Fundamentals of Combustion

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Lecture - 13

First Law and Second Law of Thermodynamics Applied to Combustion - Part 05

Chemical Equilibrium (Contd.)

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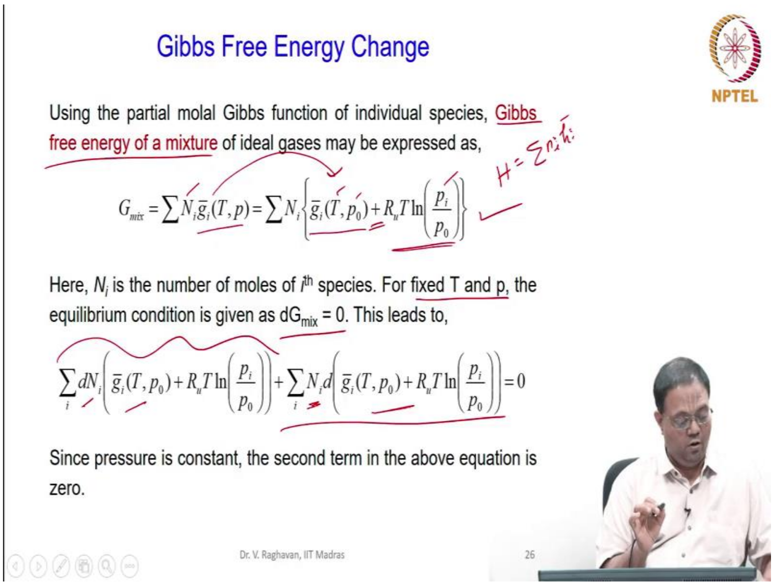

Gibbs Free Energy Change

Using the partial molal Gibbs function of individual species, Gibbs free energy of a mixture of ideal gases may be expressed as,

$$G_{mix} = \sum N_i \bar{g}_i(T,p) = \sum N_i \left\{ \bar{g}_i(T,p_0) + R_u T \ln\left(\frac{p_i}{p_0}\right) \right\}$$

$H = \sum n_i h_i$

Here, N_i is the number of moles of i^{th} species. For fixed T and p, the equilibrium condition is given as $dG_{mix} = 0$. This leads to,

$$\sum_i dN_i \left(\bar{g}_i(T,p_0) + R_u T \ln\left(\frac{p_i}{p_0}\right) \right) + \sum_i N_i d\left(\bar{g}_i(T,p_0) + R_u T \ln\left(\frac{p_i}{p_0}\right) \right) = 0$$

Since pressure is constant, the second term in the above equation is zero.

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Ok now, once you know the Gibbs function or Gibbs free energy for a particular species i then the Gibbs free energy of a mixture of ideal gases can be calculated by just same as H, $\sum n_i H_i$. Same thing I am using here $\sum n_i g_i$ but calculated at a particular temperature and pressure.

So, that you can now expand this term here and write. $\sum ni[gi(T,p_0) + R_u T\times\ln(p_i/p_o)]$. So, this is the Gibbs function at a particular temperature calculated at atmospheric pressure. Again, we have tables for this and this even you can calculate knowing the mole fraction of the particular species. In fact, if you want to determine mole fraction, this term is which is going to be useful for us.

Now, this is the equation

$$G_{mix} = \sum N_i \bar{g}_i(T,p) = \sum N_i \left\{ \bar{g}_i(T,p_0) + R_u T \ln\left(\frac{p_i}{p_0}\right) \right\}$$

Now, the condition for equilibrium at a given temperature and pressure is $dG_{mix} = 0$. So, you have to just differentiate this by chain rule.

$$\sum_i dN_i\left(\bar{g}_i(T,p_0)+R_uT\ln\left(\frac{p_i}{p_0}\right)\right)+\sum_i N_i d\left(\bar{g}_i(T,p_0)+R_uT\ln\left(\frac{p_i}{p_0}\right)\right)=0$$

So, dN_i g plus N_i dg. Now, you can see that the second term here goes to 0 because at a given temperature g has a constant value. Similarly, pressure is constant; partial pressure is depend on the total pressure that is constant. When you sum all the partial pressure you get the total pressure and total pressure is held constant. So, this second term goes to 0. That means, dG_{mix} will be just equal the first term.

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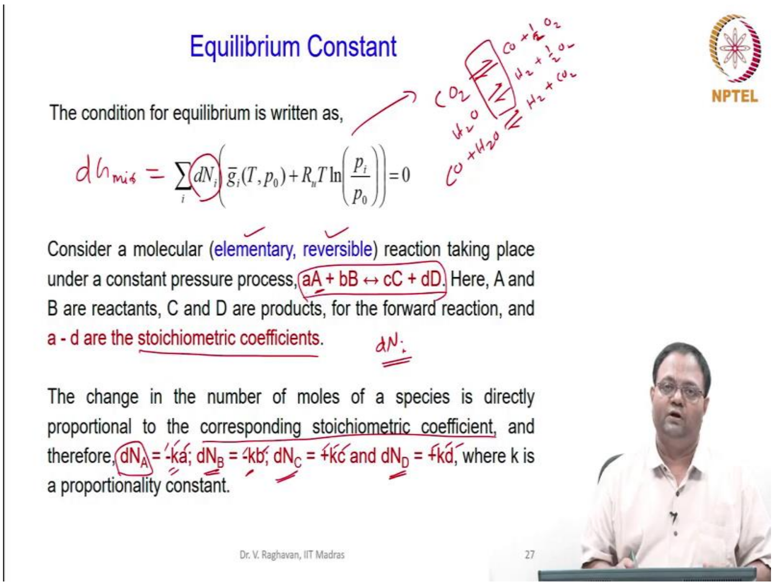

Equilibrium Constant

The condition for equilibrium is written as,

$$dG_{mix} = \sum_i \boxed{dN_i}\left(\bar{g}_i(T,p_0)+R_uT\ln\left(\frac{p_i}{p_0}\right)\right)=0$$

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

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

$CO + H_2O \rightleftharpoons H_2 + CO_2$

Consider a molecular (elementary, reversible) reaction taking place under a constant pressure process, aA + bB ↔ cC + dD. Here, A and B are reactants, C and D are products, for the forward reaction, and a - d are the stoichiometric coefficients.

dN_i

The change in the number of moles of a species is directly proportional to the corresponding stoichiometric coefficient, and therefore, $dN_A = -ka$; $dN_B = -kb$; $dN_C = +kc$ and $dN_D = +kd$, where k is a proportionality constant.

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$$dG_{mix} = \sum_i dN_i\left(\bar{g}_i(T,p_0)+R_uT\ln\left(\frac{p_i}{p_0}\right)\right)=0$$

So, this is the condition for equilibrium.

Now, this has to be implemented for any reaction. So, for example, when I said equilibrium reactions, I consider $CO_2 \rightarrow CO + \frac{1}{2} O_2$. Similarly, $H_2O \rightarrow H_2 + \frac{1}{2} O_2$. These are all equilibrium reaction. I have to apply this condition to the equilibrium reaction to get the equilibrium products.

Now, let us consider elementary reactions which are reversible in nature. So, let us consider an arbitrary elementary reaction written like this capital A, B, C, D represent the species and small a, b, c, d represent the stoichiometric coefficients.

$$aA + bB \leftrightarrow cC + dD$$

So, aA + bB reversibly giving small cC + dD, that is the general equation we are trying to consider here.

We can also have a bi-molecular reaction like this. Now, you get any general equation written like this and try to apply this condition and see how to evaluate this.

So, before going to this evaluation, we should understand what is the change in number of moles dN_i. So, the change in the number of moles of a species is directly proportional to the corresponding stoichiometric coefficient.

$$dN_A = -ka; \; dN_B = -kb;$$

So, for the species A, if a, small a is the stoichiometric coefficient, then the change in the number of moles of the species a will be proportional to stoichiometric coefficient. So, I add a constant of proportionality k. I also put a minus sign here because that is the reactant.

So, we definitely know that if I consider forward reaction here, then the reactants are consumed. So, dN_A and dN_B should be negative. So, I put a negative sign and the change in the number of moles is proportional to the corresponding stoichiometric coefficients a, b etcetera here. So, I put proportionality constant k.

$$dN_C = +kc \text{ and } dN_D = +kd$$

Coming to the products, the change in number of products will be correspondingly proportional to their coefficients. So, dN_C will be proportional to c, dN_D will be proportional to small d and I put a plus sign because they are produced the forward reaction and the constant of proportionality is k.

So, you can now replace dN's by ka, kb, etcetera for the particular reaction here with the sign.

When I consider the reverse reaction then dN_A will be positive, dN_B will be positive. On the other hand, dN_C and dN_D will be negative. So, the kb value etcetera what we are going to calculate next will be dependent on which direction you consider this reaction.

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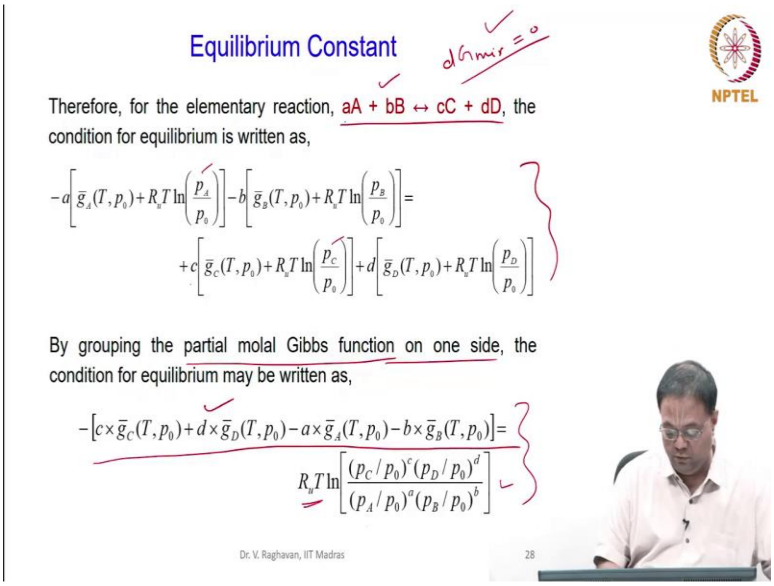

Equilibrium Constant

$dG_{mix} = 0$

Therefore, for the elementary reaction, aA + bB ↔ cC + dD, the condition for equilibrium is written as,

$$-a\left[\bar{g}_A(T,p_0)+R_uT\ln\left(\frac{p_A}{p_0}\right)\right]-b\left[\bar{g}_B(T,p_0)+R_uT\ln\left(\frac{p_B}{p_0}\right)\right]= +c\left[\bar{g}_C(T,p_0)+R_uT\ln\left(\frac{p_C}{p_0}\right)\right]+d\left[\bar{g}_D(T,p_0)+R_uT\ln\left(\frac{p_D}{p_0}\right)\right]$$

By grouping the partial molal Gibbs function on one side, the condition for equilibrium may be written as,

$$-\left[c\times\bar{g}_C(T,p_0)+d\times\bar{g}_D(T,p_0)-a\times\bar{g}_A(T,p_0)-b\times\bar{g}_B(T,p_0)\right]= R_uT\ln\left[\frac{(p_C/p_0)^c(p_D/p_0)^d}{(p_A/p_0)^a(p_B/p_0)^b}\right]$$

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$$a\left[\bar{g}_A(T,p_0)+R_uT\ln\left(\frac{p_A}{p_0}\right)\right]+b\left[\bar{g}_B(T,p_0)+R_uT\ln\left(\frac{p_B}{p_0}\right)\right]= +c\left[\bar{g}_C(T,p_0)+R_uT\ln\left(\frac{p_C}{p_0}\right)\right]+d\left[\bar{g}_D(T,p_0)+R_uT\ln\left(\frac{p_D}{p_0}\right)\right]$$

Now, let us apply this rule and calculate dG_{mix} for the reaction. When I make it equal to 0 then I get this. So, k cancels out, $a\times g_A(T,p_0)$ + $R_uT\times\ln(p_A/p_o)$ + $b\times g_B(T,p_0)$ + $R_uT\times\ln(p_B/p_o)$ that is equal to the c and d's correct.

So, the products, c is the coefficient of the species C that into $g_C(T,p_0)$ + $R_uT\times\ln(p_C/p_0)$. Similarly, you can do this for D. So, this is the equation I get when I subject this equation to dG_{mix} equal to 0.

Now, you now try to group the Gibbs functions in one side and the partial pressures on the other side.

$$-\left[c\times\bar{g}_C(T,p_0)+d\times\bar{g}_D(T,p_0)-a\times\bar{g}_A(T,p_0)-b\times\bar{g}_B(T,p_0)\right]= R_uT\ln\left[\frac{(p_C/p_0)^c(p_D/p_0)^d}{(p_A/p_0)^a(p_B/p_0)^b}\right]$$

So, $-c\times g_C(T, p_0)$ + $d\times g_D(T,p_o)$ $-a\times g_A(T,p_0)$ $-b\times g_B(T,p_0)$ will be equal to now group this log terms R_uT times logarithm of the product partial pressure of product raised to the stoichiometric coefficient.

So, $(p_C/p_0)^c\times(p_D/p_0)^d$ divided by the reactants again say same products product of the reactant partial pressures $(p_A/p_0)^a\times(p_B/p_o)^b$ raised to the stoichiometric coefficient. So, this is the equation what we get and I am grouping the g's on one side, partial pressure terms on the other side and get this equation.

Now, I started from this equation, applied $dG_{mix} = 0$, I got this equation and I grouped the g's in the left-hand side and the partial pressures in the right-hand side I get this equation.

$$\Delta G(T,p_0) = c\times \bar{g}_C(T,p_0) + d\times \bar{g}_D(T,p_0) - a\times \bar{g}_A(T,p_0) - b\times \bar{g}_B(T,p_0)$$

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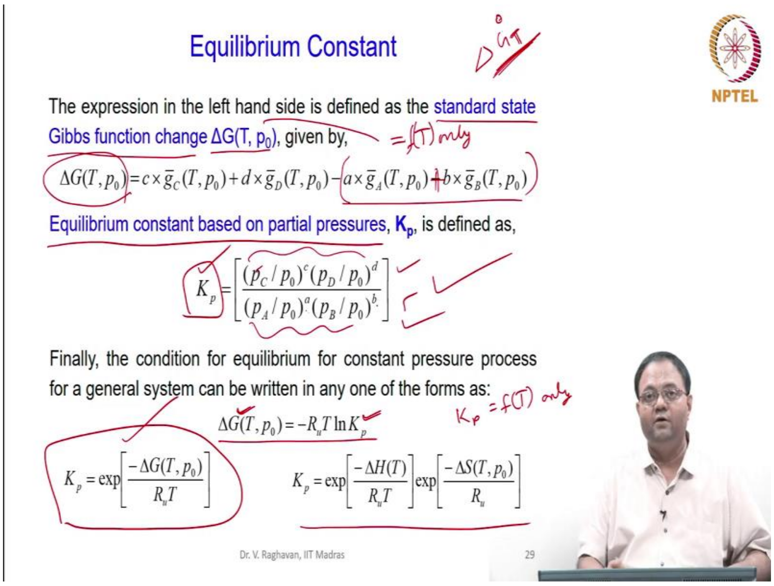

Equilibrium Constant

ΔG^0_T

The expression in the left hand side is defined as the standard state Gibbs function change ΔG(T, p_0), given by, $= f(T)$ only

$$\Delta G(T,p_0) = c\times \bar{g}_C(T,p_0) + d\times \bar{g}_D(T,p_0) - a\times \bar{g}_A(T,p_0) + b\times \bar{g}_B(T,p_0)$$

Equilibrium constant based on partial pressures, **K_p**, is defined as,

$$K_p = \left[\frac{(p_C/p_0)^c (p_D/p_0)^d}{(p_A/p_0)^a (p_B/p_0)^b}\right]$$

Finally, the condition for equilibrium for constant pressure process for a general system can be written in any one of the forms as:

$$\Delta G(T,p_0) = -R_u T \ln K_p$$

$K_p = f(T)$ only

$$K_p = \exp\left[\frac{-\Delta G(T,p_0)}{R_u T}\right] \qquad K_p = \exp\left[\frac{-\Delta H(T)}{R_u T}\right]\exp\left[\frac{-\Delta S(T,p_0)}{R_u}\right]$$

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Now, I define the left-hand side as standard state Gibbs function change ΔG(T, p_0). You can see in the Turns book, this is represented by this in a compact notation ΔG^0 that is for standard atmospheric pressure and the subscript T represent any temperature.

So, I have just written ΔG(T, p_0), you can also write like this ΔG^0_T that will be equal to the products. Gibbs free energy of the products $c\times g_C(T, p_0) + d\times g_D(T, p_0)$, then minus again add the reactant sides.

So, all the product Gibbs free energy multiplied by stoichiometric coefficients should be added and that should be subtracted to this reactants Gibbs free energy, the sum of reactants.

So, this is the Gibbs function change, standard state Gibbs function change calculated at any temperature, but only at atmospheric pressure. So, that means, ΔG is a function of temperature only.

Now, in the right-hand side, I have already grouped the partial pressures like this in the natural logarithm term. Now, that I define as equilibrium constant based on partial pressures. This partial pressure is the ratio of product of the partial pressures of products raised to the stoichiometric coefficient divided by corresponding atmospheric pressure.

Similarly, that divided by the product of the reactant partial pressure ratios raised to corresponding stoichiometric proportions. This ratio is called the equilibrium constant at partial pressure K_p.

$$K_p = \left[\frac{(p_C / p_0)^c (p_D / p_0)^d}{(p_A / p_0)^a (p_B / p_0)^b} \right]$$

So, now I can write the previous equation like this $\Delta G(T, p_0) = -R_u T \ln(K_p)$.

So, you please understand that to calculate K_p, I need this. So, temperature is known already. Since temperature is known, ΔG can be calculated because ΔG is a function of temperature only. It is done at atmospheric pressure.

Then K_p can be calculated. So, K_p is also a function of temperature only.

$$K_p = \exp\left[\frac{-\Delta G(T, p_0)}{R_u T} \right]$$

Now, how the pressure effects come, because of the definition of K_p pressure effect comes here. So, partial pressures are involved, so the partial pressures of products they are multiplied together with the ratio with atmospheric pressure raised to corresponding stoichiometric proportions and that divided by the product of the partial pressure ratio of the reactants raised to corresponding stoichiometric proportions.

So, this definition. The partial pressure itself p_C, p_D, p_A, p_B will change based upon the total pressure. So, the pressure dependence comes by the definition of K_p. K_p itself is calculated as a function of temperature and you can substitute the value of K_p in this to get the product composition.

So, in terms of H and S, K_p can be written like this. If you do not want to use G, you can also use H and S and both are same.

$$K_p = \exp\left[\frac{-\Delta H(T)}{R_u T} \right] \exp\left[\frac{-\Delta S(T, p_0)}{R_u} \right]$$

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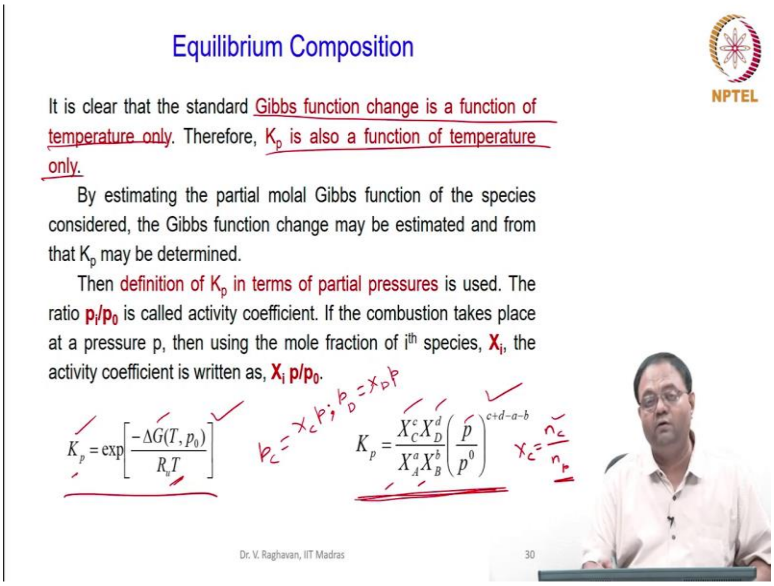

Equilibrium Composition

It is clear that the standard Gibbs function change is a function of temperature only. Therefore, K_p is also a function of temperature only.

By estimating the partial molal Gibbs function of the species considered, the Gibbs function change may be estimated and from that K_p may be determined.

Then definition of K_p in terms of partial pressures is used. The ratio p_i/p_0 is called activity coefficient. If the combustion takes place at a pressure p, then using the mole fraction of ith species, X_i, the activity coefficient is written as, $X_i\ p/p_0$.

$$K_p = \exp\left[\frac{-\Delta G(T, p_0)}{R_u T}\right]$$

$p_C = X_C p; p_D = X_D p$

$$K_p = \frac{X_C^c X_D^d}{X_A^a X_B^b}\left(\frac{p}{p^0}\right)^{c+d-a-b}$$

$X_C = \frac{n_C}{n_p}$

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Now, to summarise you know that the Gibbs function change is a function of temperature only. So, K_p is also a function of temperature only. Now, after calculating K_p like this as a function of temperature you can use this equation. So, what I have done here is instead of p_C I am putting X_C × p.

Similarly, p_D I am writing X_D × p and substitute here. This equation here when you substitute your p_C, X_C × p similarly for p_B, X_B × p etcetera you can write in terms of mole fractions and the total pressure p.

$$K_p = \frac{X_C^c X_D^d}{X_A^a X_B^b}\left(\frac{p}{p^0}\right)^{c+d-a-b}$$

So, after evaluating K_p at a given temperature with Gibbs function change, standard Gibbs function change, then you can substitute this to calculate or to generate expressions. We cannot calculate everything so, if there is only one unknown, this one equation can be used to do that. Or you have to generate equations in order to solve for the mole fractions.

So, mole fraction can be written in terms of the number of moles of a particular species see for example, mole fraction of C can be n_C/n_T or n_p; n_p I will say that is the number of moles of the product n_p. n_C is the number of moles of the C so, X_C will be this.

When you substitute, you can also substitute this equation in terms of number of moles. So, straight away we can write the equation in terms of number of moles a, b, c, d, e what we saw earlier. So, once we do that, we can calculate.

The procedure of calculating the equilibrium product is first you find the Gibbs free energy of individual species then calculate the standard Gibbs function change at a given temperature at the reference pressure of one atmosphere so, ΔG is got, then you calculate the value of K_p using this expression then substitute this for the given equation and find the number of moles or form an equation with the number of moles involved.

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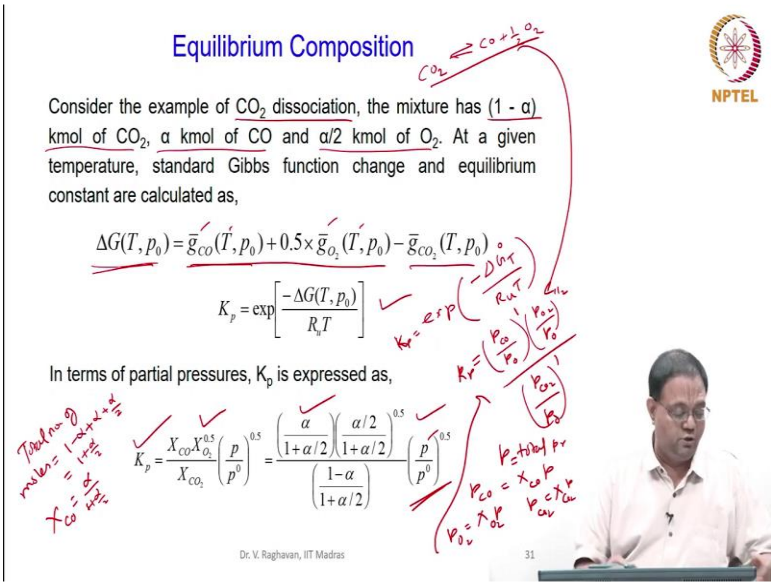

Equilibrium Composition

Consider the example of CO_2 dissociation, the mixture has $(1 - \alpha)$ kmol of CO_2, α kmol of CO and $\alpha/2$ kmol of O_2. At a given temperature, standard Gibbs function change and equilibrium constant are calculated as,

$$\Delta G(T,p_0) = \bar{g}_{CO}(T,p_0) + 0.5\times\bar{g}_{O_2}(T,p_0) - \bar{g}_{CO_2}(T,p_0)$$

$$K_p = \exp\left[\frac{-\Delta G(T,p_0)}{R_u T}\right]$$

In terms of partial pressures, K_p is expressed as,

$$K_p = \frac{X_{CO}X_{O_2}^{0.5}}{X_{CO_2}}\left(\frac{p}{p^0}\right)^{0.5} = \frac{\left(\frac{\alpha}{1+\alpha/2}\right)\left(\frac{\alpha/2}{1+\alpha/2}\right)^{0.5}}{\left(\frac{1-\alpha}{1+\alpha/2}\right)}\left(\frac{p}{p^0}\right)^{0.5}$$

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So, so, let us just take the equation what we considered in which we have some CO_2 dissociation taking place the equation is $CO_2 \rightarrow CO + \frac{1}{2} O_2$. Now, in this case, we know that the mixture has 1-α kilomole of CO_2, α kilomoles of CO and α/2 kilomoles of O_2.

At a given temperature, now we can calculate ΔG at atmospheric pressure. First of all, you have to group the products so, these were the products. So, g_{CO} at a particular temperature, then 0.5 times g_{O2} at a particular temperature calculate them add up then calculate reactant g_{CO2} at the same temperature then subtract that to this.

Now, you get ΔG, when ΔG is known calculate K_p.

$$K_p = \frac{X_{CO}X_O^{0.5}}{X_{CO}}\left(\frac{p}{p^0}\right)^{0.5} = \frac{\left(\frac{\alpha}{1+\alpha/2}\right)\left(\frac{\alpha/2}{1+\alpha/2}\right)^{0.5}}{\left(\frac{1-\alpha}{1+\alpha/2}\right)}\left(\frac{p}{p^0}\right)^{0.5}$$

So, we can write in a compact form like this. So, this is the expression you make.

Then, use the definition of K_p. K_p for this equation is written as partial pressure of product first of all so, partial pressure of $(p_{CO}/p_0)^1$ and $(p_{O2}/p_0)^{0.5}$ / $(p_{CO2}/p_0)^1$.

Now, if the pressure of the reaction is p and is equal to the total pressure, then p_{CO} will be equal to $X_{CO} \times p$. Similarly, you can write the $X_{O2} \times p$ as p_{O2} and p_{CO2} will be equal to $X_{CO2} \times p$. So, substitute this here, you get this equation.

Then, what is mole fraction? Total number of moles = $1-\alpha + \alpha + \alpha/2 = 1 + \alpha/2$. So, X_{CO} will be equal to alpha by $1 + \alpha/2$.

Similarly, you can substitute for other things and you could write this in terms of alpha. So, X_{O2} is $\alpha/2 / (1 + \alpha/2)^{0.5}$. Similarly, number of moles of CO_2 is $1-\alpha / (1 + \alpha/2)$.

If you write, then you get a non-linear equation in α. So, K_p is known, right-hand side α in a non-linear is there. The total pressure is known, so, the pressure ratio can be calculated.

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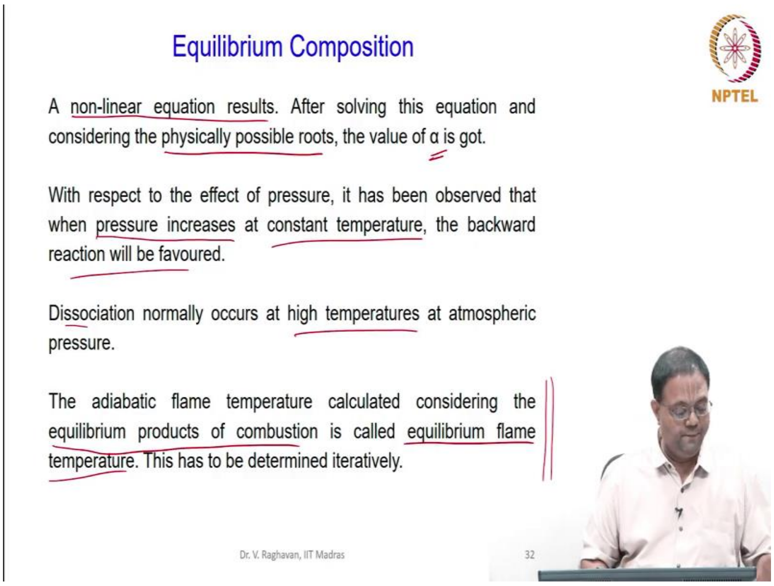

Equilibrium Composition

A non-linear equation results. After solving this equation and considering the physically possible roots, the value of α is got.

With respect to the effect of pressure, it has been observed that when pressure increases at constant temperature, the backward reaction will be favoured.

Dissociation normally occurs at high temperatures at atmospheric pressure.

The adiabatic flame temperature calculated considering the equilibrium products of combustion is called equilibrium flame temperature. This has to be determined iteratively.

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A non-linear equation results. If you are solving that, you get the value of alpha. So, it is the only one unknown, so, one equation is enough. But non-linear equation will give multiple roots. You have to choose physically possible roots that is all, that will be the value of α. We know that the Gibbs function change a is function of temperature only.

So, K_p is a function of temperature only. The temperature dependence on the products of equilibrium comes due to that. The pressure dependence comes due to the mole fraction and this pressure term here. So, with that we take into account both the effects of pressure and temperature and calculate the equilibrium value of a particular species.

Now, some observations. When pressure increases at a constant temperature, the backward reaction is favoured. Dissociation normally occurs at high temperatures at atmospheric pressure. When pressure increases, then there is a decrease in the dissociation.

Now, adiabatic flame temperature when you calculate by calculating the equilibrium products of combustion, then that value is close to the measured value. So, such a temperature is called equilibrium flame temperature. Again, as I told you it has to be determined iteratively. So, this is the completion of this particular topic

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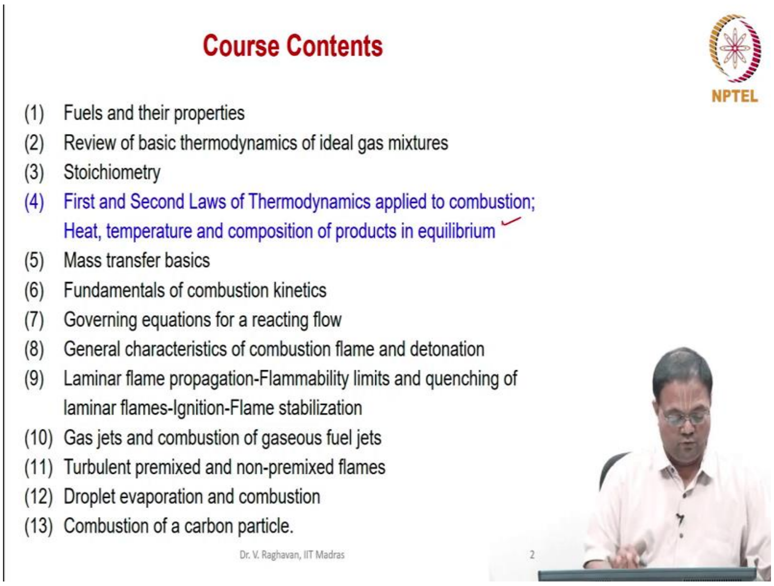

Course Contents

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(5) Mass transfer basics
(6) Fundamentals of combustion kinetics
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If you see in this particular section, we have actually dealt with this. We have seen how to calculate heat, temperature, adiabatic flame temperature iteratively. So, heat calculations require enthalpy calculations of individual species absolute enthalpy then calculate the reactant enthalpy and the product enthalpy, apply first law. In a constant volume process heat of reaction is U_P - U_R and in a constant pressure process it is H_P - H_R.

The flame temperature you calculate based upon some iterative procedure, for which you need composition of the products. The adiabatic flame temperature is the maximum temperature attainable, when the product enthalpy matches the reactant enthalpy for a constant pressure system or the product internal energy matches the reactant internal energy for a constant volume system.

Composition of the products in equilibrium is determined using second law, a variable defined using second law is entropy. So, based on entropy, two free energies have been defined one is Helmholtz free energy, another one is Gibbs free energy used in constant volume and constant pressure processes, respectively.

So, using that, we calculate the Gibbs function change and from that, we calculate the equilibrium constant which is defined as the ratio of partial pressures of product mixture and the reactant mixture and from that you calculate the equilibrium composition. So, this finishes this topic.

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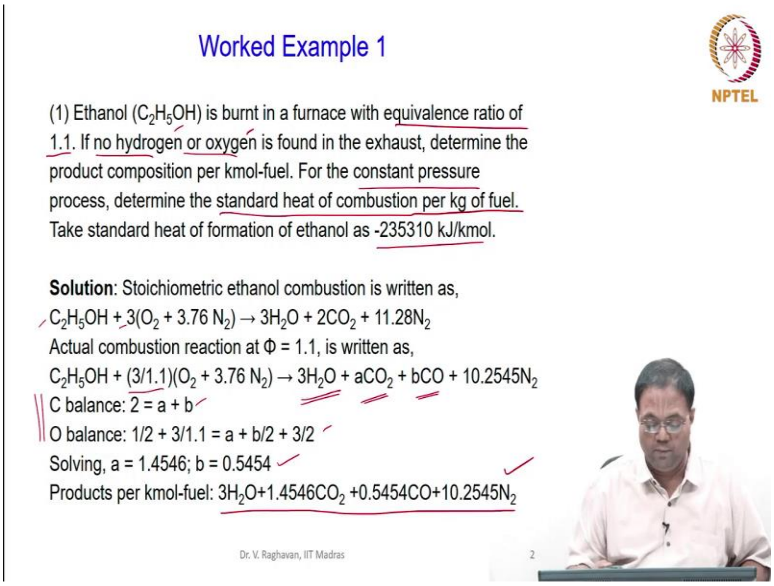

Worked Example 1

(1) Ethanol (C_2H_5OH) is burnt in a furnace with equivalence ratio of 1.1. If no hydrogen or oxygen is found in the exhaust, determine the product composition per kmol-fuel. For the constant pressure process, determine the standard heat of combustion per kg of fuel. Take standard heat of formation of ethanol as -235310 kJ/kmol.

Solution: Stoichiometric ethanol combustion is written as,

$C_2H_5OH + 3(O_2 + 3.76\ N_2) \rightarrow 3H_2O + 2CO_2 + 11.28N_2$

Actual combustion reaction at $\Phi = 1.1$, is written as,

$C_2H_5OH + (3/1.1)(O_2 + 3.76\ N_2) \rightarrow 3H_2O + aCO_2 + bCO + 10.2545N_2$

C balance: $2 = a + b$

O balance: $1/2 + 3/1.1 = a + b/2 + 3/2$

Solving, $a = 1.4546$; $b = 0.5454$

Products per kmol-fuel: $3H_2O+1.4546CO_2 +0.5454CO+10.2545N_2$

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Now, we go for worked examples. This worked example is corresponding to the heat, temperature and equilibrium calculation. Let us do some simple example first.

Let us consider the first problem, ethanol, C_2H_5OH is burnt in a furnace with a equivalence ratio of 1.1 and exhaust gas analysis specifies that there is no hydrogen or oxygen left in the exhaust gas.

Now, for a constant pressure process, you have to determine the standard heat of combustion per kg of fuel. Now, the standard heat of formation of ethanol is given here that you can use that is the problem.

$$C_2H_5OH + 3(O_2 + 3.76\ N_2) \rightarrow 3H_2O + 2CO_2 + 11.28N_2$$

So, ethanol stoichiometric combustion is written here $C_2H_5OH + 3(O_2 + 3.76\ N_2)$ giving $3H_2O + 2CO_2 + 11.28$ kilomoles of N_2. Now, actual combustion occurs at an equivalence ratio of 1. So, you rewrite the equation for the actual combustion by replacing 3 by 3 / 1.1 and it is given that no hydrogen or oxygen is left. We have already seen this in the previous worked example.

So, hydrogen combust fully to H_2O because it is highly reactive. However, the remaining oxygen is shared to form CO_2 and CO. Now, by incurring C and O balances, you get two equations involving a and b by solving you get a equal to 1.4546 and b equal to 0.5454 and the products are this

$$C_2H_5OH + (3/1.1)(O_2 + 3.76\ N_2) \rightarrow 3H_2O + aCO_2 + bCO + 10.2545N_2$$

C balance: $2 = a + b$

O balance: $1/2 + 3/1.1 = a + b/2 + 3/2$

Now we can write the equations. So, product composition is known, so, we can find the standard heat of combustion.

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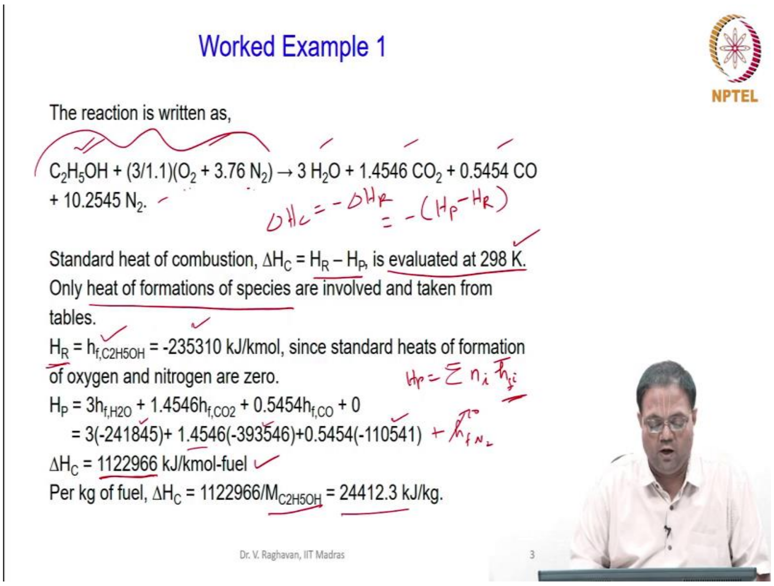

Worked Example 1

The reaction is written as,

$C_2H_5OH + (3/1.1)(O_2 + 3.76\ N_2) \rightarrow 3\ H_2O + 1.4546\ CO_2 + 0.5454\ CO + 10.2545\ N_2$.

$\Delta H_c = -\Delta H_R = -(H_P - H_R)$

Standard heat of combustion, $\Delta H_C = H_R - H_P$, is evaluated at 298 K. Only heat of formations of species are involved and taken from tables.

$H_R = h_{f,C2H5OH} = -235310$ kJ/kmol, since standard heats of formation of oxygen and nitrogen are zero.

$H_P = \sum n_i h_{fi}$

$H_P = 3h_{f,H2O} + 1.4546h_{f,CO2} + 0.5454h_{f,CO} + 0$

$= 3(-241845) + 1.4546(-393546) + 0.5454(-110541) + \overset{0}{h_{fN_2}}$

$\Delta H_C = 1122966$ kJ/kmol-fuel

Per kg of fuel, $\Delta H_C = 1122966/M_{C2H5OH} = 24412.3$ kJ/kg.

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Now, the entire equation is written here 1 kilomole of ethanol + 3 / 1.1 × air 4.76 kilomoles of air giving 3 kilomoles of water vapour, 1.4546 kilomoles of CO_2 0.5454 kilo moles of CO and 10.2545 kilomoles of nitrogen.

$$C_2H_5OH + (3/1.1)(O_2 + 3.76\ N_2) \rightarrow 3\ H_2O + 1.4546\ CO_2 + 0.5454\ CO + 10.2545\ N_2.$$

Now, standard heat of combustion ΔH_C is nothing but $-\Delta H_R$ which is nothing but $-(H_P - H_R)$, which is written as $H_R - H_P$. So, this is the standard heat of combustion.

Now, when I say standard, this has to be evaluated at 298 K, all the enthalpies have to be evaluated at 298 K. So, only heat of formation of species are involved in this.

For example, H_R the reactant mixture contains ethanol, O_2 and N_2; however, since O_2 and N_2 are basic elements heat of formation of them are 0. The H_R is contributed only by the heat of formation of ethanol which is given as -235310 kJ/kmol.

So, that is the enthalpy of reaction. Then, what is enthalpy of products? Enthalpy of product is nothing, but $\sum n_i h_i$.

$$H_P = 3h_{f,H2O} + 1.4546h_{f,CO2} + 0.5454h_{f,CO} + 0$$
$$= 3(-241845) + 1.4546(-393546) + 0.5454(-110541)$$

Now, since we are talking about 298 K, this is $n_i \times h_{fi}$, heat of formation that is it. so, now that is what we are trying to do here 3 times the enthalpy of formation of H_2O and 1.4546 times the enthalpy of formation of CO_2 + 0.5454 times enthalpy of formation of CO + 0, that is 0. There is no enthalpy of formation of nitrogen because it is a naturally occurring species.

So, when you do H_R - H_P, you will get the positive ΔH_C value because say exothermic reaction. So, 1122966 kJ/kmol of fuel so, that is this. If you want per kg of fuel, then divide by the molecular weight of fuel you will get 24412.3 kJ/kg.

So, this is a simple example where you try to find the calorific value or heat of combustion at standard state when there is a slightly rich mixture of ethanol and air reacting.