# Fundamentals of Combustion

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## Lecture - 15

## First Law and Second Law of Thermodynamics Applied to Combustion - Part 07 - Worked Examples (Contd.)

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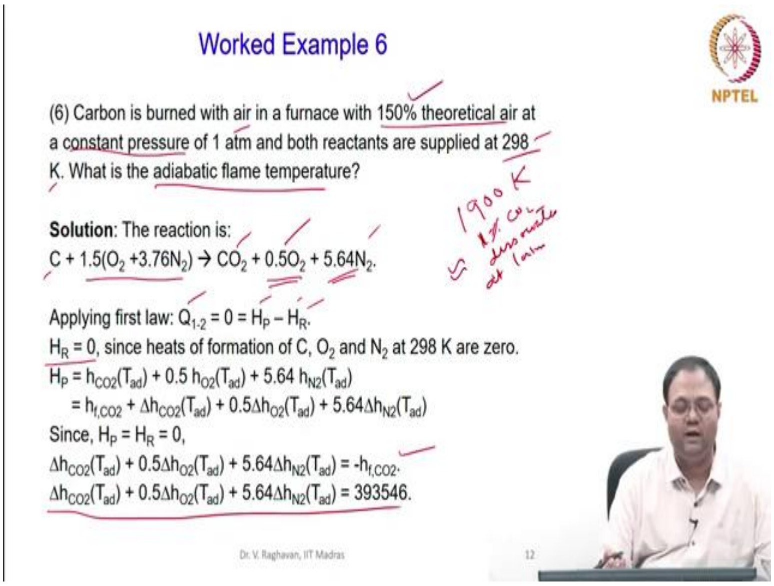

Worked Example 6

(6) Carbon is burned with air in a furnace with 150% theoretical air at a constant pressure of 1 atm and both reactants are supplied at 298 K. What is the adiabatic flame temperature?

1900 K

1% $CO_2$ dissociate at 1 atm

**Solution**: The reaction is:

$C + 1.5(O_2 + 3.76N_2) \rightarrow CO_2 + 0.5O_2 + 5.64N_2$.

Applying first law: $Q_{1\text{-}2} = 0 = H_P - H_R$.

$H_R = 0$, since heats of formation of C, $O_2$ and $N_2$ at 298 K are zero.

$H_P = h_{CO2}(T_{ad}) + 0.5\, h_{O2}(T_{ad}) + 5.64\, h_{N2}(T_{ad})$

$= h_{f,CO2} + \Delta h_{CO2}(T_{ad}) + 0.5\Delta h_{O2}(T_{ad}) + 5.64\Delta h_{N2}(T_{ad})$

Since, $H_P = H_R = 0$,

$\Delta h_{CO2}(T_{ad}) + 0.5\Delta h_{O2}(T_{ad}) + 5.64\Delta h_{N2}(T_{ad}) = -h_{f,CO2}$.

$\Delta h_{CO2}(T_{ad}) + 0.5\Delta h_{O2}(T_{ad}) + 5.64\Delta h_{N2}(T_{ad}) = 393546$.

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So, the worked example 6, carbon is burned with air in a furnace with 150% theoretical air, at a constant pressure of 1 atmosphere and both reactants are supplied at 298 K. What is the adiabatic flame temperature? So, till the previous example we saw the heat calculations.

Now, let us try to calculate the adiabatic flame temperature.

$$C + 1.5(O_2 + 3.76N_2) \rightarrow CO_2 + 0.5O_2 + 5.64N_2.$$

The reaction is C + 1.5 so, for 1 C atom we need 1 $O_2$ molecule, but here since 150% theoretical air so, we are supplying 1 1.5 × 1.5 kmol of oxygen. So, 1.5 ($O_2$ + 3.76 $N_2$), that is air giving $CO_2$, complete combustion takes place.

The excess air comes out and this 5.64 $N_2$ remains in the product. Now, from the first law you know that for a constant pressure process, the heat interaction is nothing but the enthalpy change. The final state enthalpy is $H_P$ and the initial state enthalpy is $H_R$.

$$Q_{1\text{-}2} = 0 = H_P - H_R$$

$$H_R = 0$$

Now, $H_R$ is 0 because C, $O_2$ and $N_2$ all are basic elements and they are 298 K. So, $h_f$ is equal to 0. So, $H_R = 0$. Now what is $H_P$? we should get $H_P$ at a particular temperature. Let us assume that the flame temperature is adiabatic flame temperature, $T_{ad}$, anyway we have to assume the value for that.

$$H_P = h_{CO2}(T_{ad}) + 0.5\ h_{O2}(T_{ad}) + 5.64\ h_{N2}(T_{ad})$$

$$= h_{f,CO2} + \Delta h_{CO2}(T_{ad}) + 0.5\Delta h_{O2}(T_{ad}) + 5.64\Delta h_{N2}(T_{ad})$$

So, 1 mole of $CO_2$, $h_{CO2}$ calculated at $T_{ad}$ + 0.5 kmol of $h_{O2}$ calculated at the same temperature + 5.64 $h_{N2}$ at this $T_{ad}$. Now, I can write this splitting into two as formation and the sensible parts.

So, $h_f$ of $CO_2$ + $\Delta h_{CO2}$ calculated at $T_{ad}$ + 0.5 $h_f$ is 0 for $O_2$ + $\Delta h_{O2}$ at $T_{ad}$ + 5.64 times $\Delta h_{N2}$ at $T_{ad}$. Now, since $H_P - H_R = 0$.

$$H_P = H_R = 0$$

Since $H_R = 0$, $H_P$ also should be equal to 0. So, using that I can write rewrite this Δh's as,

$$\Delta h_{CO2}(T_{ad}) + 0.5\Delta h_{O2}(T_{ad}) + 5.64\Delta h_{N2}(T_{ad}) = -h_{f,CO2}.$$

$$\Delta h_{CO2}(T_{ad}) + 0.5\Delta h_{O2}(T_{ad}) + 5.64\Delta h_{N2}(T_{ad}) = 393546.$$

I have put Δh on one side and $h_f$ of $CO_2$ I take to the other side. So, I get this equation.

So, only by referring to the tables, assume a temperature $T_{ad}$ go to the corresponding tables of $CO_2$ $O_2$ and $N_2$ retrieve the value of Δh at that particular temperature, substitute that in the left hand side and see whether it is equal to the right hand side. So, that is what the exercise we are going to do iteratively.

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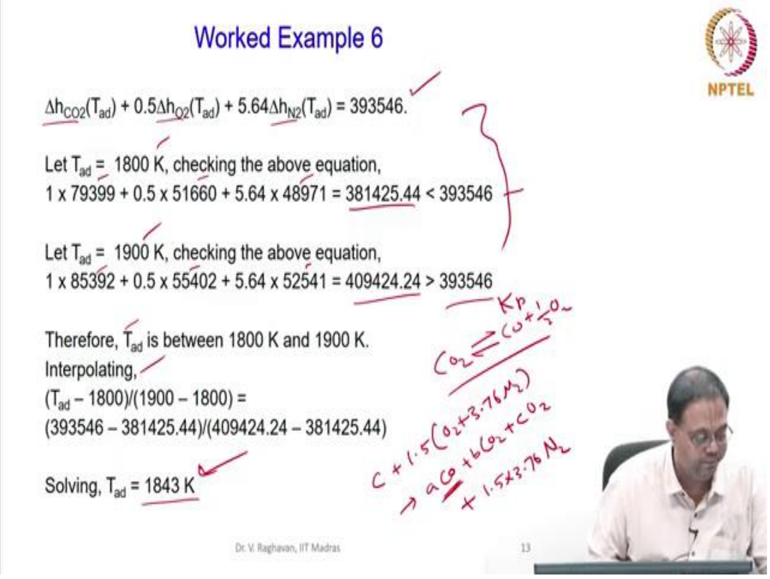

### Worked Example 6

$\Delta h_{CO2}(T_{ad}) + 0.5\Delta h_{O2}(T_{ad}) + 5.64\Delta h_{N2}(T_{ad}) = 393546.$

Let $T_{ad}$ = 1800 K, checking the above equation,
$1 \times 79399 + 0.5 \times 51660 + 5.64 \times 48971 = 381425.44 < 393546$

Let $T_{ad}$ = 1900 K, checking the above equation,
$1 \times 85392 + 0.5 \times 55402 + 5.64 \times 52541 = 409424.24 > 393546$

Therefore, $T_{ad}$ is between 1800 K and 1900 K.
Interpolating,
$(T_{ad} - 1800)/(1900 - 1800) =$
$(393546 - 381425.44)/(409424.24 - 381425.44)$

Solving, $T_{ad}$ = 1843 K

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$$\Delta h_{CO2}(T_{ad}) + 0.5\Delta h_{O2}(T_{ad}) + 5.64\Delta h_{N2}(T_{ad}) = 393546$$

So, this is the equation I have. Let us assume the adiabatic temperature to be 1800 K, why I am assuming a lower temperature is because, here you can see that it is 150% theoretical air, when you put more air you will see naturally that there is excess oxygen and more amount of $N_2$ is there. So, this is going to reduce the temperature.

$$1 \times 79399 + 0.5 \times 51660 + 5.64 \times 48971 = 381425.44 < 393546$$

I initially take a temperature of 1800 K and try to evaluate. So, go to the tables and get the value of $\Delta h_{CO2}$ at 1800 K, $\Delta h_{O2}$ at 1800 K and $\Delta h_{N2}$ at 1800 K, which are these three. Substitute this and get the value of this left hand side. You see that the left hand side is now lesser than the right hand side.

Since this is lesser, I now increase my gas temperature to 1900 K and I again retrieve the value of $\Delta h_{CO2}$ at 1900 K, $\Delta h_{O2}$ at 1900 K and $\Delta h_{N2}$ at 1900 K these three are the values.

$$1 \times 85392 + 0.5 \times 55402 + 5.64 \times 52541 = 409424.24 > 393546$$

So, when I substitute, I overshoot the value. Now I get a value which is greater than the required value.

Now, this means that the adiabatic flame temperature should be in between these two. We just interpolate this linear, we assume that it lies linearly in between these two.

$$(T_{ad} - 1800)/(1900 - 1800) =$$

$$(393546 - 381425.44)/(409424.24 - 381425.44)$$

So, assume linear interpolation like this $(T_{ad} - 1800) / (1900 - 1800)$ will be equal to the value of h at $T_{ad}$ and at 1800 K and 1900 K, respectively.

So, you get $T_{ad}$ as 1843 K. So, its a simple problem. We have not considered dissociation here, that is assumption we are making. For example, at 1800 K some small amount of $CO_2$ may dissociate, small amount but it is not so high. So, actually we can see that when the temperature is around 1900 K 1 percent of $CO_2$ dissociates at atmospheric pressure approximately, 1 percent of $CO_2$ only dissociates at 1900 K.

Since the theoretical air supplied is very high and the temperature we estimate to be within this, less than 1900 K, it is better we did not assume any dissociation. So, if you want to really calculate accurately you have to assume dissociation of $CO_2$ also; that means, you have to write this equation here.

You have to write including the dissociation as $C + 1.5(O_2 + 3.76\ N_2)$ giving $a \times CO + b \times CO_2 + c \times O_2 + 1.5 \times 3.76\ N_2$. Now, for this, carbon balance and oxygen balance will give you two equations and one more equation you will get by considering this dissociation.

$$CO_2 \leftarrow\rightarrow CO + ½\ O_2$$

So, we can solve like this, you can attempt solving this problem like this, but you will not see much change in the temperature. That is because of the excess oxygen here. Now, we can see that if you consider small amount of CO maybe produced at this temperature.

So, again if you want to solve this like this, you have to assume a temperature and calculate the equilibrium constant for this equation $K_p$ and calculate this a b c as mole fraction and write it in the mole fraction term. Then calculate the $H_P$ and do this iteration to check $H_P = H_R$ or not, then you have to finalize the temperature iteratively.

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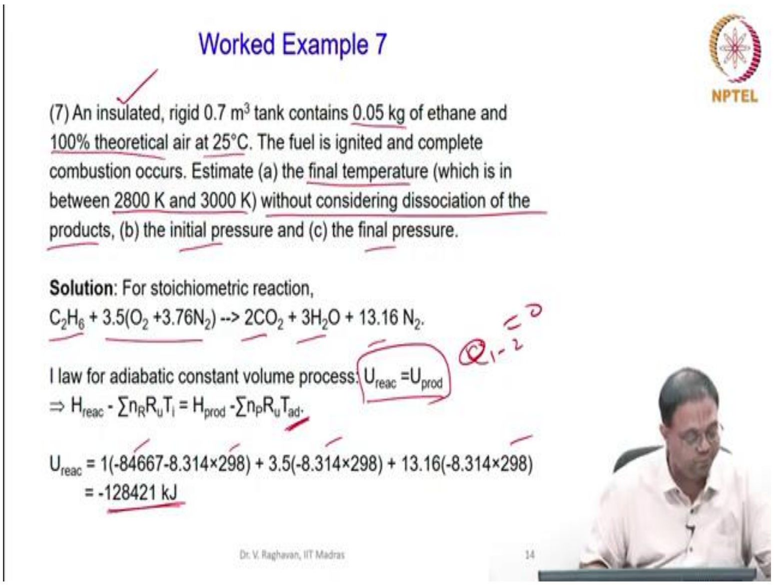

## Worked Example 7

(7) An insulated, rigid 0.7 $m^3$ tank contains 0.05 kg of ethane and 100% theoretical air at 25°C. The fuel is ignited and complete combustion occurs. Estimate (a) the final temperature (which is in between 2800 K and 3000 K) without considering dissociation of the products, (b) the initial pressure and (c) the final pressure.

**Solution**: For stoichiometric reaction,

$C_2H_6 + 3.5(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O + 13.16\,N_2$.

I law for adiabatic constant volume process: $\boxed{U_{reac} = U_{prod}}$ $Q_{1-2} = 0$

$\Rightarrow H_{reac} - \sum n_R R_u T_i = H_{prod} - \sum n_P R_u T_{ad}$.

$U_{reac} = 1(-84667 - 8.314\times298) + 3.5(-8.314\times298) + 13.16(-8.314\times298)$
$= -128421$ kJ

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Next problem, an insulated rigid 0.7 $m^3$ tank contains 0.05 kg of ethane and 100% theoretical air at 25°C that is 298 K. Fuel is ignited and complete combustion occurs.

Now, what is the final temperature? they have given this also, final temperature is between 2800 K and 3000 K. Now, to make our life easier they have asked to calculate without considering dissociation of the products. Then you have to find the initial pressure and final pressure also. So, that is the equation here. So, ethane $C_2H_6$ + 100% theoretical air so, just to use 2 + 6 / 4.

$$C_2H_6 + 3.5(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O + 13.16\,N_2$$

So, that will be this 3.5 × ($O_2$ + 3.76 $N_2$) giving 2 $CO_2$ + 3 $H_2O$ + 13.16 $N_2$. Now, for constant volume process $U_{react} = U_{prod}$, because its adiabatic. So, we need to actually calculate the final temperature of the insulated vessel. So, $Q_{1-2} = 0$, adiabatic insulated vessel. So, when you apply the first law to this U reactant will be equal to U products.

$$U_{reac} = U_{prod}$$

$$\Rightarrow H_{reac} - \sum n_R R_u T_i = H_{prod} - \sum n_P R_u T_{ad}.$$

Now, $H_{reac}$ - $\sum n_R R_u T_i$ will be equal to $H_{prod}$ - $\sum n_P R_u T_{ad}$. So, this is the adiabatic flame temperature or final temperature. I am assuming it as adiabatic flame temperature. Now, you calculate the equation like this. So, sigma I am putting here because, I am considering each and every species here.

$$U_{reac} = 1(-84667-8.314\times298) + 3.5(-8.314\times298) + 13.16(-8.314\times298)$$
$$= -128421 \text{ kJ}$$

So, for this $C_2H_2$ you have 1 × 84667 is the $h_f$ of $C_2H_2$ – 1 × 8.314 × 298. So, that is for fuel + 3.5 × $O_2$, $h_f$ is 0, but -3.5 × 8.314 × 298 will be there + again nitrogen 3.5 × 3.76 × $h_f$, which is 0, but 8.314 × 298 remains. So, this will be the $U_{reac}$, the internal energy of the reactants.

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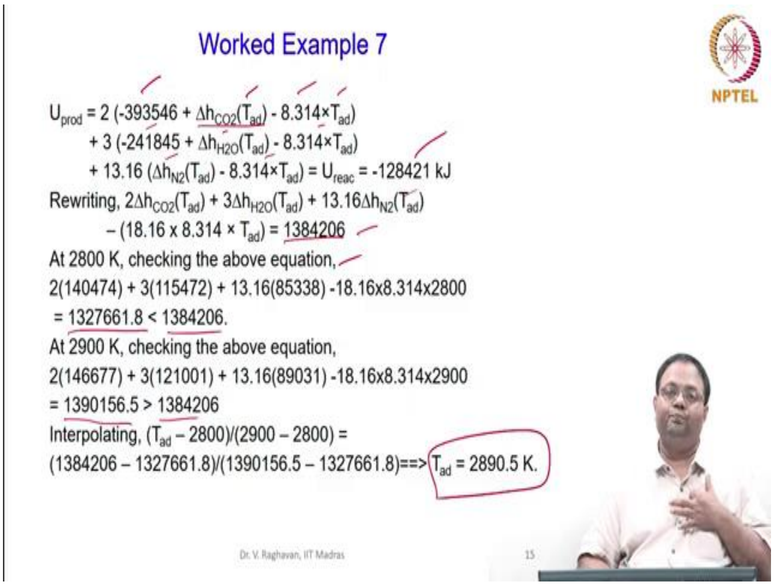

## Worked Example 7

$U_{prod} = 2\,(-393546 + \underline{\Delta h_{CO2}(T_{ad})} - 8.314\times T_{ad})$
$\quad + 3\,(-241845 + \Delta h_{H2O}(T_{ad}) - 8.314\times T_{ad})$
$\quad + 13.16\,(\Delta h_{N2}(T_{ad}) - 8.314\times T_{ad}) = U_{reac} = -128421$ kJ

Rewriting, $2\Delta h_{CO2}(T_{ad}) + 3\Delta h_{H2O}(T_{ad}) + 13.16\Delta h_{N2}(T_{ad})$
$\quad - (18.16 \times 8.314 \times T_{ad}) = \underline{1384206}$

At 2800 K, checking the above equation,
2(140474) + 3(115472) + 13.16(85338) -18.16x8.314x2800
= $\underline{1327661.8} < \underline{1384206}$.

At 2900 K, checking the above equation,
2(146677) + 3(121001) + 13.16(89031) -18.16x8.314x2900
= $\underline{1390156.5} > \underline{1384206}$

Interpolating, $(T_{ad} - 2800)/(2900 - 2800)$ =
(1384206 – 1327661.8)/(1390156.5 – 1327661.8)==> $\boxed{T_{ad} = 2890.5 \text{ K.}}$

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$$U_{prod} = 2\,(-393546 + \Delta h_{CO2}(T_{ad}) - 8.314\times T_{ad})$$
$$+ 3\,(-241845 + \Delta h_{H2O}(T_{ad}) - 8.314\times T_{ad})$$
$$+ 13.16\,(\Delta h_{N2}(T_{ad}) - 8.314\times T_{ad}) = U_{reac} = -128421 \text{ kJ}$$

Now, internal energy of the products is 2 × $h_f$ of $CO_2$, then adiabatic flame temperature, we do not know, but you write just write the sensible enthalpy of $CO_2$ calculated at $T_{ad}$, which we are going to assume. Similarly, 2 is there here. So, 2 × $R_u$ × $T_{ad}$ also appears here.

Similarly, for 3 × $H_2O$, enthalpy of formation and Δh at $T_{ad}$ and $R_u$ × $T_{ad}$ is calculated. Similarly, for nitrogen, there is no $h_f$ straight away sensible enthalpy of nitrogen at $T_{ad}$ and $R_u$ × $T_{ad}$ is calculated. So, this should be equal to $U_{reac}$.

So, rearrange the equation to get all the sensible enthalpies two times sensible enthalpy of $CO_2$ at $T_{ad}$ + three times sensible enthalpy of $H_2$ at $T_{ad}$ + 13.16 times sensible enthalpy of $N_2$ at $T_{ad}$ - the number of moles of products × $R_u$ × $T_{ad}$ will be equal to, whatever be the constant I am taking to right hand side and added to this. So, this will be the equation I get.

$$2\Delta h_{CO2}(T_{ad}) + 3\Delta h_{H2O}(T_{ad}) + 13.16\Delta h_{N2}(T_{ad})$$
$$– (18.16 \text{ x } 8.314 \times T_{ad}) = 1384206$$

So, once you assume $T_{ad}$ I can substitute it in the left hand side, retrieve the values of Δh's from the tables and calculate the left hand side and compare it with the right hand side. They have given that the temperature is in between 2800 K and 2900 K.

At 2800 K, checking the above equation,

$$2(140474) + 3(115472) + 13.16(85338) -18.16\text{x}8.314\text{x}2800$$
$$= 1327661.8 < 1384206$$

At 2900 K, checking the above equation,

$$2(146677) + 3(121001) + 13.16(89031) -18.16\text{x}8.314\text{x}2900$$
$$= 1390156.5 > 1384206$$

Interpolating,

$$(T_{ad} – 2800)/(2900 – 2800) =$$
$$(1384206 – 1327661.8)/(1390156.5 – 1327661.8) \text{==>} T_{ad} = 2890.5 \text{ K}$$

So, starting with 2800 K I see that the left hand side is less than right hand side, but for 2900 K I see the other way, right hand side is less than the left hand side. So, interpolating again what we did in the previous case, I get the adiabatic flame temperature as 2890.5 K, as they have given this is in between these two.

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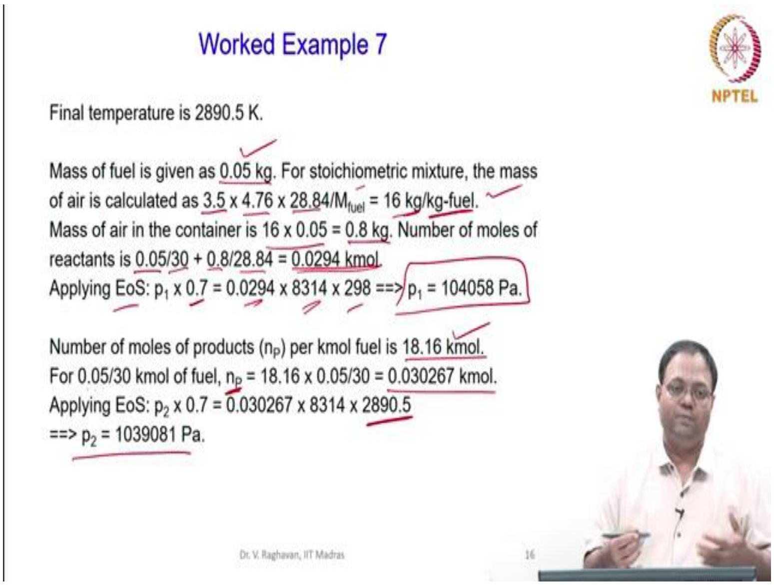

## Worked Example 7

Final temperature is 2890.5 K.

Mass of fuel is given as 0.05 kg. For stoichiometric mixture, the mass of air is calculated as $3.5 \times 4.76 \times 28.84/M_{fuel} = 16$ kg/kg-fuel.
Mass of air in the container is $16 \times 0.05 = 0.8$ kg. Number of moles of reactants is $0.05/30 + 0.8/28.84 = 0.0294$ kmol.
Applying EoS: $p_1 \times 0.7 = 0.0294 \times 8314 \times 298 \Longrightarrow \boxed{p_1 = 104058 \text{ Pa.}}$

Number of moles of products ($n_P$) per kmol fuel is 18.16 kmol.
For 0.05/30 kmol of fuel, $n_P = 18.16 \times 0.05/30 = 0.030267$ kmol.
Applying EoS: $p_2 \times 0.7 = 0.030267 \times 8314 \times 2890.5$
$\Longrightarrow p_2 = 1039081$ Pa.

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Now, final temperature is got. So, what is the initial pressure? Now, they have given some data on mass of fuel as 0.05 kg, for stoichiometric mixture.

For stoichiometric mixture, the mass of air is calculated as

$$3.5 \times 4.76 \times 28.84/M_{fuel} = 16 \text{ kg/kg-fuel.}$$

At stoichiometric its 100% theoretical air so, 3.5 × 4.76 number of moles of air × molecular weight of air / molecular weight of fuel. So, that will be 16 kg/kg of fuel.

$$\text{Mass of air in the container is } 16 \times 0.05 = 0.8 \text{ kg.}$$

$$\text{Number of moles of reactants is } 0.05/30 + 0.8/28.84 = 0.0294 \text{ kmol.}$$

So, mass of air in the container will be, if 1 kg of fuel is present, then 16 kg of air will be present. Now, you have only 0.05 kg of fuel in the vessel; that means, 16 × 0.05 that is 0.8 kg of air will be present in the vessel.

Number of moles of reactant will be now, the mass of the fuel / molecular weight of fuel. So, $C_2H_6$ molecular weight + mass of the air / molecular weight of air. So, this will be the kilomoles of fuel.

Now, you use the equation of state ideal gas equation of state $p_1$ which you do not know.

$$\text{Applying EoS: } p_1 \times 0.7 = 0.0294 \times 8314 \times 298 \Longrightarrow p_1 = 104058 \text{ Pa}$$

So, $p_1$ × V, 0.7 $m^3$ is equal to number of moles of reactant × universal gas constant × 298. So, it will give the $p_1$. its about 100 kPa, so, 104 kPa. Now, number of moles of products is 18.16 × number of kmol of products per kmol of fuel. For 0.05 / 30 kmol of fuel, only this much kilo mole of product is formed.

$$\text{For } 0.05/30 \text{ kmol of fuel, } n_P = 18.16 \times 0.05/30 = 0.030267 \text{ kmol}$$

Since mass is given mass of the fuel is given as 0.05 kgs. So, corresponding to that will be 0.05 / 30 kmol of fuel. So, when one kmol of fuel burns, you will get 18.16 kmol of products. Now, how much kmol of fuel is burning, 0.05 / 30 kilo mole of fuel is burning, corresponding to that the number of product moles will be 0.030267 kmol.

$$\text{Applying EoS: } p_2 \times 0.7 = 0.030267 \times 8314 \times 2890.5$$

$$\Longrightarrow p_2 = 1039081 \text{ Pa.}$$

Now, use this in the equation of state, $p_2 \times 0.7 = 0.030267 \times R_u \times T_{ad}$, now you get the pressure here. So, we get about 10 times pressure raise approximately. This is a constant volume combustion, where the temperature rises and pressure also raises tremendously.

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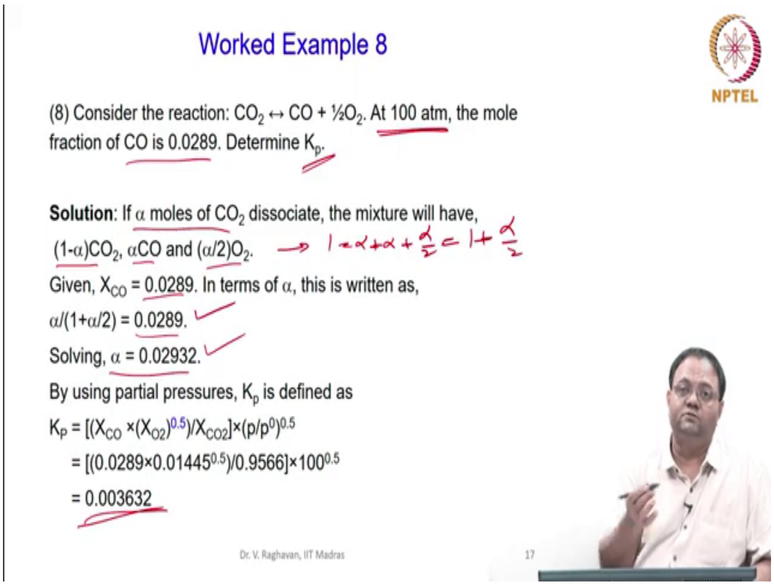

## Worked Example 8

(8) Consider the reaction: $CO_2 \leftrightarrow CO + ½O_2$. At 100 atm, the mole fraction of CO is 0.0289. Determine $K_p$.

**Solution**: If $\alpha$ moles of $CO_2$ dissociate, the mixture will have, $(1-\alpha)CO_2$, $\alpha CO$ and $(\alpha/2)O_2$. $\rightarrow 1-\alpha+\alpha+\frac{\alpha}{2} = 1+\frac{\alpha}{2}$

Given, $X_{CO} = 0.0289$. In terms of $\alpha$, this is written as,

$\alpha/(1+\alpha/2) = 0.0289$. ✓

Solving, $\alpha = 0.02932$. ✓

By using partial pressures, $K_p$ is defined as

$K_P = [(X_{CO} \times (X_{O2})^{0.5})/X_{CO2}] \times (p/p^0)^{0.5}$

$= [(0.0289 \times 0.01445^{0.5})/0.9566] \times 100^{0.5}$

$= 0.003632$

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Now, the next example, consider the reactions $CO_2 \leftarrow\rightarrow CO + ½ O_2$ at 100 atmosphere, the mole fraction of CO is given as 0.0289 mole fraction at 100 atmospheric pressure.

What is $K_p$? Now, we have to use the definition of $K_p$. Again, the same thing what we have already seen α moles of $CO_2$ dissociate so, the mixture will have 1-α $CO_2$, α moles of CO and α/2 moles of $O_2$.

Now, the mole fraction of CO is given as this; that means, α / (1+α/2) the total number of moles will be 1 - α + α + α/2, this is equal to 1 + α/2. So, that will be the total number of moles. Now, α / (1+α/2) is the mole fraction of CO which is equal to 0.0289. So, from that you can calculate α.

Now, once you know the α define $K_p$ in terms of partial pressures.

$$K_P = [(X_{CO} \times (X_{O2})^{0.5})/X_{CO2}] \times (p/p^0)^{0.5}$$

$$= [(0.0289 \times 0.01445^{0.5})/0.9566] \times 100^{0.5}$$

$$= 0.003632$$

So, the product $[X_{CO} \times (X_{O2})^{0.5} / X_{CO2}] \times (p / p^0)^{0.5}$. Now, p is 100 atmosphere. $(p/p^o)^{0.5} = (100)^{0.5}$. So, substitute for this, you know once your α is got, you can find all other number of moles or mole fractions calculate that and find this. So, $K_p$ value is this.

So, this light demonstration, once you know one of the component you can find the $K_p$ directly, when the pressure is given so, that is what is this, but its not easy to calculate the temperature from this.

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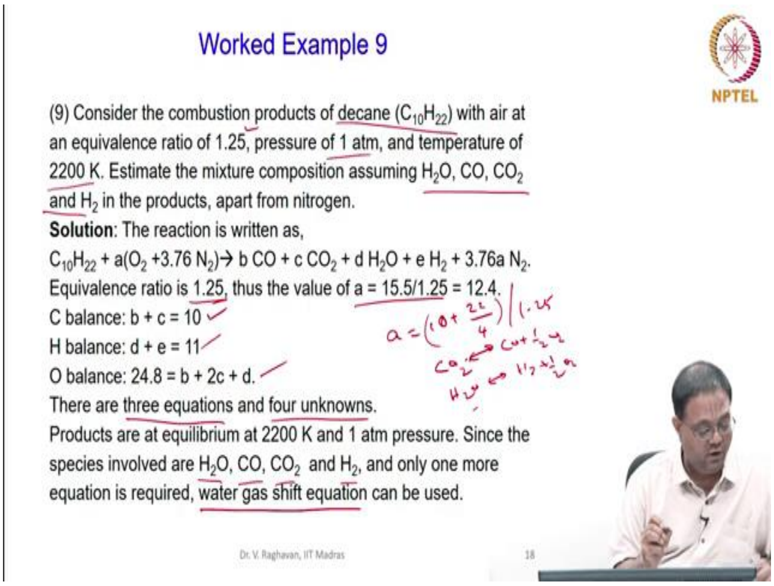

## Worked Example 9

(9) Consider the combustion products of decane ($C_{10}H_{22}$) with air at an equivalence ratio of 1.25, pressure of 1 atm, and temperature of 2200 K. Estimate the mixture composition assuming $H_2O$, CO, $CO_2$ and $H_2$ in the products, apart from nitrogen.

**Solution**: The reaction is written as,

$C_{10}H_{22} + a(O_2 + 3.76\ N_2) \rightarrow b\ CO + c\ CO_2 + d\ H_2O + e\ H_2 + 3.76a\ N_2$.

Equivalence ratio is 1.25, thus the value of a = 15.5/1.25 = 12.4.

C balance: b + c = 10 ✓

H balance: d + e = 11 ✓

O balance: 24.8 = b + 2c + d. ✓

There are three equations and four unknowns.

Products are at equilibrium at 2200 K and 1 atm pressure. Since the species involved are $H_2O$, CO, $CO_2$ and $H_2$, and only one more equation is required, water gas shift equation can be used.

$a = \left(10 + \frac{22}{4}\right) / 1.25$

$CO_2 \leftrightarrow CO + \frac{1}{2}O_2$

$H_2O \leftrightarrow H_2 + \frac{1}{2}O_2$

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The next problem is combustion, consider the combustion products of decane with air at equivalence ratio is 1.25. So, rich combustion, pressure is 1 atmosphere, temperature is 2200 K. Now, we estimate the mixture composition assuming $H_2O$, CO, $CO_2$ and $H_2$ in the products apart from nitrogen.

$$C_{10}H_{22} + a(O_2 + 3.76\ N_2) \rightarrow b\ CO + c\ CO_2 + d\ H_2O + e\ H_2 + 3.76a\ N_2$$

So that means, I write the equation as $C_{10}H_{22} + a \times (O_2 + 3.76\ N_2)$ giving $b \times CO + c \times CO_2 + d \times H_2O + e \times H_2 + 3.76a \times N_2$, $N_2$ is whatever coming from the oxidizer side $3.76 \times a \times N_2$ that is it.

Now, this is the equation and equivalence ratio is given as 1.25. So, the value of a is 10 + (22 / 4) / 1.25.

$$a = 15.5/1.25 = 12.4$$

S, that is 12.4.

$$\text{C balance: } b + c = 10$$

$$\text{H balance: } d + e = 11$$

$$\text{O balance: } 24.8 = b + 2c + d.$$

Now, carbon balance will give rise to one equation b + c = 10. So, the right hand side b and c corresponding to CO and $CO_2$ will be in left hand side, 10. H balance, d + e = 22 / 2 = 11.

Then O balance will give you a equation 24.8 = b + 2c + d. So, in the right hand side here since you know the value of a, 12.4 × 2 = 24.8. So, that will be the O balance. So, you get three equations, but there are four unknowns because a is also known now.

So, only four unknowns b, c, d and e are there and only three equations are available. So, you need only one more equation. So, you need to generate one equation. Now, since the species involved are $H_2O$, CO, $CO_2$ and $H_2$. We can discard $N_2$, even if it is a product. But we have to construct equations with the unknown number of moles which corresponds to the species of CO, $CO_2$, $H_2O$ and $H_2$, so, one more equation is required. We can explore the choice of using $CO_2 \leftarrow\rightarrow CO + ½ O_2$ and $H_2O \leftarrow\rightarrow H_2 + ½ O_2$, you can use these two equations.

But you need only one equation, if I select say one equation like $CO_2$ splitting into CO, then $H_2$ will not appear at all if you take this equation CO will not appear at all. So, we have to take a equation in which both are present.

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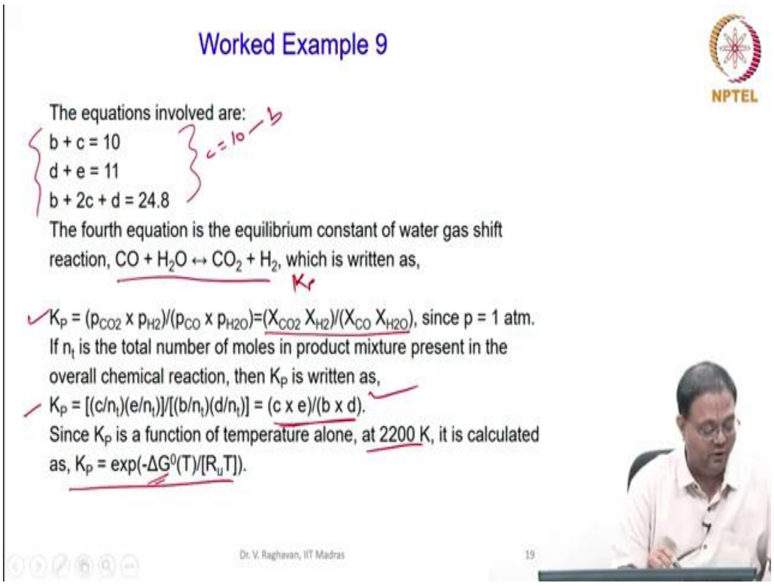

Worked Example 9

The equations involved are:

$$\left\{\begin{array}{l} b + c = 10 \\ d + e = 11 \\ b + 2c + d = 24.8 \end{array}\right\} c = 10 - b$$

The fourth equation is the equilibrium constant of water gas shift reaction, $\underline{CO + H_2O \leftrightarrow CO_2 + H_2}$, which is written as, Kr

✓ $K_p = (p_{CO2} \times p_{H2})/(p_{CO} \times p_{H2O}) = \underline{(X_{CO2}\, X_{H2})/(X_{CO}\, X_{H2O})}$, since p = 1 atm.

If $n_t$ is the total number of moles in product mixture present in the overall chemical reaction, then $K_p$ is written as,

✓ $K_p = [(c/n_t)(e/n_t)]/[(b/n_t)(d/n_t)] = \underline{(c \times e)/(b \times d)}$.

Since $K_p$ is a function of temperature alone, at $\underline{2200\ K}$, it is calculated as, $\underline{K_p = \exp(-\Delta G^0(T)/[R_uT])}$.

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$$CO + H_2O \leftrightarrow CO_2 + H_2$$

So, that for that we use what is called water gas shift equation which is this CO + $H_2O$ giving $CO_2$ + $H_2$. For example, when CO is formed to reform the CO you use steam, so that $CO_2$ and $H_2$ are formed. So, $H_2$ can be got from that. This is called water gas shift reaction. We use this reaction and find the $K_P$ for this.

Then you can write the $K_P$ in terms of b, c, d and e which are the four unknowns. So, apart from the three equations got from the atom balances a fourth equation can be generated and that can be used. So, since temperature is known as 2200 K, we can calculate the $K_P$ value here. Once the $K_P$ is known define $K_P$ using the partial pressures or mole fractions like this and get the $K_P$ in terms of b, c, d and e.

$$K_P = (p_{CO2} \times p_{H2})/(p_{CO} \times p_{H2O})=(X_{CO2}\ X_{H2})/(X_{CO}\ X_{H2O}),$$

$$K_P = [(c/n_t)(e/n_t)]/[(b/n_t)(d/n_t)] = (c \times e)/(b \times d).$$

So, I am getting the $K_P$ value like this. I know the $K_P$ value in terms of number of moles of the CO, $CO_2$, $H_2O$ and $H_2$, so, that is what I have written here. Now, how to calculate $K_P$, its only a function of temperature, use the Gibbs function change, that is what we are going to do next.

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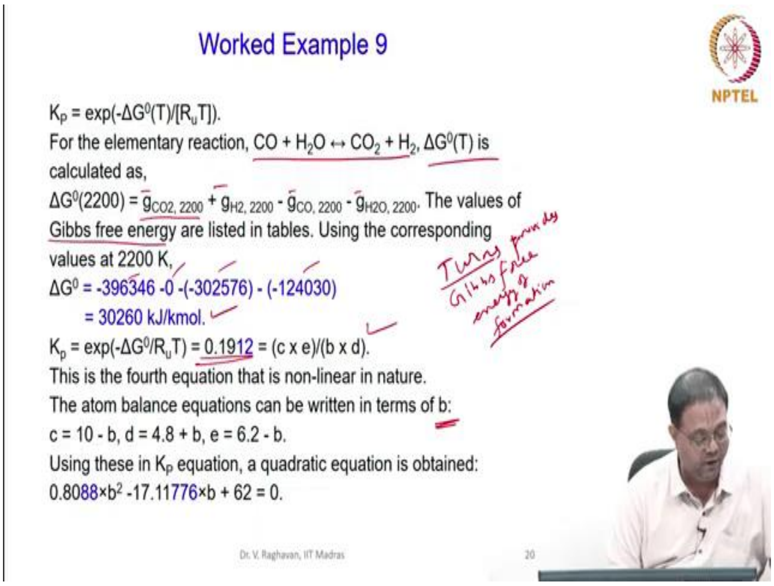

## Worked Example 9

$K_p = \exp(-\Delta G^0(T)/[R_uT])$.

For the elementary reaction, $CO + H_2O \leftrightarrow CO_2 + H_2$, $\Delta G^0(T)$ is calculated as,

$\Delta G^0(2200) = \bar{g}_{CO2,\ 2200} + \bar{g}_{H2,\ 2200} - \bar{g}_{CO,\ 2200} - \bar{g}_{H2O,\ 2200}$. The values of Gibbs free energy are listed in tables. Using the corresponding values at 2200 K,

$\Delta G^0 = -396346 - 0 - (-302576) - (-124030)$

$= 30260$ kJ/kmol.

$K_p = \exp(-\Delta G^0/R_uT) = 0.1912 = (c \times e)/(b \times d)$.

This is the fourth equation that is non-linear in nature.

The atom balance equations can be written in terms of b:

$c = 10 - b$, $d = 4.8 + b$, $e = 6.2 - b$.

Using these in $K_p$ equation, a quadratic equation is obtained:

$0.8088 \times b^2 - 17.11776 \times b + 62 = 0$.

Turns provides Gibbs free energy of formation

$$K_P = \exp(-\Delta G^0(T)/[R_uT]).$$

$$\Delta G^0(2200) = g_{CO2,\ 2200} + g_{H2,\ 2200} - g_{CO,\ 2200} - g_{H2O,\ 2200}$$

So, the elementary reaction is this. So, ΔG is got as $g_{CO2}$ at 2000 these product side first $g_{CO2}$ at 2200. You can also put the overhead bar, for simplicity I have removed it + $g_{H2}$ at 2200 - the reactant side $g_{CO}$ at 2200 - $g_{H2}$ at 2200. So, again you can go to the tables, please understand that the Stephen Turns book lists what is called Gibbs free energy of formation.

$$\Delta G^0 = -396346 - 0 - (-302576) - (-124030)$$

$$= 30260 \text{ kJ/kmol}.$$

You can use that. That is not a problem. You can use any table. So, if you use this table, then you get the values corresponding to this. Say Turns book provides Gibbs free energy of formation.

So, in which actually he says Gibbs free energy of formation for $H_2$ and $O_2$ is zero similar to enthalpy of formation.

Similarly, Gibbs free energy of formation is always set to 0. Let us follow the Turns book for this particular example, you can also use NIST tables and other things, but I do not think there will be any big change in the values. So, the Gibbs free energy corresponding to 2200 K for $CO_2$ is -396346. $H_2$ is a basic element, so, Gibbs energy of formation is 0 and for CO, it is -302576 at 2200 K. Similarly, for $H_2O$, it is -124030.

You can also calculate this as H - Ts that is also possible. So, when you calculate Gibbs function, you get this value and calculate the $K_P$ based upon the expression exp($-\Delta G/R_uT$), so, you get this value. So, $K_P$ is known now and the expressions of $K_P$ in terms of b, c, d and e is also known. So, this is the non-linear equation we get.

$$K_p = \exp(-\Delta G^0/R_uT) = 0.1912 = (c \times e)/(b \times d).$$

$$c = 10 - b,\ d = 4.8 + b,\ e = 6.2 - b$$

So, this equation along with the atom balance equations we have to solve. Now, if we take the atom balance equations, we can reduce the equations and write the equation only in terms of b see for example, here see here b + c = 10. So, c = 10 – b.

Similarly, here you know now c, you have written. So, in this equation you substitute for this, then d can be written in terms of b once d is written in terms of b, e also can be written in terms of b. So, in these three equations we can write everything in terms of b.

Now, you substitute this in this. So, retaining b, all other coefficients c, d and e you write in terms of this, then you get a quadratic equation in b like this.

$$0.8088\times b^2 - 17.11776\times b + 62 = 0$$

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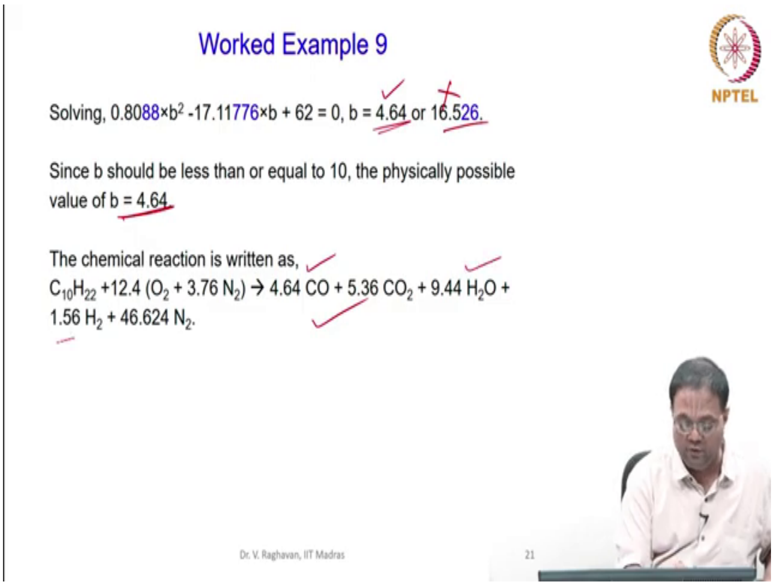

## Worked Example 9

Solving, $0.8088\times b^2 - 17.11776\times b + 62 = 0$, b = 4.64 or 16.526.

Since b should be less than or equal to 10, the physically possible value of b = 4.64.

The chemical reaction is written as,
$C_{10}H_{22} + 12.4\,(O_2 + 3.76\,N_2) \rightarrow 4.64\,CO + 5.36\,CO_2 + 9.44\,H_2O + 1.56\,H_2 + 46.624\,N_2$.

$$\text{Solving, } 0.8088\times b^2 - 17.11776\times b + 62 = 0,\ b = 4.64 \text{ or } 16.526$$

Now, if we solve the quadratic equation you will get b value as either 4.64 or 16.526. However, physically what is b in this equation? b is number of moles of CO. Total number of moles of C is only 10. So, together b + c = 10, so, b cannot be 16. This is wrong. The physically correct value of b should be 4.64. So, that you take and write the equation that is all. So, that is what is asked so, in this we have used equilibrium to find the proper products at a given temperature, when temperature changes these values will change. You can see that more amount of dissociation has taken place for both $CO_2$ and also a significant amount of hydrogen is present.

$$C_{10}H_{22} + 12.4\,(O_2 + 3.76\,N_2) \rightarrow 4.64\,CO + 5.36\,CO_2 + 9.44\,H_2O + 1.56\,H_2 + 46.624\,N_2$$

So, this is what? You can also use additional equations if you want. We can have say OH or H etcetera or O, you can add them to the products side and you have to use appropriate number of equilibrium equations and say $K_{P1}$, $K_{P2}$, $K_{P3}$ etcetera and solve that. So, multiple equations also can be used to solve for a particular composition. So, if you use N number of product species you need N number of equilibrium equations to solve them.

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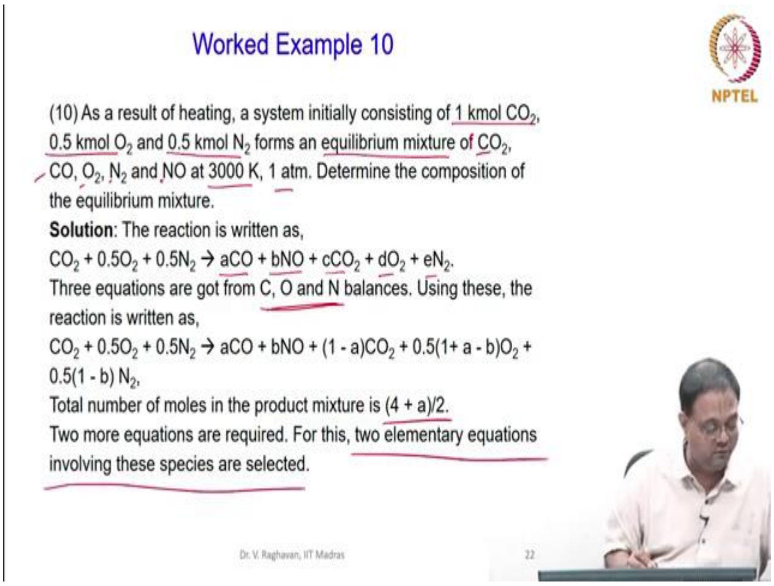

## Worked Example 10

(10) As a result of heating, a system initially consisting of 1 kmol $CO_2$, 0.5 kmol $O_2$ and 0.5 kmol $N_2$ forms an equilibrium mixture of $CO_2$, CO, $O_2$, $N_2$ and NO at 3000 K, 1 atm. Determine the composition of the equilibrium mixture.

**Solution**: The reaction is written as,

$CO_2 + 0.5O_2 + 0.5N_2 \rightarrow aCO + bNO + cCO_2 + dO_2 + eN_2$.

Three equations are got from C, O and N balances. Using these, the reaction is written as,

$CO_2 + 0.5O_2 + 0.5N_2 \rightarrow aCO + bNO + (1 - a)CO_2 + 0.5(1+ a - b)O_2 + 0.5(1 - b) N_2$,

Total number of moles in the product mixture is (4 + a)/2.

Two more equations are required. For this, two elementary equations involving these species are selected.

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This is the last example. The 10th example is the last one. Here, we have a system in which 1 kilomole of $CO_2$, 0.5 kilomole of $O_2$ and 0.5 kilomole of $N_2$ are present. Now, this is heated, when it is heated then the mixture is formed at the equilibrium.

$$CO_2 + 0.5O_2 + 0.5N_2 \rightarrow aCO + bNO + cCO_2 + dO_2 + eN_2$$

So, at the temperate of 3000 K and 1 atmosphere, equilibrium mixture is composed of $CO_2$, CO, $O_2$ and $N_2$ and also nitric oxide NO. Now, what is the composition do you understand?

$$CO_2 + 0.5O_2 + 0.5N_2 \rightarrow aCO + bNO + (1 - a)CO_2 + 0.5(1+ a - b)O_2 + 0.5(1 - b) N_2$$

So, initially the vessel has $CO_2$ 1 kilo mole, 0.5 kilo moles of $O_2$ and 0.5 kilo moles of $N_2$. Now, due to heating dissociation happens and $N_2$ and $O_2$ also dissociates.

So, that finally, you get NO, CO etcetera in the product apart from what was present previously. So, the reaction is written as $CO_2$ + ½ $O_2$ + ½ $N_2$ giving a × CO + b × NO + c × $CO_2$ + d × $O_2$ + e × $N_2$. This is the equation I have. So, I do not know anything in the right hand side now because of NO formation, $N_2$ also is not known now.

So, three equations are got from the balances again as we previously did. So, three balance C, O and N balances will give three equations. Now, again I reduce the number of constants using 3, but how many unknowns are there? five unknowns are there. So, try to use these three balances and arrive at two unknowns. So, that is what I am trying to do. Only a and b are kept as unknown others are written in terms of a and b itself.

So, $CO_2$ + 0.5 $O_2$ + 0.5 $N_2$, reactant, we can forget about this. Now, the product is a CO + b NO, then I am writing c in terms of a, (1 – a) CO and d in terms of a and b. So, 0.5 × (1 + a – b), similarly, $N_2$ is written in terms of b because of NO formation. Now, only two unknowns are there. We have already used the atom balances. So, you cannot use the atom balance anymore. Two unknowns should be solved by using equilibrium equations. So, the total number of moles comes out to be 4 + (a / 2) just we have to use it for total number of moles later. Now, two elementary equilibrium equations are going to be used for this.

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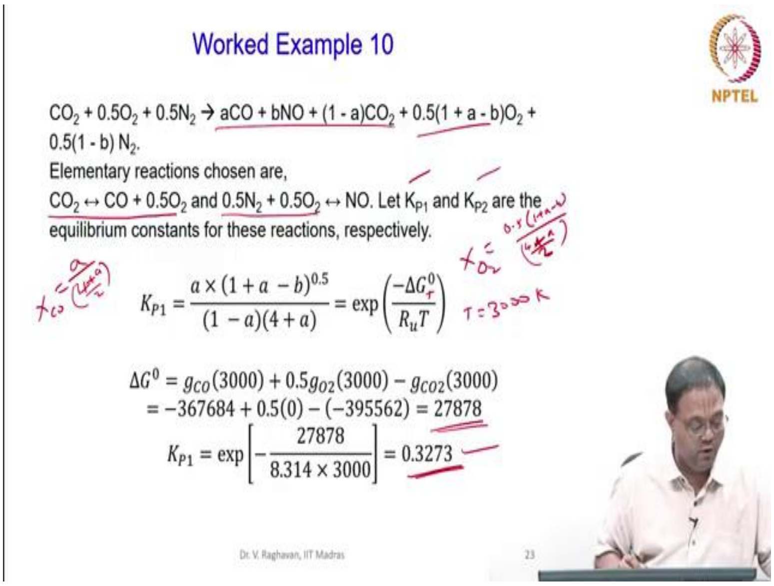

## Worked Example 10

$CO_2 + 0.5O_2 + 0.5N_2 \rightarrow aCO + bNO + (1 - a)CO_2 + 0.5(1 + a - b)O_2 + 0.5(1 - b)N_2$.

Elementary reactions chosen are,

$CO_2 \leftrightarrow CO + 0.5O_2$ and $0.5N_2 + 0.5O_2 \leftrightarrow NO$. Let $K_{P1}$ and $K_{P2}$ are the equilibrium constants for these reactions, respectively.

$x_{CO} = \frac{a}{\left(4+\frac{a}{2}\right)}$

$x_{O_2} = \frac{0.5(1+a-b)}{\left(4+\frac{a}{2}\right)}$

$$K_{P1} = \frac{a \times (1 + a - b)^{0.5}}{(1 - a)(4 + a)} = \exp\left(\frac{-\Delta G_T^0}{R_u T}\right)$$

$T = 3000$ K

$$\Delta G^0 = g_{CO}(3000) + 0.5 g_{O2}(3000) - g_{CO2}(3000)$$
$$= -367684 + 0.5(0) - (-395562) = 27878$$
$$K_{P1} = \exp\left[-\frac{27878}{8.314 \times 3000}\right] = 0.3273$$

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So, what are they; obviously, this $CO_2$ ←→ CO + ½ $O_2$ will be the first one, then $N_2$ + $O_2$ ←→ 2 NO or ½ $N_2$ + ½ $O_2$ ←→ NO that is the second equation we use. Let $K_{P1}$ be the equilibrium constant for the first equation and $K_{P2}$ be the equilibrium constant for the second equation.

Now, based upon definition what is the number of moles and total number of moles, so, mole fractions. Please understand that this is occurring at 1 atmospheric pressure only, but temperature is 3000 K.

So, a CO and then you have $O_2$. So, a CO and $O_2$ are the product side $O_2$ is 0.5(1 + a – b)$^{0.5}$. So, that divided by (1-a) and this (4 + a) / 2. So, total number of moles should be divided in each term.

So, for example, for $X_{CO}$ we write as a / total number of moles, which is nothing but (4 + a / 2). Similarly, for $O_2$, you can write $X_{O2}$ as 0.5(1 + a – b) / (4 + a / 2).

So, when you substitute all the mole fractions here, you will get this expression.

$$K_{p1} = \frac{a \times (1 + a - b)^{0.5}}{(1 - a) \times (4 + a)} = \exp\left(\frac{-\Delta G^0}{R_u T}\right)$$

That is equal to exp(-ΔG / $R_u$T), this is actually at a particular temperature. Now, here T equal to 3000 K as per the problem. I calculate ΔG at 3000 K and get the value of this. So, $K_P$ is known.

$$\Delta G^0 = g_{CO}(3000) + 0.5\ g_{O2}(3000) - g_{CO2}(3000) = -367864 + 0.5(0) - (-395562) = 27878$$

So, $K_{P1}$ = 0.3273. This will be equal to this non-linear equation involving a and b.

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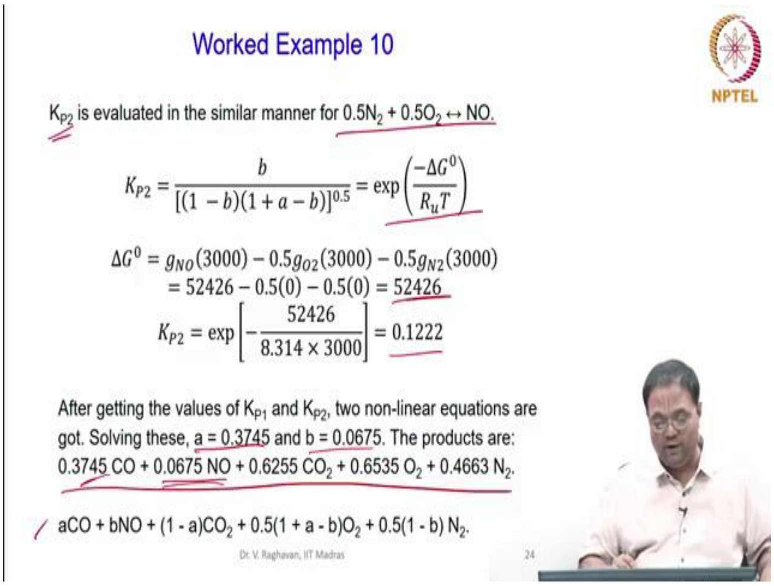

## Worked Example 10

$K_{P2}$ is evaluated in the similar manner for $0.5N_2 + 0.5O_2 \leftrightarrow NO$.

$$K_{P2} = \frac{b}{[(1-b)(1+a-b)]^{0.5}} = \exp\left(\frac{-\Delta G^0}{R_u T}\right)$$

$$\Delta G^0 = g_{NO}(3000) - 0.5g_{O2}(3000) - 0.5g_{N2}(3000)$$
$$= 52426 - 0.5(0) - 0.5(0) = 52426$$
$$K_{P2} = \exp\left[-\frac{52426}{8.314 \times 3000}\right] = 0.1222$$

After getting the values of $K_{P1}$ and $K_{P2}$, two non-linear equations are got. Solving these, a = 0.3745 and b = 0.0675. The products are: $0.3745\ CO + 0.0675\ NO + 0.6255\ CO_2 + 0.6535\ O_2 + 0.4663\ N_2$.

$aCO + bNO + (1 - a)CO_2 + 0.5(1 + a - b)O_2 + 0.5(1 - b)\ N_2$.

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Now, go to the next equation $K_{P2}$ similarly for this equation you have to evaluate. So, $K_{P2}$ is defined as b / [(1 – b) × (1 + a – b)$^{0.5}$] = exp(-Δ$G^0$/$R_u$T), again you calculate ΔG for this equation.

$$g_{NO}(3000) - 0.5\ g_{O2}(3000) - 0.5g_{N2}(3000) = 52426 - 0.5(0) -0.5(0) = 52426$$

From Turns tables, Gibbs free energy of formation for $O_2$ and $N_2$ will be 0.

So, the value of $K_{P2}$ = 0.1222, that will be equal to this equation. So, you have formed now two non-linear equations involving a and b and while solving those in two non-linear equations, you will get a = 0.3745 and b = 0.0675.

Now, I calculate c, d and e because they are dependent on a and b values and you can write the mixture as this. So, here you have seen using two equations and please understand that since non-linear are involved, you cannot always solve this by hand you have to use some computer programs. Especially when more number of equations are involved and more number of unknowns are there. So, these are the equilibrium equations. So, you can see some amount of NO is formed here and also a good amount of CO is formed at the very high temperatures. So, at very high temperatures we cannot avoid formation of NO. So, this will be the equation.

$$0.3745\ CO + 0.0675\ NO + 0.6255\ CO_2 + 0.6535\ O_2 + 0.4663\ N_2.$$