Fundamentals of Aerospace Propulsion
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Lecture - 19

Let us start this lecture with a thought process from Jim Eadon from Sheffield university.

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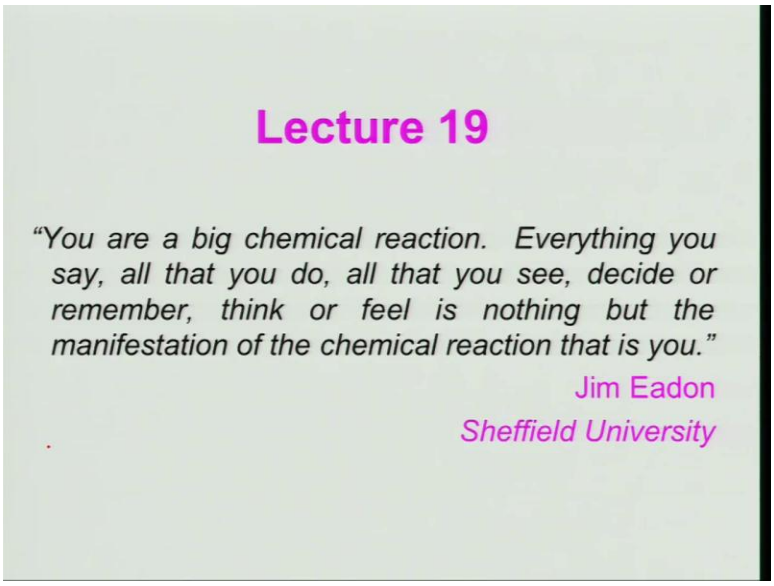

Lecture 19

"You are a big chemical reaction. Everything you say, all that you do, all that you see, decide or remember, think or feel is nothing but the manifestation of the chemical reaction that is you."

Jim Eadon

Sheffield University

He says that you are a big chemical reaction, everything you say, all that you do, all that you see, decide or remember, think or feel is nothing. But, the manifestation of the chemical reaction that is you, it is a very profound statement and I told you nature does a lot of activity through us with the help of chemistry that is the beauty of this. And let us recall briefly what we had learned in the last lecture, we basically discussed about hays law and then we moved to how to find out adiabatic temperature.

Then adiabatic temperature we found out that it is function of equivalence ratio, it is a function of inlet temperature, it is a function of also the pressure. And keep in mind that what I had derived in the last class that is mean for constant pressure process; however, some of the process occurs in the constant volume process, you need to think we will have to find out adiabatic temperature for that. And remember that I did those things keeping that you know this chemical composition being known, but; however, in the real situation chemical composition is not be known and if both are inherent.

And then be moved into equilibrium because, from at equilibrium we can find out we learn the by minimization of the Gibb's free energy, we can find out the equilibrium composition right. And keep again I must draw your attention that this minimization of Gibb's free energy can be applied only for the control volume process at what you call or the constant pressure process right. And if I want to go for a constant volume heat addition, like in a combustion form or a for use as a calorimeter or for a nice engine then I need to use the helmets Gibb's free energy.

That means, we need to minimize that you will have to look at it I would not be covering, I will be concentrating on the minimization of Gibb's free energy.

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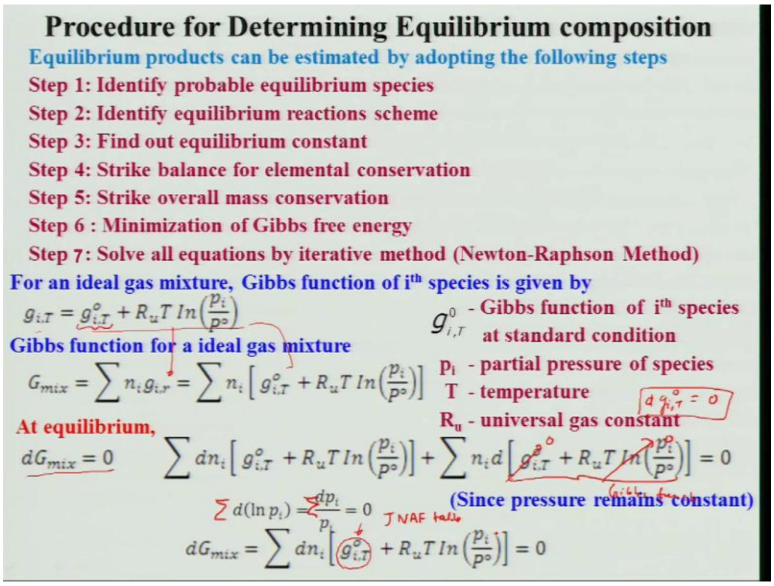

Procedure for Determining Equilibrium composition

Equilibrium products can be estimated by adopting the following steps

Step 1: Identify probable equilibrium species

Step 2: Identify equilibrium reactions scheme

Step 3: Find out equilibrium constant

Step 4: Strike balance for elemental conservation

Step 5: Strike overall mass conservation

Step 6 : Minimization of Gibbs free energy

Step 7: Solve all equations by iterative method (Newton-Raphson Method)

For an ideal gas mixture, Gibbs function of ith species is given by

$$g_{i,T} = \underline{g^o_{i,T}} + R_u T\, ln\left(\frac{p_i}{p^o}\right)$$

$g^0_{i,T}$ - Gibbs function of ith species at standard condition

Gibbs function for a ideal gas mixture

$$G_{mix} = \sum n_i g_{i,T} = \sum n_i \left[g^o_{i,T} + R_u T\, ln\left(\frac{p_i}{p^o}\right)\right]$$

p_i - partial pressure of species

T - temperature

R_u - universal gas constant

$\boxed{d\, g^o_{i,T} = 0}$

At equilibrium,

$$\underline{dG_{mix} = 0} \qquad \sum dn_i \left[g^o_{i,T} + R_u T\, ln\left(\frac{p_i}{p^o}\right)\right] + \sum n_i d\left[\cancel{g^o_{i,T}} + R_u T\, \cancel{ln}\left(\frac{p^o_i}{p^o}\right)\right] = 0$$

Gibbs funct

(Since pressure remains constant)

$$\sum d(\ln p_i) = \sum \frac{dp_i}{p_i} = 0$$

JNAF table

$$dG_{mix} = \sum dn_i \left[\boxed{g^o_{i,T}} + R_u T\, ln\left(\frac{p_i}{p^o}\right)\right] = 0$$

Let us look at how we will be dealing with it, and as I well we will have to basically look at the procedure for determining the equilibrium compositions. And I have just identified few steps of course, first of all you know one has to look at what reaction, it is when you talk about reaction, you will have to identify probable equilibrium spaces. You may ask a question, how I will know that of course, you need to have some experience, and even if you choose something you know just by guessing then you can figure it out the end of this calculation, whether it is of worth doing that are not.

Because, the composition if it is very, very less you know as compared to the major components, you can say I can neglect it. But, you will have to pay price for that because, number of equations will be increasing, then you need to what you call identify the equilibrium reaction scheme that is also is the important aspect what are the alone. And then this reactions must be elementary in nature that is a very important point, then you need to find out equilibrium constant, what is that equilibrium constant some of you might be aware.

Because, it is being taught in the you know your engineering and other things, so we need to determine that equilibrium constant right. And then of course, for that will have to for you know next step would be strike a balance for elemental conservation, strike over mass conservation, and then minimization of Gibb's free energy right, and solve all equation you know by iterative method because, all are coupled equations. So, you cannot really solve like that although it is algebraic, but it will be you know a couple.

So, you need to use iterative method one of the numerical tool, which is being used in the Newton Raphson method for solving. So, we will as I told it will be considering ideal gas mixture all the times, so Gibb's function for i'th species can be written as g i T; that means, this is the i'th the species Gibb's free energy at particular temperature. And this is at standard state, you know like temperature and pressure, and then less R u T l n P i by P naught you keep in mind that P i is basically partial pressure of the i'th species, and T is the temperature R u is the universal gas constant right.

That means, this expression is meant for a particular species it can be methane, it can be propane, it can be oxygen, it can be o h any other things. So, what it indicates is depends on temperature, it depends on also partial pressure and P naught is your what you call the standard pressure, in this case ambient pressure which is being considered. So, Gibb's function for an ideal gas mixture, we know that g mixture will be summation of n i g i r and n i into g i T R u can just write down this expression over here.

You know if you look at this expression can be put it over here that is all rather it this expression can be put it here and you will get this thing. So, what we will do now, we will have to basically find out the d capital G of mixture is 0 right at equilibrium because, at equilibrium this will be 0. So, then what I will do I will just differentiate this expression and d n i keeping this as a constant, this I will be keeping a constant. So, I will get d n i g i in the bracket you know naught plus R u T l n P i by P naught.

And similarly, n i you will keep it constant and I will be differentiating this, what you call Gibb's function because, this is Gibb's function right and I am differentiating what I get if I differentiate d g i T what will happen it will be constant. So, therefore, that this term will be 0 right similarly because, if I look at basically you know it will be d g i T 0 is 0. Because, it is not changing with respect to it is with respect to what I mean like whatever the temperature a standard temperature kind of things you know it will be at with a certain temperature.

So, it would not be really changing, so that will be 0 and we will find that this T l n P i by P is basically d p i by P. And if I take a summation of that partial pressure you know it is equal to when you take about partial summation of all partial pressure over the all you know of each individual species, then what you will get, you will get the total pressure. So, that will also be would not be change right, so if I take a summation of that you know summation because, since the pressure is remain constant in this you know you can have a 0.

So, therefore, this term will be 0, so what you will get the d G mixture is nothing, but d n i into this Gibb's you know function for a i'th species. So, this is a very important, you know expression you should keep in mind which is being used for finding out, you know composition. Keep in mind that these values you know these values from where I will get, I will get from J NAF table and in my book fundamental combustion it is given on the back subtle of the data’s.

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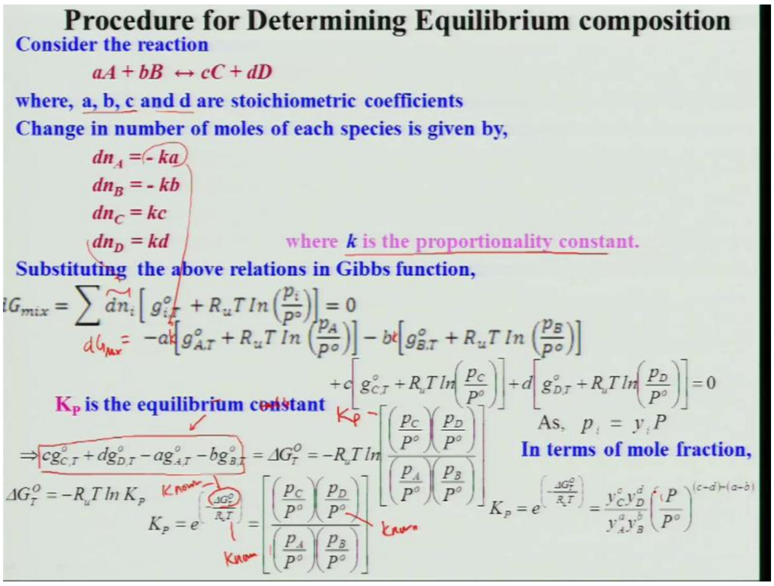

Procedure for Determining Equilibrium composition

Consider the reaction

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

where, a, b, c and d are stoichiometric coefficients

Change in number of moles of each species is given by,

$$dn_A = -ka$$
$$dn_B = -kb$$
$$dn_C = kc$$
$$dn_D = kd$$

where k is the proportionality constant.

Substituting the above relations in Gibbs function,

$$dG_{mix} = \sum dn_i \left[g^o_{i,T} + R_u T \ln\left(\frac{p_i}{P^o}\right)\right] = 0$$

$$dG_{mix} = -ak\left[g^o_{A,T} + R_u T \ln\left(\frac{p_A}{P^o}\right)\right] - bk\left[g^o_{B,T} + R_u T \ln\left(\frac{p_B}{P^o}\right)\right]$$
$$+ c\left[g^o_{C,T} + R_u T \ln\left(\frac{p_C}{P^o}\right)\right] + d\left[g^o_{D,T} + R_u T \ln\left(\frac{p_D}{P^o}\right)\right] = 0$$

K

K_P is the equilibrium constant

$$\Rightarrow \boxed{c g^o_{C,T} + d g^o_{D,T} - a g^o_{A,T} - b g^o_{B,T}} = \Delta G^O_T = -R_u T \ln \overset{K_P}{\left[\frac{\left(\frac{p_C}{P^o}\right)\left(\frac{p_D}{P^o}\right)}{\left(\frac{p_A}{P^o}\right)\left(\frac{p_B}{P^o}\right)}\right]}$$

As, $p_i = y_i P$

In terms of mole fraction,

$$\Delta G^O_T = -R_u T \ln K_P$$

Know

$$K_P = e^{\left(-\frac{\Delta G^O_T}{R_u T}\right)} = \left[\frac{\left(\frac{p_C}{P^o}\right)\left(\frac{p_D}{P^o}\right)}{\left(\frac{p_A}{P^o}\right)\left(\frac{p_B}{P^o}\right)}\right]$$

Know

Know

$$K_P = e^{\left(-\frac{\Delta G^O_T}{R_u T}\right)} = \frac{y_C^c y_D^d}{y_A^a y_B^b}\left(\frac{P}{P^o}\right)^{(c-d)-(a-b)}$$

And of course, partial pressure and this is the total pressure from which we will be getting basically the mole fraction that I will see, you know in the next slide or we will discuss about it.

So, let us consider a arbitrary reaction that a moles of species a is reacting with b moles of species b, and it is going to the c moles of species c and d moles of species d, it can be n any numbers. But, I have considered only 2 reactants and 2 products just for simplicity, and what are these a, b, c if you look at a, b, c and d are corresponding stoichiometric coefficients. That means, you know how many moles it is participating that is saying, and change in number of moles of each species.

For examples species a will be proportional to the coefficient of that species a in that case d n A is equal to minus k a, k is what k is you are proportionality constant. And why it is minus because, the reactant is getting consumed therefore, it is minus similarly d n B is equal to minus k b and whereas, the d n C is equal to k c keep in mind this is positive because, it is being produced.

Similarly, d n D is equal to k d and k is the basically proportionality constant right, what will do now we will substitute this above relation with Gibb's function what we have derived at equilibrium this d G mixture will be equal to 0, and we will be substituting here you know all those expression and sum it over.

For example, if I take for a you know for a and b it will be minus a and keep in mind that this is a k here because, a k this portion I am taking from here and putting it here and g A naught T plus R u T l n p A by P naught. Because, the species is a similarly minus there will be k here, and g B T naught plus R u T l n p B by P naught, just write and then similarly I can write down for species c and species d is that clear, which is equal to 0 right.

Because, this is nothing, but what this is basically G mixture right d G mixture is equal to 0 at equilibrium, you keep in mind and we will be knowing the temperature, will be knowing the pressure right. So, and then if I will do what I will do now, I will basically rearrange this equations, what I will do I will put this you know g c T kind of corresponding to the standard state like c and d for and then this thing, if you look at this portion is basically delta G naught that is corresponding to the what you call standard state and temperature and this you can get from J NAF table right.

That means, delta G naught is known to you, and then minus R u T l n is equal to P c by P naught then P D by P naught divided by P A by P naught P B by and this we call it is basically this term you know this bracket term we call it as a K p, what is this K p, K p is the equilibrium constant right. And this equilibrium constant you know I can write down K p is basically e power to the minus delta G naught R u T right into this portion that is K p.

That means, this is known if you look at this portion is nothing, but that and then this is known I am right. Similarly, I must be knowing the temperature at which I am finding out the equilibrium; that means, in real situation it will be adiabatic temperature you know. So, T will be known and of course, the R u is known, so you know this term; that means, you know basically K p value, and then you will have to find out this basically P naught is known to your naught P naught is known.

But, do you know P D P C P A P B you really do not know that right, you do not those things right can be expressed this partial pressure of species like P C P D and then P A P B in terms of mole fractions right. Let us the power to the c plus d minus a minus, but if this pressure this pressure is what, this is the pressure at which you are trying to find out equilibrium composition, if this happens to be atmosphere pressure or standard pressure is this term will be P by P naught will be 1.

That means, this term will be basically 1 you need not to worry about, but; however, sometimes we will be looking at a higher pressure or a lower pressure than P naught. So, this you know for the generality I have kept, but in some book you may find it is not there.

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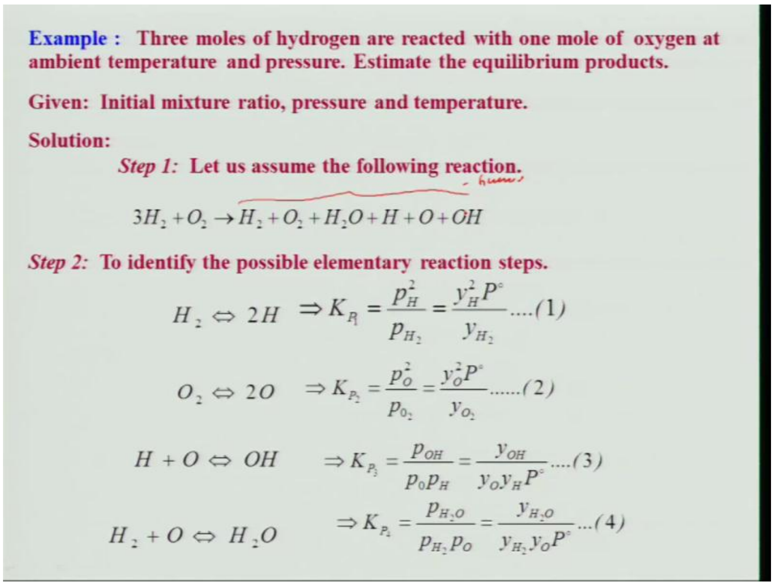

Example : **Three moles of hydrogen are reacted with one mole of oxygen at ambient temperature and pressure. Estimate the equilibrium products.**

Given: Initial mixture ratio, pressure and temperature.

Solution:

Step 1: **Let us assume the following reaction.** [illegible]

$$3H_2 + O_2 \rightarrow H_2 + O_2 + H_2O + H + O + OH$$

Step 2: **To identify the possible elementary reaction steps.**

$$H_2 \Leftrightarrow 2H \quad \Rightarrow K_{P_1} = \frac{p_H^2}{p_{H_2}} = \frac{y_H^2 P^\circ}{y_{H_2}} \quad ....(1)$$

$$O_2 \Leftrightarrow 2O \quad \Rightarrow K_{P_2} = \frac{p_O^2}{p_{O_2}} = \frac{y_O^2 P^\circ}{y_{O_2}} \quad ......(2)$$

$$H + O \Leftrightarrow OH \quad \Rightarrow K_{P_3} = \frac{p_{OH}}{p_O p_H} = \frac{y_{OH}}{y_O y_H P^\circ} \quad ....(3)$$

$$H_2 + O \Leftrightarrow H_2O \quad \Rightarrow K_{P_4} = \frac{p_{H_2O}}{p_{H_2} p_O} = \frac{y_{H_2O}}{y_{H_2} y_O P^\circ} \quad ...(4)$$

So, now, will take an example and illustrate how we can you know determine this naught equilibrium compositions and also I will tell you the steps, how you can find out the both equilibrium composition, and adiabatic temperature right that I will have to show you. And then of course, this you cannot do in you know in your day to day life or in your as a part of curriculum. So, we will be taking a simple example where which can be done in classroom.

So, let us look at three moles of hydrogen are reacted with one mole of oxygen at ambient temperature and pressure right, we need to determine the equilibrium products. So, what is given, given is that initial mixture ratio is given; that means, three moles of hydrogen is reacting with one mole of oxygen I know that, and pressure is given temperature is given. So, what I will have to do, I will have to first assume the certain reactions for example, I can write down three moles of hydrogen 3 as 2 plus you know is reacting with one moles of oxygen; that means, O 2.

What are the products I think of can I guess it will be definitely water will be oxygen, will be definitely will be there right maybe there may not be there right and O will be there, O H will be there right and several other things. But, we will consider few of them like hydrogen, oxygen, water H O and O H and several other species one can think of keep in mind that more species I take more it will be number of equations I need to consider.

So; that means, this I have guess you know this species this is being you know guess, so then I need to identify the possible elementary reactions. Keep in mind we need to always consider elementary reaction, and that is hydrogen you know can be converted into 2 H when I talk about it I can determine what is K p. So, K p by definition it will be P H square divided P H square if I talk in terms of mole fraction, it will be y H square P naught divided by y H 2 why it is because, 1 P naught is cancel it off are you getting my point.

Because, in this case the P naught is being cancel it out, in the denominator right, so similarly this is our equation 1 and I will take oxygen is going to 2 O O 2 is going to 2 O. Then, similarly I can you know get a relationship for equilibrium constant that is K p 2 P o 2 divide by P o 2 right P o is equal to basically y o 2 square you know mole fraction in P naught divided by y o 2 right.

Similarly, I will be considering H plus O going to the O H right and I can write down K p 3 will be P o H divide by P o and P H, you keep in mind that these are all mole fraction y o H divided by y o y H and P naught comes in the denominator right. And then I will have to look at H 2 plus O H 2 O and K p 4 P H 2 o divide by P H 2 P o and you will get the in terms of mole fraction.

That means, I am getting these 4 equations, if you look at we need to find out 1, 2, 3, 4, 5, 6 right, but we are only considering the 4 equations here or we are getting 4 equations because, as your considering 4 elementary reactions right. Keep in mind that I can I may take not take this combination, but I may take some other combination as well, then we need to actually maybe it will be clear little later on that why we need 4 why not 6 as I told you previously.

In the procedure we need to talk about elementary balance right and those things are important as well, otherwise you will be in deep trouble right. So, we will be getting to equation from that let us see what we will get.

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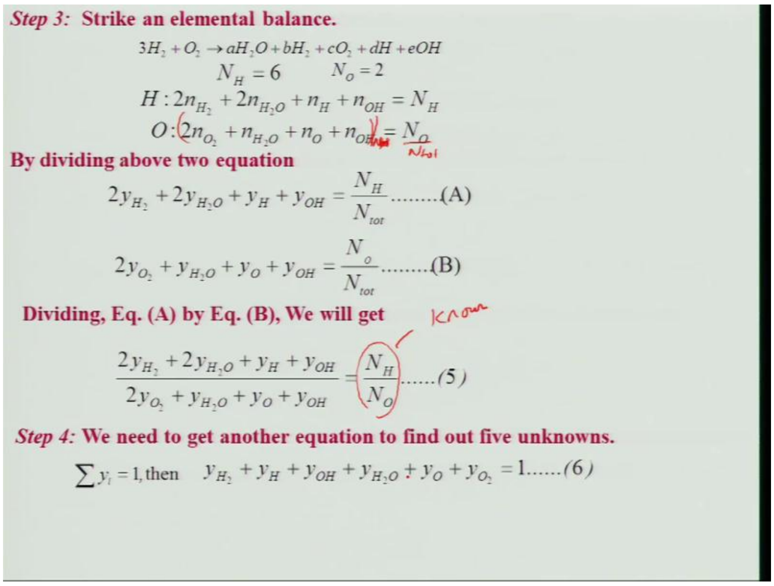

Step 3: **Strike an elemental balance.**

$$3H_2 + O_2 \rightarrow aH_2O + bH_2 + cO_2 + dH + eOH$$

$$N_H = 6 \qquad N_o = 2$$

$$H: 2n_{H_2} + 2n_{H_2O} + n_H + n_{OH} = N_H$$

$$O: 2n_{O_2} + n_{H_2O} + n_O + n_{OH} = \frac{N_O}{N_{tot}}$$

By dividing above two equation

$$2y_{H_2} + 2y_{H_2O} + y_H + y_{OH} = \frac{N_H}{N_{tot}} \text{........(A)}$$

$$2y_{O_2} + y_{H_2O} + y_O + y_{OH} = \frac{N_o}{N_{tot}} \text{........(B)}$$

Dividing, Eq. (A) by Eq. (B), We will get

Known

$$\frac{2y_{H_2} + 2y_{H_2O} + y_H + y_{OH}}{2y_{O_2} + y_{H_2O} + y_O + y_{OH}} = \frac{N_H}{N_O} \text{......(5)}$$

Step 4: **We need to get another equation to find out five unknowns.**

$$\sum y_i = 1, \text{then} \quad y_{H_2} + y_H + y_{OH} + y_{H_2O} + y_O + y_{O_2} = 1\text{......(6)}$$

Let us say that 3 H 2 O is reacting with oxygen going to a of water, b moles of hydrogen, c moles of oxygen, d moles of H, e moles of O H, just for the simplicity I have written. So, if you look at number of H is equal to what 6 given yes or no 3 H 2; that means, 6 a number of O atom is basically 2, so if I take this H what I can write down 2 n H 2 because, 2 are there in H 2.

So, similarly in the water 2 n H 2 O plus H it is the only one, so n H plus n O H is equal to N H that is the product what I should get you know if I look at the product balance all the things I am talking about in the product, wherever it is there if you look at hydrogen water H O H. Similarly, I will be looking at oxygen, if you look at 2 n O 2, n H 2 o is there n o, n O H and N; that means, these numbers you know reactant in the product should match.

So, what I will do I will just divide this by the total number of you know elements whatever is there. So, if I divide this equation for H right I will get you know 2 y H plus 2 y water and plus y H plus y O H is N H by N total and similarly when I divide this by N total right. So, I will get 2 y o 2 plus y H 2 O O plus y O plus y O H N o divided by now what I will do I will just divide equation A by B right what I will get this will be when I divide this thing that N total N total cancel it out I get 2 y H 2 plus 2 y water plus y H plus y O H divided by 2 y o 2 plus y H 2 O plus y O O H.

So, this is known if you look at this is known what is that, That is basically 6 divided by 2 right which is given. So, this is one expression equation number 5, and another we need to get another equation to find out 5 unknowns, 6 unknown basically, so that is y i is equal to y H, y H, y O H, y H 2 O O plus O 2 right. These are the species and then I will get 1 and we can look at this you know 6 solve this equation, and such that we can get this you know values.

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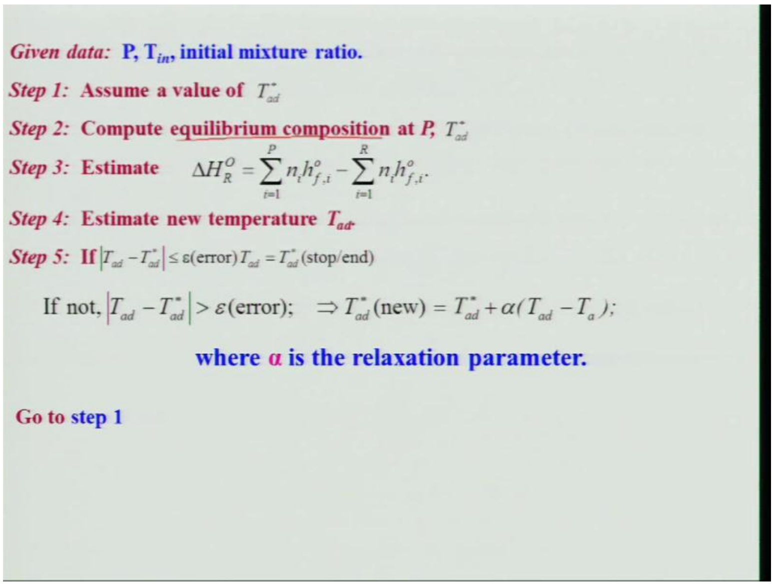

Given data: **P, T_{in}, initial mixture ratio.**

Step 1: **Assume a value of** T_{ad}^{*}

Step 2: **Compute equilibrium composition at** P, T_{ad}^{*}

Step 3: **Estimate** $\Delta H_R^O = \sum_{i=1}^{P} n_i h_{f,i}^o - \sum_{i=1}^{R} n_i h_{f,i}^o.$

Step 4: **Estimate new temperature** T_{ad}.

Step 5: **If** $|T_{ad} - T_{ad}^{*}| \leq \varepsilon(\text{error}) T_{ad} = T_{ad}^{*}$ (stop/end)

If not, $|T_{ad} - T_{ad}^{*}| > \varepsilon(\text{error}); \Rightarrow T_{ad}^{*}(\text{new}) = T_{ad}^{*} + \alpha(T_{ad} - T_a);$

where α is the relaxation parameter.

Go to step 1

So, what I will tell you; that means, let us look at how we can go about this, we know that P is given, T initial temperature is given what is that an initial mixture ratio is given right. So, initial temperature must be given because, that is the point and then what we will do, you will have to assume value of adiabatic temperature right, and after assuming those adiabatic temperature, then you will have to compute this equilibrium compositions you know like P and T by using this give minimization of Gibb's free energy right.

And then estimates that heat of reaction what I am getting right, so if you look at whatever this thing I have told like in the previously like you need to solve 6 equations to get those compositions you know because, K p and other things will be known. So, you will get composition, then you will have to estimate heat of reactions because, you have assumed adiabatic you do not know really adiabatic. Then estimates the new adiabatic temperature from this heat of reaction, which we have done already by invoking the first law of thermodynamics right.

And by knowing this you know you will have to find out you have guessed this value, you have obtained this value, then what is the error you are getting. For example, I will just assume 2000 Kelvin then I am getting 2100 Kelvin, so naturally there is a error you know which I cannot tolerate. For example, but if you can say look it is only 5 percent error I need not to worry about it, then you can manage if it is less than error.

Then if it is T adiabatic is equal to T in a adiabatic star of the guessed value, then you can stop right, if you are happy with the error whatever it is coming let us say 1 percent, 2 percent, 3 percent you can tolerate then you can stop. But, suppose you are not happy like if T adiabatic T adiabatic star is greater than the error tolerable error, then you will have to find out there what will be the new guessed value.

That means, this T adiabatic plus alpha minus T adiabatic minus T you know star kind of things, so right. So, what we will have to do, so we will have to basically use a relaxation parameter, generally people use under relaxation parameter you know alpha is less than 1S kind of things. And because, if you give a over relaxation sometimes you may get a instability problems, so then if you are not happy with these then you will have to guess value this is a new guessed value, you will have to go to the step 1.

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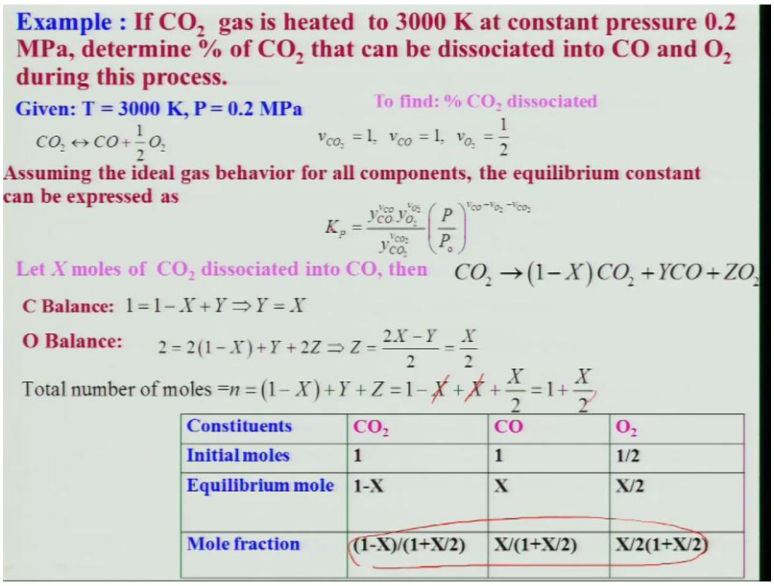

Example : If CO_2 gas is heated to 3000 K at constant pressure 0.2 MPa, determine % of CO_2 that can be dissociated into CO and O_2 during this process.

Given: T = 3000 K, P = 0.2 MPa

To find: % CO_2 dissociated

$$CO_2 \leftrightarrow CO + \frac{1}{2}O_2 \qquad \nu_{CO_2} = 1,\ \nu_{CO} = 1,\ \nu_{O_2} = \frac{1}{2}$$

Assuming the ideal gas behavior for all components, the equilibrium constant can be expressed as

$$K_p = \frac{y_{CO}^{\nu_{CO}}\, y_{O_2}^{\nu_{O_2}}}{y_{CO_2}^{\nu_{CO_2}}}\left(\frac{P}{P_o}\right)^{\nu_{CO}-\nu_{O_2}-\nu_{CO_2}}$$

Let X moles of CO_2 dissociated into CO, then $CO_2 \rightarrow (1-X)CO_2 + YCO + ZO_2$

C Balance: $1 = 1 - X + Y \Rightarrow Y = X$

O Balance: $2 = 2(1-X) + Y + 2Z \Rightarrow Z = \frac{2X-Y}{2} = \frac{X}{2}$

Total number of moles $= n = (1-X) + Y + Z = 1 - \cancel{X} + \cancel{X} + \frac{X}{2} = 1 + \frac{X}{2}$

Constituents	CO_2	CO	O_2
Initial moles	1	1	1/2
Equilibrium mole	1-X	X	X/2
Mole fraction	(1-X)/(1+X/2)	X/(1+X/2)	X/2(1+X/2)

And then you know that is the way it will go on iterating and you will do, and then estimates those values right. So, now let us look at an example which you will be dealing in the classroom kind of thing if C O 2 gas is heated to 3000 Kelvin at a constant pressure of 0.2 mega paschal, we need to determine percentage of C O 2 that can be dissociated into C O and O 2 during this process.

So, if you look at the temperature is given, and the pressure is given right here it is temperature is known unlike the previous case where you do not know the temperature right. Therefore, we need to go on and we need to find out percent of carbon dioxide, so carbon dioxide is basically react you know reacting going to the C O plus half O 2 right. And if you look at the what are the coefficients, coefficient for this case C O 2 is 1, C O is also 1, but oxygen is half these are the stoichiometric of the coefficients you know.

So, assuming ideal gas waiver for all component, equilibrium constant can be expressed as you know K p y C O C O you know new C O that is coefficient and y O 2 it is corresponding coefficient divided by y C O 2 corresponding coefficient, stoichiometric coefficient of carbon dioxide P by P naught, and these are the coefficients right. And what we will have to do we will let us assume X moles of C O 2 dissociated into C O, then what will be the reaction that will be C O 2 will be half you know 1 minus X C O 2, and we are assuming that Y C O and there will be some oxygen Z O 2 right.

Because, the reaction can proceed this way and there can be go that way right, so therefore, we need to find out we are assuming that this will be the product the C O 2 C O and O 2, again this is an you know kind of assumption one has to make. So, we will have to do you C balance, if I look at this is the left-hand side is 1 is equal to 1 minus X plus Y right because, there is in the Z there is no oxygen here, this is now carbon here, so Y is equal to X.

So, O balance we can get 2 that is for the O 2 into 1 minus X plus Y 2 Z, so Z is basically X by 2 right. So, total number of moles will be basically 1 plus X by 2 because, this will cancel it outright 1 plus X by 2, so if I look at that in a tabular form you know is the constituents gas as C O 2 C O and O 2. And these are initial moles, these are equilibrium moles what we are you know assuming because, X is not known we need to find out X basically then mole fraction you can say 1 minus x divided by this total.

And, similarly for carbon monoxide X divided by 1 plus X by 2, and for oxygen X divided by 2 you know into 1 minus 1 plus X by 2 right. So, what we will do now we will substitute these values you know these values over in the K p that is equilibrium constant. And we must be knowing that you know equilibrium constant from knowing the change in Gibb's free energy at a standard state.

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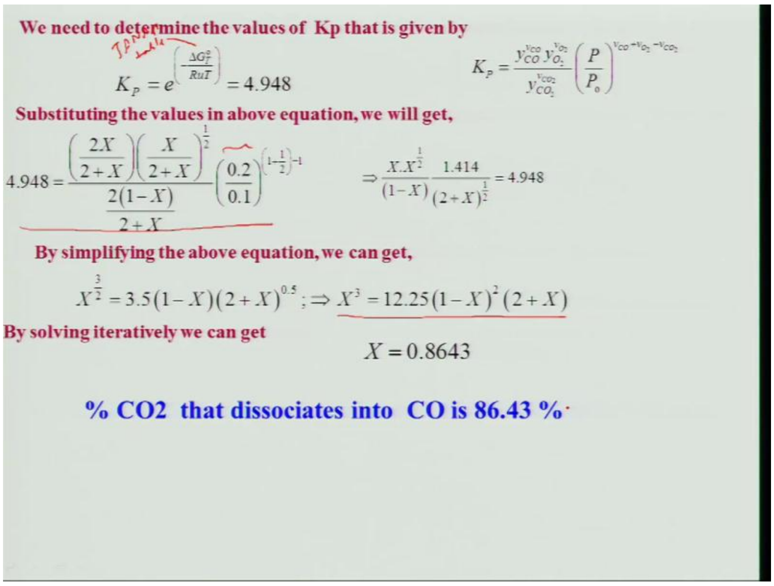

We need to determine the values of Kp that is given by

JANAF table

$$K_p = e^{\left(-\frac{\Delta G_T^0}{R_u T}\right)} = 4.948 \qquad K_p = \frac{y_{CO}^{\nu_{CO}} y_{O_2}^{\nu_{O_2}}}{y_{CO_2}^{\nu_{CO_2}}} \left(\frac{P}{P_o}\right)^{\nu_{CO}+\nu_{O_2}-\nu_{CO_2}}$$

Substituting the values in above equation, we will get,

$$4.948 = \frac{\left(\frac{2X}{2+X}\right)\left(\frac{X}{2+X}\right)^{\frac{1}{2}}}{\frac{2(1-X)}{2+X}} \left(\frac{0.2}{0.1}\right)^{\left(1-\frac{1}{2}\right)-1} \qquad \Rightarrow \frac{X.X^{\frac{1}{2}}}{(1-X)} \frac{1.414}{(2+X)^{\frac{1}{2}}} = 4.948$$

By simplifying the above equation, we can get,

$$X^{\frac{3}{2}} = 3.5(1-X)(2+X)^{0.5}; \Rightarrow X^3 = 12.25(1-X)^2(2+X)$$

By solving iteratively we can get

$$X = 0.8643$$

% CO2 that dissociates into CO is 86.43 %

So, what we will do we will basically K p is equal to e minus delta G by R u T, so we know the temperature. So, we will substitute this value 3000 Kelvin, this and this values from the J NAF table, if you look at this I can take from J NAF table right, and then I know this values right from J NAF because, delta G T I know, if you express that will be G you know like all those things and then you will get those from the table. So, these values will be known, but whereas, K p is y C O and all those things we know.

And we will substitute this in place of this mole fraction from the table of this values right I will get and then this is known. So, we need to solve because, if you look at this expression is basically, you know in terms of X only right, so if I will get this X then I can get what will be the equilibrium composition for the species being considered like C O C O 2 and oxygen. So, what I will do if you simplify this you will get this 4.948 and then this and then you will have to simplify further, and you will get a basically a expression which is cubic in nature.

Sometimes very rarely of course, you will get a unit of quadratic equation, if it is quadratic you can get easily of course, some of the calculator you are having you can solve cubic equations. Otherwise you will have to do a iterative method, and keep in mind that here the pressure comes into picture 0.2 and this is 0.1, you know in this example it is very important, this term we cannot really neglect.

So, iteratively if you solve this equation you get X is equal to 0.8643; that means, the percentage of carbon dioxide you know that that dissociate into C O is basically 86.43 percent, and you can get other composition as it is a major one in this temperature. The temperature is low what will happen, naturally this percentage will be much lower values right.

If you consider the ambient temperature, it is really would not be nothing will be happening you know kind of things right. So, now this you know we have discussed about chemical equilibrium composition right and now we will move into basically kinetic’s.

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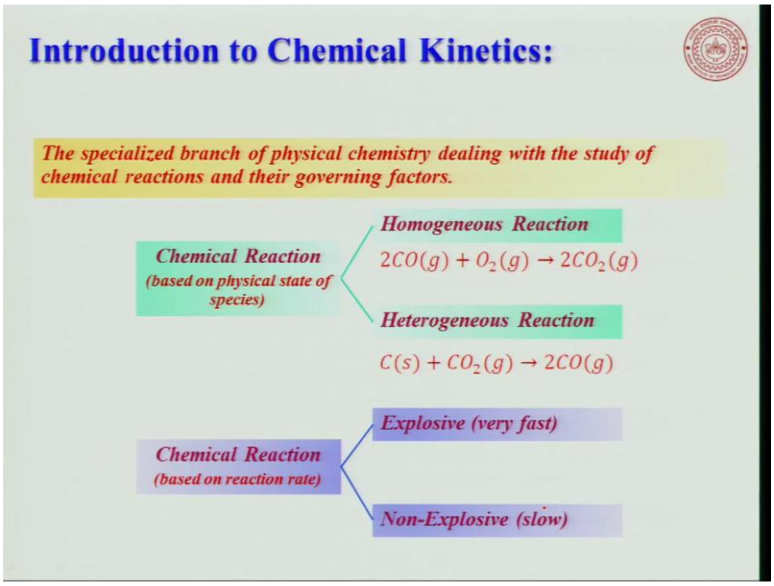

Introduction to Chemical Kinetics:

The specialized branch of physical chemistry dealing with the study of chemical reactions and their governing factors.

Chemical Reaction *(based on physical state of species)*
- *Homogeneous Reaction* $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
- *Heterogeneous Reaction* $C(s) + CO_2(g) \rightarrow 2CO(g)$

Chemical Reaction *(based on reaction rate)*
- *Explosive (very fast)*
- *Non-Explosive (slow)*

So, if you look at this is basically a specialized branch of physical chemistry dealing with study of chemical reactions, and their governing factors. So, when you talk about this chemical reaction it can be homogeneous reaction, it can be a heterogeneous reaction. So, when you talk about homogeneous I have taken one example 2 C O gas plus reacting with oxygen going to the 2 moles of carbon dioxide. Keep in mind that all are in gaseous phase, but you know in what you call in a propulsive devices we may need to deal with heterogeneous reaction.

Particularly when you are looking at solid propellant combustion right, so; that means, where one of this you know reactant or even product. You know suit and other things you know happen in combustion is the carbon C s is in solid form, it is reacting with carbon dioxide you know is a gaseous and going into the 2 C O. So, this is basically based on the physical state whether it is a you know gaseous phase all the components of the participating species in reaction or one of them is the, what you call different physical state like solid or liquid right.

Then we call it as a heterogeneous reaction, but if all in the same phase we call it as a homogeneous reaction. So, chemical reaction can be you know divided into categories, based on the fastness of reaction one is explosive which is quite very fast as compared to the a non-explosive reaction, and is a slow we call it a reflag ration, where is explosive reaction we call it a donation kind of thing will be discussing little later on.

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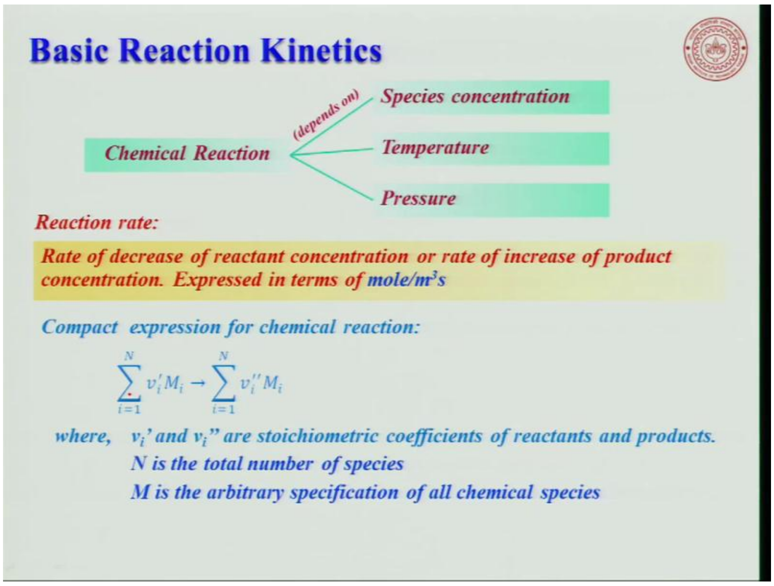

Basic Reaction Kinetics

Chemical Reaction (depends on) Species concentration

Temperature

Pressure

Reaction rate:

Rate of decrease of reactant concentration or rate of increase of product concentration. Expressed in terms of mole/m^{3}s

Compact expression for chemical reaction:

$$\sum_{i=1}^{N} v_i' M_i \rightarrow \sum_{i=1}^{N} v_i'' M_i$$

where, v_i' and v_i" are stoichiometric coefficients of reactants and products.

N is the total number of species

M is the arbitrary specification of all chemical species

And then chemical reaction depends on if you look at on the species concentration, temperature and pressure right. We have seen already from the equilibrium point of view, but reaction rate when you talk about it will be, you know we will see little later on that it will depend on that. So, if you look at reaction rate, it is basically rate of decrease of reactant concentration or rate of increase a product of concentration, generally it is expressed in terms of mole per meter cube second.

But, in some cases will be looking at k g per meter cube second you know how much marks it is being consumed for you need volume from kind of things. So, if I look at a compact expression of chemical reactions, which you can look at like you know v i dash M i going to the product v i double dash M i keep in mind that these a summation, which is a various phases i is can be 1 to N.

Similarly, in the react inside i is equal to 1 to N than number and v i, v i dash double dash are stoichiometric coefficient reactants of product of course, M is the arbitrary specification of all chemicals species we are considering, but I will taken example. So, what is a looks to be little quite complex, but in you know it is quite simple, and it is being used when you are basically using a coding kind of thing, suppose you are doing a modeling it is very useful, but in our case if may not be that useful.

But, when you want to model the chemical reaction using basically numerical tools this is a very, very handy way of expiration, you know chemical reactions.

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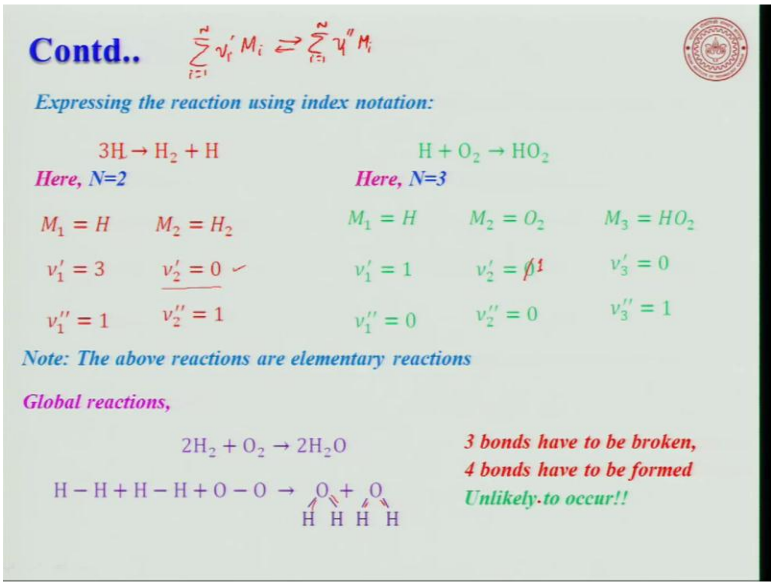

Contd.. $\sum_{i=1}^{N} \nu_i' M_i \rightleftarrows \sum_{i=1}^{N} \nu_i'' M_i$

Expressing the reaction using index notation:

$3H \rightarrow H_2 + H$

Here, N=2

$M_1 = H$ $\quad M_2 = H_2$

$\nu_1' = 3$ $\quad \underline{\nu_2' = 0}$ ✓

$\nu_1'' = 1$ $\quad \nu_2'' = 1$

$H + O_2 \rightarrow HO_2$

Here, N=3

$M_1 = H$ $\quad M_2 = O_2$ $\quad M_3 = HO_2$

$\nu_1' = 1$ $\quad \nu_2' = \cancel{0}1$ $\quad \nu_3' = 0$

$\nu_1'' = 0$ $\quad \nu_2'' = 0$ $\quad \nu_3'' = 1$

Note: The above reactions are elementary reactions

Global reactions,

$2H_2 + O_2 \rightarrow 2H_2O$

$H-H+H-H+O-O \rightarrow \underset{H\quad H}{O} + \underset{H\quad H}{O}$

3 bonds have to be broken,
4 bonds have to be formed
Unlikely to occur!!

So, let us take an example that if I take you know 3 H plus hydrogen going to the hydrogen an H, you know H than in this case what is N, N is the number of species, what is that N, N is equal to basically 2 because, 1 is hydrogen and other is H. So, and similarly if I take H plus O 2 going to the H O 2 in this case N is equal to 3 right because, 1 is oxygen, other is hydrogen, other is H O 2. Keep it mind, these are reaction what I am considering in elementary nature. So, if I want to right down this in the compact form, what it would be M 1 is H, M 2 is H 2 right.

If I look at this is my this thing i is equal to 1 to n i dash M i you know i double dash M i right i is equal to 1 to N. So, if I look at what is this v i 1 in this case it is what you call 3 because, H is there whatever v 2 dash, v 2 dash will be 0 because, there is no a you know H 2 here, if I look at M 2 is H 2, the left-hand side is not there, so therefore, this will be 0 right. And similarly, you look at in the right hand side that is H if you look at v 1 dash is equal to 1 whereas, in the what you call for the hydrogen in the right side v 2 is equal to 1 because hydrogen is there.

And similarly I will you know you can think of about this, this is similar way like in the left-hand side if I consider the hydrogen you know v 1 dash is equal to 1 for the product what you will be v 1 double dash 0. Similarly, oxygen you know there is a mistake actually, so this will be 1 right and v 2 dash will be 0, and M 3 is basically H O 2 and v 3 is equal to 0 there is nothing on the left hand side right hand side is equal to 1.

So, the above reactions are elementary as I have told you, so global reactions will be like you know 2 moles of hydrogen reacting with oxygen going to the product of 2 moles of water. And if you look at what is really happening, this is one you know hydrogen, and another hydrogen, and oxygen you know there will come and collide with each other, so that the bonds are broken. And if you look at there is a 1 bond which is having you know formed that is a water.

That means, many bonds this is the 1, 2, 3 you know 3 bonds are being broken, 4 bond are being formed you know like kind of thing. So, it is quite sorry this is I mean if you look at this quite difficult things to happen right, so the 3 bonds are to be broken, and 4 bonds or to be formed because, you know which is unlikely to occur right So, therefore, it is you know global reactions you know is very unlikely to occur and I take it will be clear when I will be talking about this what you call collision theory.

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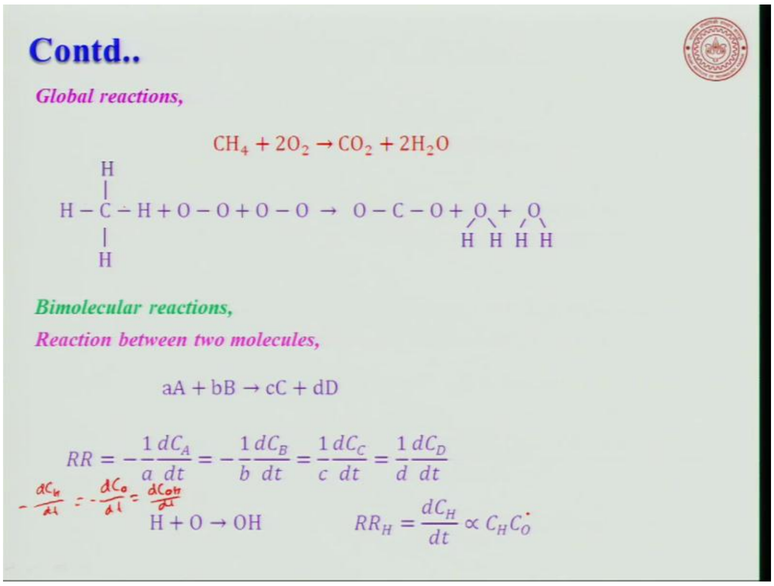

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Global reactions,

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$H-\underset{H}{\overset{H}{C}}-H + O-O + O-O \rightarrow O-C-O + \underset{H\ \ H}{O} + \underset{H\ \ H}{O}$$

Bimolecular reactions,

Reaction between two molecules,

$$aA + bB \rightarrow cC + dD$$

$$RR = -\frac{1}{a}\frac{dC_A}{dt} = -\frac{1}{b}\frac{dC_B}{dt} = \frac{1}{c}\frac{dC_C}{dt} = \frac{1}{d}\frac{dC_D}{dt}$$

$$-\frac{dC_H}{dt} = -\frac{dC_O}{dt} = \frac{dC_{OH}}{dt}$$

$$H + O \rightarrow OH \qquad RR_H = \frac{dC_H}{dt} \propto C_H C_{\dot{O}}$$

So, similarly you can see that one mole of methane reacting with to moles of a oxygen going to the carbon dioxide, and water if you look at this is 1, 2, 3, 4, 4 bonds are there you know. And similarly, oxygen 1, 2 you know like at 6 and 1, 2, 3, 4, 5, 6, so if look at this is a quite difficult to happen in real situations because, too many bonds are broken to many bonds and we should come together. So, that it will be having a ((Refer Time: 39:40))

So, therefore, global reaction is really only possible in real situations, and if you note that just now having invoke the concept of breaking of bonds and the forming the bonds explaining a global reaction for both methane, and air, and hydrogen air. But, this is just to explain you the thing you must keep in mind that such kind of breaking of bond and forming of new bonds are not really being taking place in the global kinetics. In other words these breaking a bond or the forming of new bonds are likely to occur in the elementary reaction only, just to explain I have invoked this concept.

But, you must keep in mind that this is the wrong to say that this process of breaking a bond and forming of bonds are occurring for global reactions. So, but whereas, what is likely to occur is the bimolecular and try molecular reactions may occur, so let us consider reaction between 2 molecules that is a in a moles of species a reacting with b moles of species b go to the product c moles of species c and d moles of species d. So, I can write down this reaction rate is basically 1 over a d C A by d t right, and this is a minus sign because, it is getting consumed.

And similarly, equal to the d C B by d t 1 over b minus sign because, b you know reactant is getting consumed is equal to 1 over c d C by d t and 1 over d d C by d t. So, if you look at what is saying, it is saying you know like the reaction rate for each species one case it is getting consumed, other cases by getting produced. For example, if I take H plus reacting with O is going to the O H and I can write down in similar way like you know d C H by what you call by d I can write down this is d C H by d t minus is equal to d C O by d t minus is equal to d C O H by d t.

Keep in mind that this reaction rate when you talk about in this example d C H by d t is proportional to what concentration of hydrogen, and oxygen. When you talk about this concentration of hydrogen and oxygen, then you know it has to be constant.

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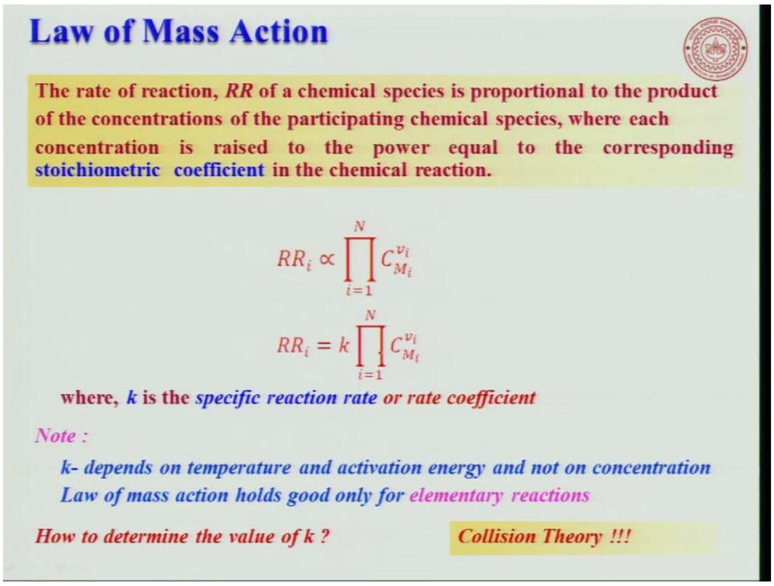

Law of Mass Action

The rate of reaction, *RR* of a chemical species is proportional to the product of the concentrations of the participating chemical species, where each concentration is raised to the power equal to the corresponding stoichiometric coefficient in the chemical reaction.

$$RR_i \propto \prod_{i=1}^{N} C_{M_i}^{\nu_i}$$

$$RR_i = k \prod_{i=1}^{N} C_{M_i}^{\nu_i}$$

where, *k* is the *specific reaction rate or rate coefficient*

Note :

k- depends on temperature and activation energy and not on concentration

Law of mass action holds good only for elementary reactions

How to determine the value of k ? *Collision Theory !!!*

So, that constant we call it as a basically rate of you know reaction kind of thing, so if I sum it off this discussion, then we need to invoke the law of mass action. Because, how this I have I could write than the law of mass action states that the rate of reaction of a chemical species is proportional to the product of concentration of participating chemical species. Where each concentration is raised to the power equal to the corresponding stoichiometric coefficient of chemical reaction.

So, this is a very important statement right, which governance the reaction rate and other thing. So, for example if I say that you know in a very compact form reaction rate of higher species, you know will be proportional to the product of all the species which will be participating on the, you know you can consider as a reactant side, and corresponding to their stoichiometric coefficient. So, I can write down this is a proportional, so therefore, k R R i is equal to k summation of C M i v i and k as I told it is a specific reaction rate are the rate coefficient right.

So, these we need to determining right how to determine that is the very important aspect. So, k depends on the temperature and it will be independence activation energy of course, it does not depend on the concentration because, the you know is already according to the mass law, mass action that it is basically proportionality constant already the concentration are there. Keep in mind at this law of mass action holds could only for the elementary reaction, it cannot be holds good for the global reaction what we have will be using you know that is a very important statement, you must keep in mind.

So, question arises how to determine the value of k right that is a very important aspect, so we need to look at collision theory right, what is the collision theory, collision theory is may says you know a molecules will be moving randomly, and it will be colliding with each other.

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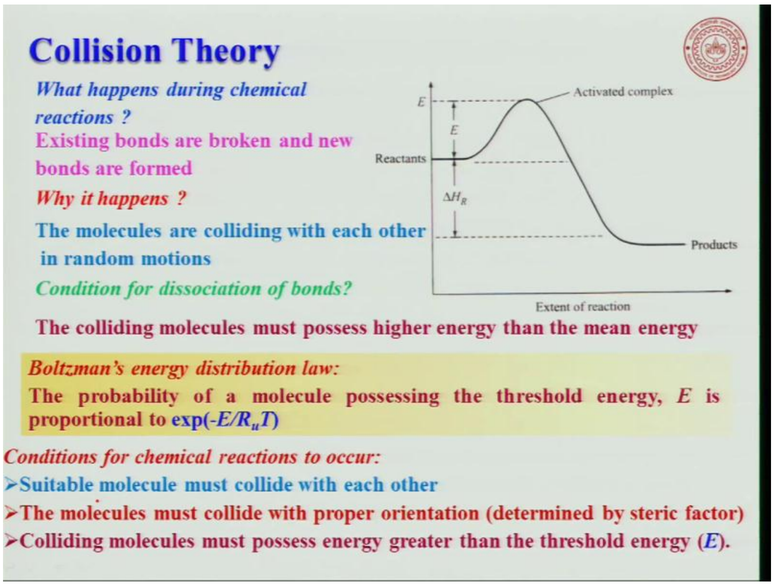

Collision Theory

What happens during chemical reactions ?

Existing bonds are broken and new bonds are formed

Why it happens ?

The molecules are colliding with each other in random motions

Condition for dissociation of bonds?

The colliding molecules must possess higher energy than the mean energy

Boltzman's energy distribution law:

The probability of a molecule possessing the threshold energy, E is proportional to exp($-E/R_uT$)

Conditions for chemical reactions to occur:

➢Suitable molecule must collide with each other

➢The molecules must collide with proper orientation (determined by steric factor)

➢Colliding molecules must possess energy greater than the threshold energy (E).

And when these a colliding with each other it will be having you know collide in a proper orientation that is first important thing. And then it should have enough energy to what to break the bond, so that is basically one as to look it. As I told you what happens during chemical reaction, I must repeat that it is basically existing bonds are there broken, and new bonds are formed and that is the way of life you know like you know old things goes out, and new things coming in then only life will be there otherwise known right. So, similarly for that you need to have enough energy right because, the molecules you know are colliding with each other in random motion.

So, therefore, you know whenever there is a problem, you know it will be something new things would come out of it when there is collision, and it should have a enough energy kind of things. So, but what is the condition of dissociation of bonds because, the bond is broken, if it is a broken then it must have enough energy, and when you talk about this enough energy you know and all, so this as to molecule as to be collided in a proper dire orientation right.

Then it should go a very higher-level and then of course, it comes a this is what to call as I told colliding molecule must have for just higher energy, then the mean energy level otherwise it would not really make in impact. So, what will happen during this reaction, so what will happen this having a reactant little bit colliding, little go to the activated complex kind of a higher energy level, and then it will be drop out and it gets will be product, keep in mind that this diagram have told soon here is meant for a exothermic reaction.

Because, if look at the product is you know energy level is lower than the reactant, and this difference of course, what to call is the heat of reaction. So, the what is the probability you known of this collision being taken place, where there is a successful collision will taken place that will be depend on the you know Boltzmann energy distribution, will state that probability of molecule processing a threshold energy E what we call it as activation energy is proportional to exponential E by R u T right.

So, conditions for chemical reaction to occur what I have already told, I want to repeat that suitable molecular must collide with each other. And the molecule must collide with proper orientation that is determined by a steric factor, and colliding molecular must possess enough energy greater than the threshold value that we call it as a activation energy right.

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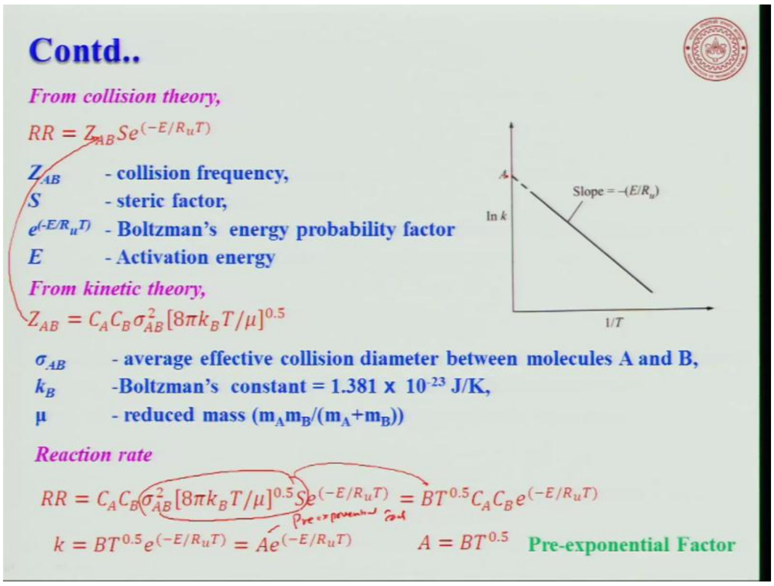

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From collision theory,

$RR = Z_{AB} S e^{(-E/R_u T)}$

Z_{AB} - collision frequency,
S - steric factor,
$e^{(-E/R_u T)}$ - Boltzman's energy probability factor
E - Activation energy

From kinetic theory,

$Z_{AB} = C_A C_B \sigma_{AB}^2 [8\pi k_B T/\mu]^{0.5}$

σ_{AB} - average effective collision diameter between molecules A and B,
k_B -Boltzman's constant = 1.381 x 10^{-23} J/K,
μ - reduced mass ($m_A m_B/(m_A+m_B)$)

Reaction rate

$RR = C_A C_B \sigma_{AB}^2 [8\pi k_B T/\mu]^{0.5} S e^{(-E/R_u T)} = BT^{0.5} C_A C_B e^{(-E/R_u T)}$

Pre exponential fact

$k = BT^{0.5} e^{(-E/R_u T)} = A e^{(-E/R_u T)}$ $A = BT^{0.5}$ **Pre-exponential Factor**

So, from the collision theory we can find out that R reaction rate is basically Z A B S e is a steric factor, and probability is basically e power to the minus capital E R u T, and this is capital E is basically activation energy. And this is of course, Boltzmann energy probability factor, and steric factor, and collision frequency what is the you know frequency with each collision will be taken place. So, from kinetic theory of gases one can get Z A B is basically C A C B sigma A B square, keep in mind that in the collision kinetic theory of gases, you considered as a spear right.

And this sigma A is basically average diameter which will be going, and this diameter will be and diameter of each molecule right. And if you remember that 8 phi k B, k B is basically Boltzmann constant right, and T divided by mu, mu I reduced mass that is m A m B divided by m A plus m B this is a collision theory I am not getting into detail, maybe you can refer some books to get that. And this is a square root of ((Refer Time: 49:21))

So, and if you look at reaction rate comes a C A C B and sigma square A B is basically 8 phi k B by T by mu as if I come and those things because, I will put it over here, and I will get this values. So, and if I club all those things you know this values together right and keeping the temperature out, you known this portion of this I can write down as B T power to the 0.5 C A C B e power to the E by R u T. So, then k if I look at k is basically B T power to the 0.5 e minus E by R u T.

So, if you look at A is basically is known as pre-exponential factor, and which is basically A is equal to B T power to the, so this you know you can put it as a law of mass section or reaction rate you can get. So, if you look at if I plate this l n k with respect to the 1 over T I will get a slope values right, and which is from this if I conduct experiments you know find out this K and other thing I can get what is there you know like activation energy from this slope.

And getting this values whenever it will be 0, you know like when the temperature is very, very is you known high and it will go you will get A value here that is your pre exponential factor, you know you can get that one.

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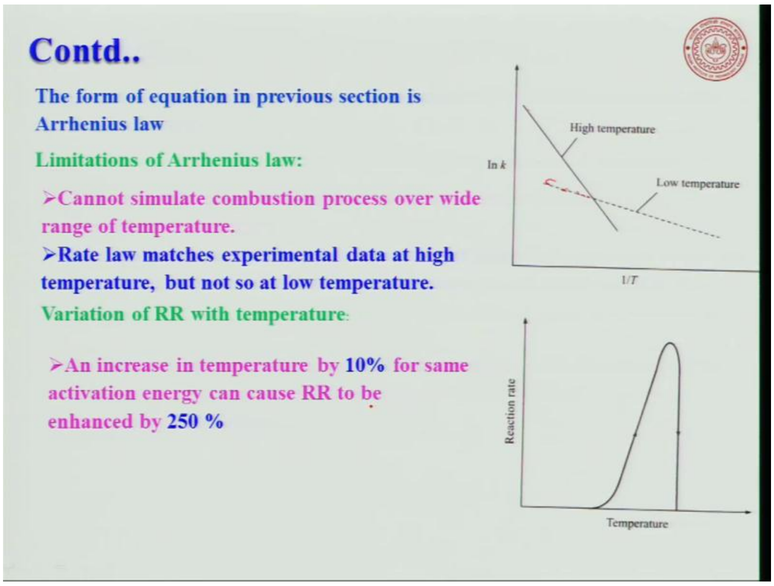

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The form of equation in previous section is Arrhenius law

Limitations of Arrhenius law:

- Cannot simulate combustion process over wide range of temperature.
- Rate law matches experimental data at high temperature, but not so at low temperature.

Variation of RR with temperature

- An increase in temperature by 10% for same activation energy can cause RR to be enhanced by 250 %

So, the form of equation in previous section we can write down, you know like a is known as Arrhenius law right. But, they will be limitations of a Arrhenius it cannot stimulate the combustion process over a wide range of temperature that is the limitation. And the rate law matches experimental data at high temperature of course, it may not match at the low temperature for example, you know this portion it may not match, but; however, it is matching in this portion you know because, this is this curve corresponding to low temperature.

So, therefore, one as to you known take care of that, and keep in mind that variation reaction with the temperature is quite really, you know interesting because, if I go on increasing will see this reaction rate goes up of course, it goes down. Because, the species would not be there to be a reacted, and keep in mind that this is goes by exponential. So, therefore, an increase in temperature by 10 percent for the same activation energy can cause are reaction rate to be enhanced by 250 percent right.

So, this is a very important aspect and one has to worry about this kinetic parts, and I will stop over here. And then we will see in next lecture about the other aspects of this you known multistep chemistry and then look at it.