

So, that plus all other things as measured by the volumetric analysis you can write. So, 10.56 kilomoles, 10.56% converts into kilomoles of CO_2, 0.92 kilomoles of CO, then 83.61 kilomoles of N_2, 4.91 kilomoles of O_2. Now, use the atom balance to solve the unknowns a, x and b.

By N balance: 3.76 a = 83.61 ==> a = 22.2367

C balance: 10 x = 10.56 + 0.92 ==> x = 1.148

H balance: 22 (1.148) = 2b ==> b = 12.628

Now, equation should be written in 1 kilomole basis. It is the customary thing we do we do not write the fuel as x kilomoles, we write it as 1 kilomole, so divide throughout by x you get the equation written in terms of 1 kilomole of decane.

$$C_{10}H_{22} + 19.37(O_2 + 3.76\,N_2) \rightarrow 11H_2O + 9.1986CO_2 + 0.801CO + 72.83N_2 + 4.277O_2$$

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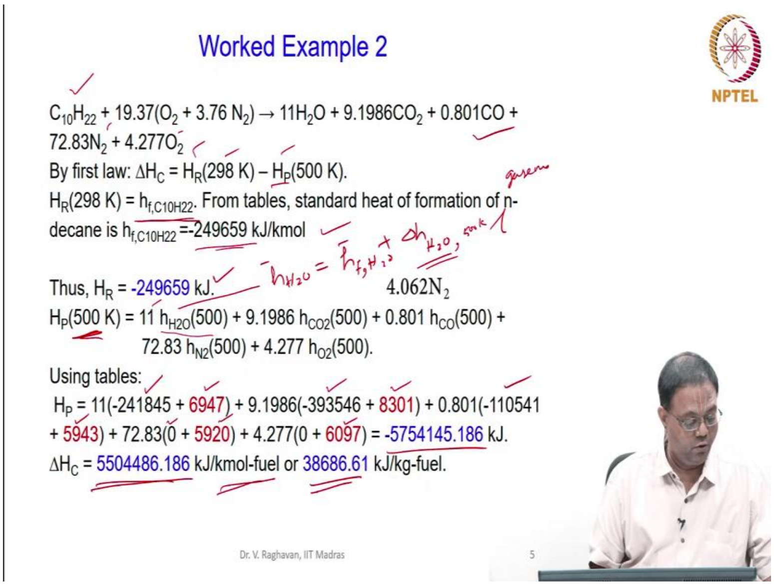

Worked Example 2

$C_{10}H_{22} + 19.37(O_2 + 3.76\,N_2) \rightarrow 11H_2O + 9.1986CO_2 + 0.801CO + 72.83N_2 + 4.277O_2$

By first law: $\Delta H_C = H_R(298\ K) - H_P(500\ K)$.

$H_R(298\ K) = h_{f,C10H22}$. From tables, standard heat of formation of n-decane is $h_{f,C10H22}$ =-249659 kJ/kmol

gaseous

$\bar{h}_{H_2O} = \bar{h}_{f,H_2O} + \Delta h_{H_2O,\,500K}$

Thus, H_R = -249659 kJ.

4.062N_2

$H_P(500\ K) = 11\ h_{H2O}(500) + 9.1986\ h_{CO2}(500) + 0.801\ h_{CO}(500) + 72.83\ h_{N2}(500) + 4.277\ h_{O2}(500)$.

Using tables:

H_P = 11(-241845 + 6947) + 9.1986(-393546 + 8301) + 0.801(-110541 + 5943) + 72.83(0 + 5920) + 4.277(0 + 6097) = -5754145.186 kJ.

ΔH_C = 5504486.186 kJ/kmol-fuel or 38686.61 kJ/kg-fuel.

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So, you can see that the products now, has this 4.277 O_2 and 11 H_2 etcetera. So, this is the thing. Now, delta H_C you have to calculate initially the reactants are 298 K. So, H_R should be calculated at 298 K only the enthalpy formation of this $C_{10}H_{22}$ is considered, O_2 and N_2 are 0. Enthalpy of formation of O_2 and N_2 are 0.

Similarly, if you take H_P, it should be calculated at 500 K; that means, that the all the species will now participate in the enthalpies, even though enthalpy formation of N_2 and

O_2 are 0, sensible enthalpy of O_2 and N_2 will contribute to the H_P value. So, let us see how to do that.

Now, from Stephen Turns tables or any other NIST website, you can take the h_f, heat of formation of decane. So, gaseous decane, you have to again choose the enthalpy formation for liquid or gas based upon what is the problem you are solving.

In this case, we have clearly given that we are dealing with gaseous decane. So, you have to take this enthalpy formation, of gaseous n-decane. So, that is taken from the tables. So, Stephen Turns gives this value for the gaseous thing.

$$\text{By first law: } \Delta H_C = H_R(298\text{ K}) - H_P(500\text{ K}).$$

$$H_R(298\text{ K}) = h_{f,C10H22}.$$

From tables, standard heat of formation of n-decane is $h_{f,C10H22}$ =-249659 kJ/kmol

Now, that should be substituted for H_R. Now H_R is known H_P at 500 K will be number of moles of H_2O that is 11 times the molar enthalpy of H_2O plus take this number of moles of CO_2 times h_{CO2}. Similarly, you write for other species. Now, using tables what is this h_{H2O} will be nothing but $h_{f,H2O}$ plus Δh_{H2O} at given temperature say 500 K.

Now, that is what I am writing here. For example, H_2O enthalpy formation is -241845 kJ/kmol and a sensible enthalpy which I have given here 6947 kJ/kmol, that is the sensible enthalpy of H_2O.

Similarly, for CO_2 enthalpy formation is -393546 kJ/kmol and a sensible enthalpy calculated from the tables at 500 K is 8301 kJ/kmol. Similarly, you can write for CO enthalpy formation is -110541 kJ/kmol, and the sensible enthalpy is 5943 kJ/kmol.

But if you see for say nitrogen, 72.83 kilomoles of nitrogen, enthalpy formation is zero, but it has a sensible enthalpy at 500 K as 5920 kJ/kmol. Similarly, for oxygen, the sensible enthalpy at 500 K is 6097 kJ/kmol.

$$H_P(500\text{ K}) = 11\, h_{H2O}(500) + 9.1986\, h_{CO2}(500) + 0.801\, h_{CO}(500) +$$
$$72.83\, h_{N2}(500) + 4.277\, h_{O2}(500).$$

$$H_P = 11(-241845 + 6947) + 9.1986(-393546 + 8301) + 0.801(-110541 + 5943) + 72.83(0$$
$$+ 5920) + 4.277(0 + 6097) = -5754145.186\text{ kJ}.$$

ΔH_C = 5504486.186 kJ/kmol-fuel or 38686.61 kJ/kg-fuel

So, when you add up this, you get the enthalpy of products, then H_R - H_P will give you the ΔH_C per kilomole of fuel, or dividing by the molecular weight of the fuel you will get per kg of fuel, ΔH_C value is 38686.61 kJ/kg of fuel. So, this is the way you do the heat calculation for a mixture.

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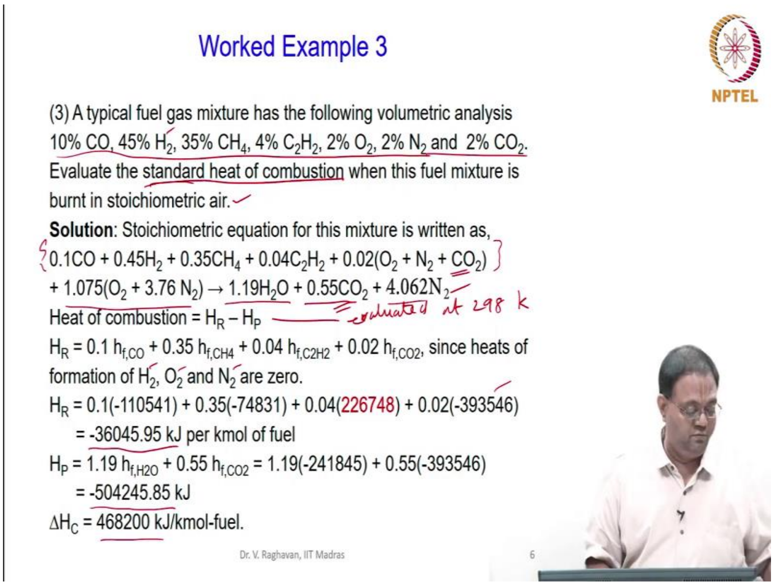

Worked Example 3

(3) A typical fuel gas mixture has the following volumetric analysis 10% CO, 45% H_2, 35% CH_4, 4% C_2H_2, 2% O_2, 2% N_2 and 2% CO_2. Evaluate the standard heat of combustion when this fuel mixture is burnt in stoichiometric air.

Solution: Stoichiometric equation for this mixture is written as,

$$0.1CO + 0.45H_2 + 0.35CH_4 + 0.04C_2H_2 + 0.02(O_2 + N_2 + CO_2)$$

$$+ 1.075(O_2 + 3.76\ N_2) \rightarrow 1.19H_2O + 0.55CO_2 + 4.062N_2$$

Heat of combustion = $H_R - H_P$ evaluated at 298 K

$H_R = 0.1\ h_{f,CO} + 0.35\ h_{f,CH4} + 0.04\ h_{f,C2H2} + 0.02\ h_{f,CO2}$, since heats of formation of H_2, O_2 and N_2 are zero.

$H_R = 0.1(-110541) + 0.35(-74831) + 0.04(226748) + 0.02(-393546)$

$= -36045.95$ kJ per kmol of fuel

$H_P = 1.19\ h_{f,H2O} + 0.55\ h_{f,CO2} = 1.19(-241845) + 0.55(-393546)$

$= -504245.85$ kJ

$\Delta H_C = 468200$ kJ/kmol-fuel.

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Now, again this example we saw how to calculate the stoichiometric proportions etcetera in the previous tutorial. But here we are trying to find the standard heat of combustion when the fuel mixture is burnt in stoichiometric.

So, standard heat of combustion is nothing but when the reactants are at 298 K whatever be the mixture, the products are got and the products are cooled to 298 K. But here we are trying to do it for stoichiometric combustion. So, only sufficient amount of air is added, but the assumption made is that CO_2 remains CO_2, no dissociation. Similarly, H_2O do not dissociate.

Now, the equation this is fuel mixture plus oxygen, we can write by balances. So, we can just write the equation and balance this, and get all the CO_2. Please understand that here the CO_2 formed plus CO_2 already present in the reactant should be added. We already seen the example how to get this in the previous tutorial, worked examples previously done for the stoichiometry.

$$0.1CO + 0.45H_2 + 0.35CH_4 + 0.04C_2H_2 + 0.02(O_2 + N_2 + CO_2)$$

$$+ 1.075(O_2 + 3.76\ N_2) \rightarrow 1.19H_2O + 0.55CO_2 + 4.062N_2$$

This is the equation you get. Now, find the H_R. Here, please understand that all the h_f, if you want standard heat of combustion, that means, H_R should be calculated at 298 K. Now, that means, h_f's are involved here. So, CO has h_f, 0.1 $h_{f,CO}$ + 0.35 $h_{f,CH4}$, H_2 I am not including here because h_f is 0 for H_2.

$$H_R = 0.1\ h_{f,CO} + 0.35\ h_{f,CH4} + 0.04\ h_{f,C2H2} + 0.02\ h_{f,CO2}$$

So, you can see hydrogen, oxygen and nitrogen are not involved in this because they are basic elements and the heat of formation is 0, so you should discard. So, 0.35 times $h_{f,CH4}$

+ 0.04 h_{f,C_2H_2} + 0.02 times h_{f,CO_2} in the fuel. Whatever in the fuel that will be reactant enthalpy H_R. Basic elements are discarded here.

$$H_R = 0.1(-110541) + 0.35(-74831) + 0.04(226748) + 0.02(-393546)$$
$$= -36045.95 \text{ kJ/kmol of fuel}$$

Similarly, if you take products, now I am substituting the values, so 0.1 times $h_{f,CO}$ is -110541 kJ/kmol, h_{f,CH_4} is -74831 kJ/kmol and h_{f,C_2H_2} is 226748 kJ/kmol. So, again you can get it from the tables and substitute it, similarly you have already seen that for carbon dioxide -393546 kJ/kmol. So, once you get this you can get the h_f value.

Now, H_P value, you have to take this mixture 1.19 times water vapor, 0.55 times carbon dioxide and 4.062 times nitrogen, but anyway N_2 will not appear here because it is a basic element, and at 298 K heat of formation is 0.

$$H_P = 1.19\, h_{f,H_2O} + 0.55\, h_{f,CO_2} = 1.19(-241845) + 0.55(-393546)$$
$$= -504245.85 \text{ kJ}$$
$$\Delta H_C = 468200 \text{ kJ/kmol-fuel.}$$

So, 1.19 × h_{f,H_2O} + 0.5 × h_{f,CO_2} that will be this. We will substitute this. Then you find ΔH_C by subtracting H_P to H_R, H_R - H_P that will be this. So, for a fuel you have to calculate this. But if the reactant or product are at different temperatures when they enter and exit, then you have to add appropriate sensible enthalpies.

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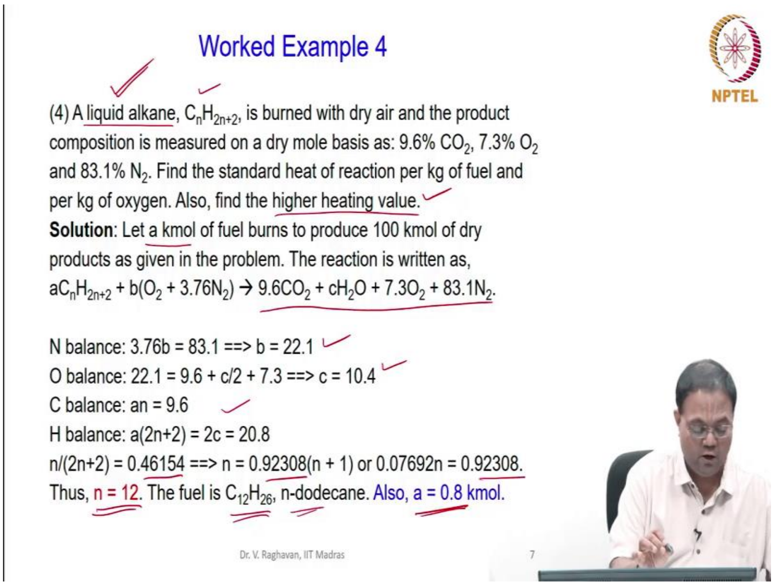

Worked Example 4

(4) A liquid alkane, C_nH_{2n+2}, is burned with dry air and the product composition is measured on a dry mole basis as: 9.6% CO_2, 7.3% O_2 and 83.1% N_2. Find the standard heat of reaction per kg of fuel and per kg of oxygen. Also, find the higher heating value.

Solution: Let a kmol of fuel burns to produce 100 kmol of dry products as given in the problem. The reaction is written as,

$aC_nH_{2n+2} + b(O_2 + 3.76N_2) \rightarrow 9.6CO_2 + cH_2O + 7.3O_2 + 83.1N_2$.

N balance: 3.76b = 83.1 ==> b = 22.1

O balance: 22.1 = 9.6 + c/2 + 7.3 ==> c = 10.4

C balance: an = 9.6

H balance: a(2n+2) = 2c = 20.8

n/(2n+2) = 0.46154 ==> n = 0.92308(n + 1) or 0.07692n = 0.92308.

Thus, n = 12. The fuel is $C_{12}H_{26}$, n-dodecane. Also, a = 0.8 kmol.

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The next problem a liquid alkane like this C_nH_{2n+2} is burned, we do not know what is that. It is burned with dry air and the product composition measured on dry mole basis are 9.6% CO_2 7.3% O_2, and 83.1% N_2, that is the product composition dry basis. So, H_2O we have to determine.

So, what is the standard heat of reaction per kg of fuel and also per kg of oxygen? So, you can write the ΔH_R or ΔH_C in both per kmol of fuel and kg of fuel or per kmol of oxygen or per kg of this, even per kg of product.

So, whatever way you want you can write that. Also find the higher heating value. We have different higher heating value. When the products water vapor is in liquid state then we get a higher heating value.

So, how to do that? We will see. Now, you have to importantly understand that this is a liquid fuel, appropriate value of heat of formation should be used. Similarly, when I talk about higher heating value, I should use the enthalpy of water vapor at formation of water vapor in the products as that of the liquids.

Now, again when the dry composition is given, I mean they sum up to 100 here like this excluding H_2O, now we will assume that a kilomole of fuel burns to produce this 100 kilomole of dry products.

$$aC_nH_{2n+2} + b(O_2 + 3.76N_2) \rightarrow 9.6CO_2 + cH_2O + 7.3O_2 + 83.1N_2.$$

So, a × C_nH_{2n+2} + b × O_2 + 3.76 N_2 giving 9.6 × CO_2 + c × H_2O + 7.3 × O_2 and 83.1 × N_2.

Now, by N balance you get b, O balance you get c. C balance and H balance will give the values of this a n and a(2n + 2).

$$\text{N balance: } 3.76b = 83.1 \implies b = 22.1$$

$$\text{O balance: } 22.1 = 9.6 + c/2 + 7.3 \implies c = 10.4$$

$$\text{C balance: } an = 9.6$$

$$\text{H balance: } a(2n+2) = 2c = 20.8$$

$$n/(2n+2) = 0.46154 \implies n = 0.92308(n + 1) \text{ or } 0.07692n = 0.92308.$$

Now, from this, you can solve for n, and n comes out to be 12. One more thing is if you want to do these calculations, you should have enough number of digits after the decimal point. If you do not do that, you will not get 12.

You have enough number of decimal points because very low values are involved. So, enough number of decimal points you have to use after that digits in order to get a number like this.

So, now the fuel is nothing but n-dodecane. And the value of a is 0.8. So, 0.8 kilomoles you burn you get this product of combustion, but anyway you can divide it and make it 1 kilomole of fuel. But the important thing is by the dry basis analysis, since you know the C and H ratio here, we have got the fuel itself as n dodecane.

$$C_{12}H_{26} + 27.625(O_2 + 3.76N_2) \rightarrow 12CO_2 + 13H_2O + 9.125O_2 + 103.87N_2$$

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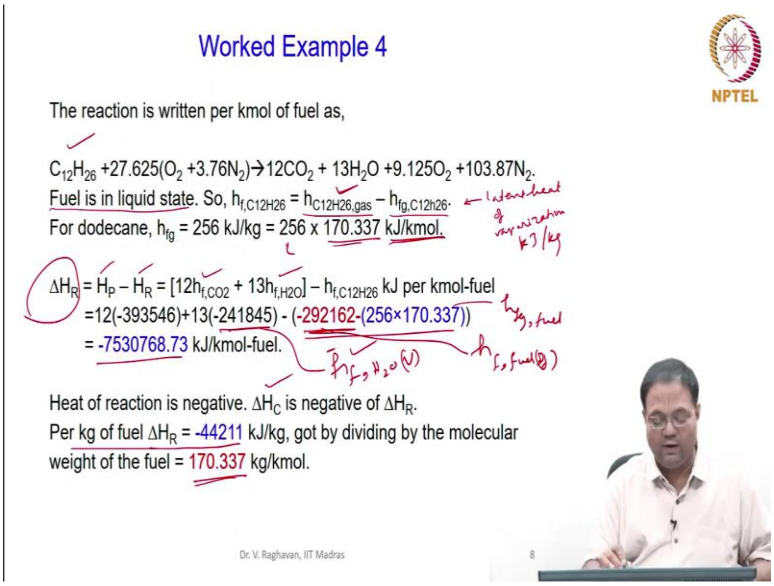

Worked Example 4

The reaction is written per kmol of fuel as,

$C_{12}H_{26}$ +27.625(O_2 +3.76N_2)→12CO_2 + 13H_2O +9.125O_2 +103.87N_2.

Fuel is in liquid state. So, $h_{f,C12H26} = h_{C12H26,gas} - h_{fg,C12h26}$.

For dodecane, h_{fg} = 256 kJ/kg = 256 x 170.337 kJ/kmol.

$\Delta H_R = H_P - H_R = [12h_{f,CO2} + 13h_{f,H2O}] - h_{f,C12H26}$ kJ per kmol-fuel

=12(-393546)+13(-241845) - (-292162-(256×170.337))

= -7530768.73 kJ/kmol-fuel.

Heat of reaction is negative. ΔH_C is negative of ΔH_R.

Per kg of fuel ΔH_R = -44211 kJ/kg, got by dividing by the molecular weight of the fuel = 170.337 kg/kmol.

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We can refer the tables and get the values, but it should be liquid. So, dividing by 0.8 throughout you get the equation per kilomole of fuel. So, $C_{12}H_{26}$ + 27.625 O_2 + 3.76 N_2 giving 12 CO_2 + 13 H_2O + 9.125 O_2 + 103.87 N_2. So, it is excess air, that comes out in the product also.

So, fuel is in liquid state, what you get as enthalpy of formation in the Turn's book tables is the gaseous enthalpy formation, so you get this value. Turns book also list the h_{fg} value, the latent heat of vaporization. Noe, both these values are available.

But please understand that this enthalpy of formation is given in kJ/kmol, but h_{fg} is given in kJ/kg. So, I multiply by molecular weight to get the value in terms of kmol, then I have to calculate the value of this.

Fuel is in liquid state. So, $h_{f,C12H26} = h_{C12H26,gas} - h_{fg,C12h26}$.

For dodecane, h_{fg} = 256 kJ/kg = 256 x 170.337 kJ/kmol.

This is the H_R value I get. H_P value is the heat of formation of CO_2, enthalpy formation of H_2O multiplied by corresponding number of moles, and we get this value kJ/kmol of fuel.

$$\Delta H_R = H_P - H_R = [12h_{f,CO2} + 13h_{f,H2O}] - h_{f,C12H26} \text{ kJ per kmol-fuel}$$

$$=12(-393546)+13(-241845) - (-292162-(256\times170.337))$$

$$= -7530768.73 \text{ kJ/kmol-fuel.}$$

Please understand here this ΔH_R, H_P - H_R we put so its negative, ΔH_C will be positive. So, when you say calorific value, I have to use Δh_c value.

Now, ΔH_R here per kg of fuel is just dividing this by molecular weight. Again, it is given in the tables you can use this and divide this by 170.337 to get ΔH_R as -44211 kJ/kg of dodecane.

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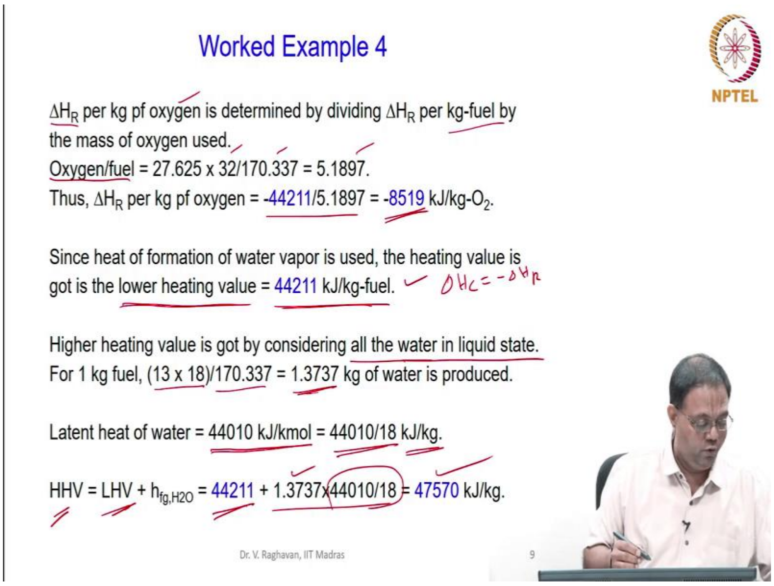

Worked Example 4

ΔH_R per kg pf oxygen is determined by dividing ΔH_R per kg-fuel by the mass of oxygen used.

Oxygen/fuel = 27.625 x 32/170.337 = 5.1897.

Thus, ΔH_R per kg pf oxygen = -44211/5.1897 = -8519 kJ/kg-O_2.

Since heat of formation of water vapor is used, the heating value is got is the lower heating value = 44211 kJ/kg-fuel. $\Delta H_C = -\Delta H_R$

Higher heating value is got by considering all the water in liquid state. For 1 kg fuel, (13 x 18)/170.337 = 1.3737 kg of water is produced.

Latent heat of water = 44010 kJ/kmol = 44010/18 kJ/kg.

HHV = LHV + $h_{fg,H2O}$ = 44211 + 1.3737x44010/18 = 47570 kJ/kg.

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Now, per kg of oxygen we want, so ΔH_R per kg of oxygen is determined by dividing ΔH_R per kg of fuel by the mass of oxygen used for 1 kg of fuel. So, find the oxygen to fuel ratio.

$$\text{Oxygen/fuel} = 27.625 \times 32/170.337 = 5.1897.$$

$$\text{Thus, } \Delta H_R \text{ per kg pf oxygen} = -44211/5.1897 = -8519 \text{ kJ/kg-}O_2$$

So, 27.625 kmol of oxygen is used, that multiplied by the molecular weight of oxygen divided by the molecular weight of fuel that will be the kg of oxygen used per kg of fuel. Now, if you divide the ΔH_R per kg of fuel by what you get here, you get the ΔH_R value per kg of oxygen burnt.

Now, what is higher calorific value? So, what we have got here is for 1 kg of fuel. You get, $\Delta H_C = -\Delta H_R$. So, per kg of fuel is positive now, ΔH_R was negative. So, negative of the negative will be positive here.

So, this is the lower heating value, 44211 kJ/kg-fuel.

Why it is lower heating value, because the product water vapor is in liquid state. The product 13 × $h_{f,H2O}$ vapor, we have used that.

So, we have assumed that when you calculate H_P the heat of formation and of H_2O is in vapor state, so you get lower heating value. For getting the higher heating value you have to consider all the water in the liquid state that means, for 1 kg fuel 13 × 18 / 170 = 1.3737 kilogram of water is produced.

So, latent of water is given in kJ/kmol as 44010. So, per kg it is 44010 / 18 kJ/kg, so you should add that to the lower heating value. So, higher heating value is nothing but lower heating value + h_{fg}.

Now, for 1 kg of fuel, you get 44010 /18 kJ/kg, but you are producing 1.3737 kg of water. So, 1.3737 kg of water produced into its latent heat in kJ/kg that will be added to the lower calorific value to get the higher calorific value or high heating value.

So, this is the way you solve this. As I told you for the liquid fuel you have to properly choose the enthalpy of formation. Gases fuel enthalpy of formation is readily given.

So, you have to appropriately use the latent heat of vaporization to get this. So, I have to subtract here. Here it is actually a vapor, I am subtracting that to get the liquid, because I want liquid. The reactor condition here is liquid alkane. So, what I get from the tables here is actually h_f fuel which is in gaseous state, so that minus this is h_{fg} of fuel.

When I subtract the h_f of a fuel which is in vapor state minus the h_{fg} of fuel to this, then you get this h_f of the fuel in liquid state, that is what the initial condition is, liquid alkane. So, I subtract this ok. Now, when they do a higher heating value calculation, you see that the LHV is added with the h_{fg} of H_2O which is produced.

So, what is the mass of water will produce that into h_{fg} that energy has to be added to this. So, that is what we are getting. This illustrates that you have to be careful when choosing the enthalpy of formation by seeing state of the fuel in the fuel stream and the H_2O in the product stream.

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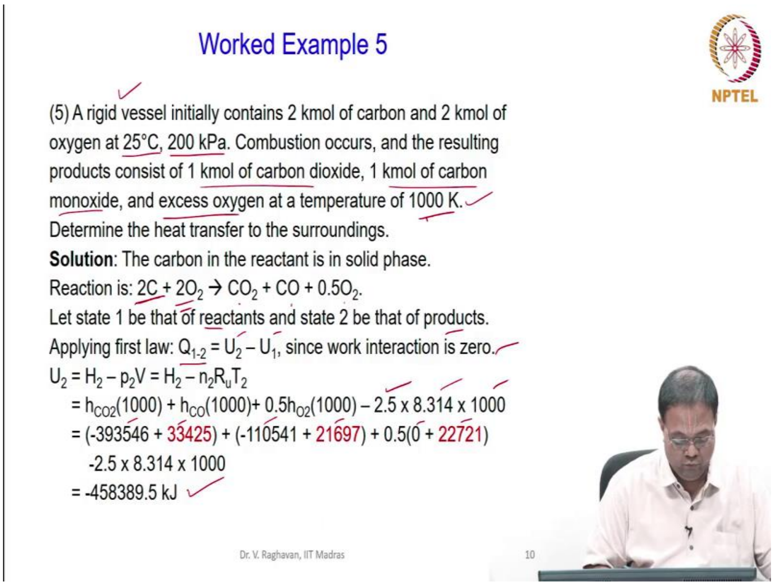

Worked Example 5

(5) A rigid vessel initially contains 2 kmol of carbon and 2 kmol of oxygen at 25°C, 200 kPa. Combustion occurs, and the resulting products consist of 1 kmol of carbon dioxide, 1 kmol of carbon monoxide, and excess oxygen at a temperature of 1000 K. Determine the heat transfer to the surroundings.

Solution: The carbon in the reactant is in solid phase.

Reaction is: $2C + 2O_2 \rightarrow CO_2 + CO + 0.5O_2$.

Let state 1 be that of reactants and state 2 be that of products.

Applying first law: $Q_{1\text{-}2} = U_2 - U_1$, since work interaction is zero.

$$\begin{aligned} U_2 &= H_2 - p_2V = H_2 - n_2R_uT_2 \\ &= h_{CO2}(1000) + h_{CO}(1000) + 0.5h_{O2}(1000) - 2.5 \times 8.314 \times 1000 \\ &= (-393546 + 33425) + (-110541 + 21697) + 0.5(0 + 22721) \\ &\quad -2.5 \times 8.314 \times 1000 \\ &= -458389.5 \text{ kJ} \end{aligned}$$

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Now, worked example 5. A rigid vessel initially contains 2 kmol of carbon and 2 kmol of oxygen at 25 degrees and 200 kilo pascals. Combustion occurs, it is a rigid vessel.

So, vessel will not have any volume change, so combustion occurs at a constant volume and resulting products consist of 1 kmol of carbon dioxide and 1 kmol of carbon monoxide and excess oxygen. And the products are at temperature of 1000 K, what is the heat transfer to the surroundings.

The same problem you have done already in the stoichiometry. Now, we are trying to calculate the heat transfer. The product contains CO_2, CO and O_2, so 1 mole, 1 mole and 2.5 moles. But if you take reactants carbon is in graphite state that is solid state and oxygen is in gas state, so that you have to remember. We have already seen that.

$$2C + 2O_2 \rightarrow CO_2 + CO + 0.5O_2$$

So, the state 1 is the reactant state and the state 2 is the product state. So, when I apply the first law to the constant volume process the heat interaction Q_{1-2} will be equal to the change in internal energy, final internal energy U_2 - initial internal energy U_1 that is the product internal energy minus reactant internal energy, the work interaction is 0.

Now, as we saw earlier, we have to use the definition of enthalpy, and I evaluate internal energy in terms of enthalpy. So, U_2 is nothing but $H_2 - p_2V$, so that is written as $H_2 - n_2R_uT_2$.

$$U_2 = H_2 – p_2V = H_2 – n_2R_uT_2$$

$$= h_{CO2}(1000) + h_{CO}(1000)+ 0.5h_{O2}(1000) – 2.5 \times 8.314 \times 1000$$

$$= (-393546 + 33425) + (-110541 + 21697) + 0.5(0 + 22721)$$

$$-2.5 \times 8.314 \times 1000$$

$$= -458389.5 \text{ kJ}$$

So, number of moles of n, n_2 is number of moles of product, T_2 is the temperature which is given as 1000 K. So, H_2 you have to evaluate. H_2 is nothing but for this mixture, you have to calculate the H_2 at 1000 K.

So, 1 mole of CO_2, so $h_{CO2}(1000)$, hCO(1000), and 0.5 $h_{O2}(1000)$, $-nR_uT_2$, that is n is 2.5, 1 kmol of CO_2, 1 kmol of CO and 0.5 kmol of O_2, so 2.5 × R_u is 8.314 in kJ/kmole-K, and T is 1000 K.

Now, at 1000 K, you see that for CO_2 you have enthalpy of formation + sensible enthalpy at 1000 K. Similarly, for CO enthalpy of formation + sensible enthalpy; for O_2 enthalpy of formation is 0 and sensible enthalpy is added. Now, if you do this, this is the U_2.

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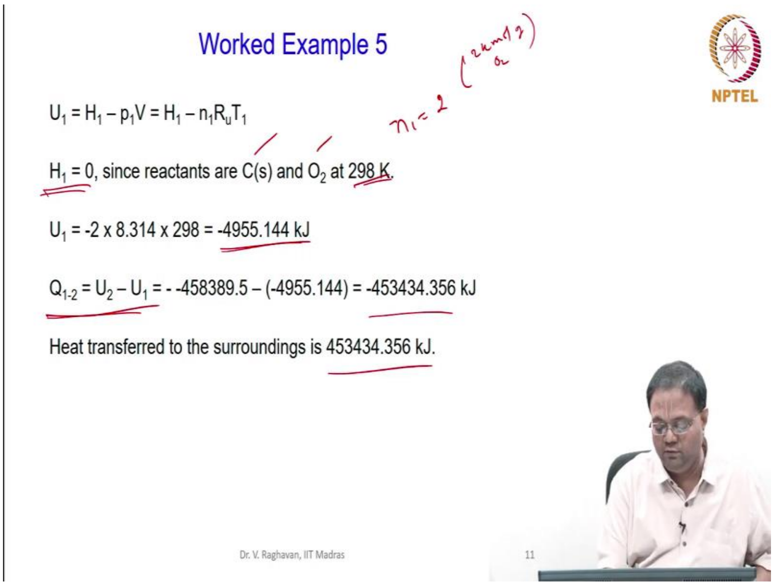

Worked Example 5

$n_1 = 2$ $\left(2\,\text{kmol}\ O_2\right)$

$U_1 = H_1 - p_1V = H_1 - n_1R_uT_1$

$H_1 = 0$, since reactants are C(s) and O_2 at 298 K.

$U_1 = -2 \times 8.314 \times 298 = -4955.144$ kJ

$Q_{1\text{-}2} = U_2 - U_1 = - -458389.5 - (-4955.144) = -453434.356$ kJ

Heat transferred to the surroundings is 453434.356 kJ.

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So, U_2, you calculate now. U_1 is $H_1 - p_1V = H_1 - n_1R_uT$.

$$U_1 = H_1 - p_1V = H_1 - n_1R_uT_1$$

$H_1 = 0$, since reactants are C(s) and O_2 at 298 K.

$$U_1 = -2 \times 8.314 \times 298 = -4955.144 \text{ kJ}$$

$$Q_{1\text{-}2} = U_2 - U_1 = - -458389.5 - (-4955.144) = -453434.356 \text{ kJ}$$

Heat transferred to the surroundings is 453434.356 kJ

Now, $H_1 = 0$, Please understand why because C is in solid state and O_2 is a basic element. Both are basic elements, and the enthalpy of formation at 298 K is 0. The reactants are at 298 K.

So, the enthalpy is 0 for the reactants. But U is not 0. U is -2 × 8.314 × 298. Please see that $n_1 = 2$ that is 2 kmol of O_2. The solid will not contribute to the n. So, $n_1 = 2$, so 2 × 8.314 × 298.

So, even though the reactants are at 298 K, enthalpy is 0, but internal energy is not 0, that is having some value here. So, when you do this $Q_{1\text{-}2}$ heat interaction will be -453434.356 kJ. And since this is negative, that means, the heat is transferred to the surroundings, and that is this.