Advanced Thermodynamics and Combustion
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Module - VI
Chemical Kinetics
Lecture - 23
Fundamentals of Chemical Reactions

Dear learners, greetings from IIT Guwahati. I welcome you to this course Advanced Thermodynamics and Combustions. In this class we will start a new module that is module 6, Chemical Kinetics. The study of chemical kinetics is very vital for combustion analysis. So, basically when the reactants consisting of fuel and air reacts, they produce products. So, in between we are going to discuss what are the different possible reactions that are going to happen.

So, that we get a final product. The other aspect is that what parameters that governs, what mathematical parameters which we can identify and that will clearly tell us in which directions the reaction should proceed. Such parameters are like rate coefficients we are going to introduce in this module.

Apart from that we are also going to discuss different reaction mechanisms. Like unimolecular reaction, bimolecular reaction, tertiary molecular reactions and so on. And these reactions are although we see the final equilibrium products. But in between the reactions, lot of elementary reaction that happens and we normally are not aware of such reactions because our interest lies only in the equilibrium products. So, all those aspects we are going to discuss.

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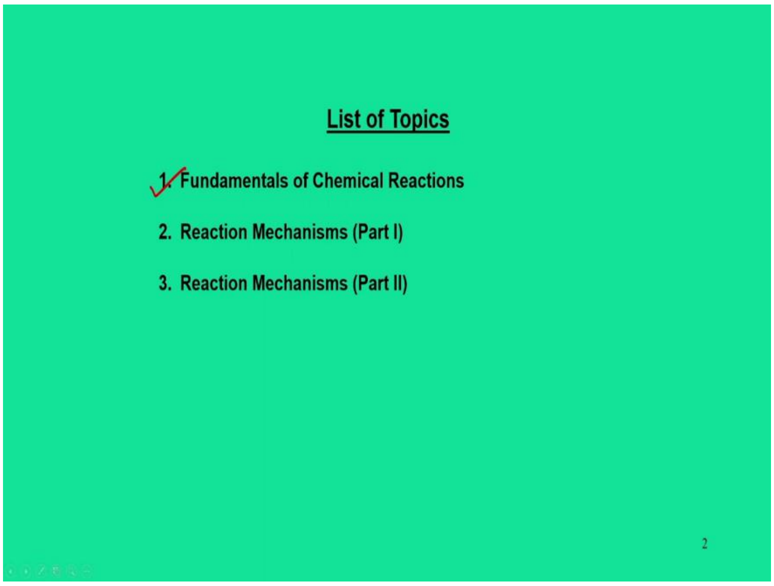

List of Topics

1. Fundamentals of Chemical Reactions
2. Reaction Mechanisms (Part I)
3. Reaction Mechanisms (Part II)

So, this model consists of following topics. In the first lecture that is today we are going to discuss about the Fundamentals of Chemical Reactions. In the next lecture we will discuss about different Reaction Mechanisms.

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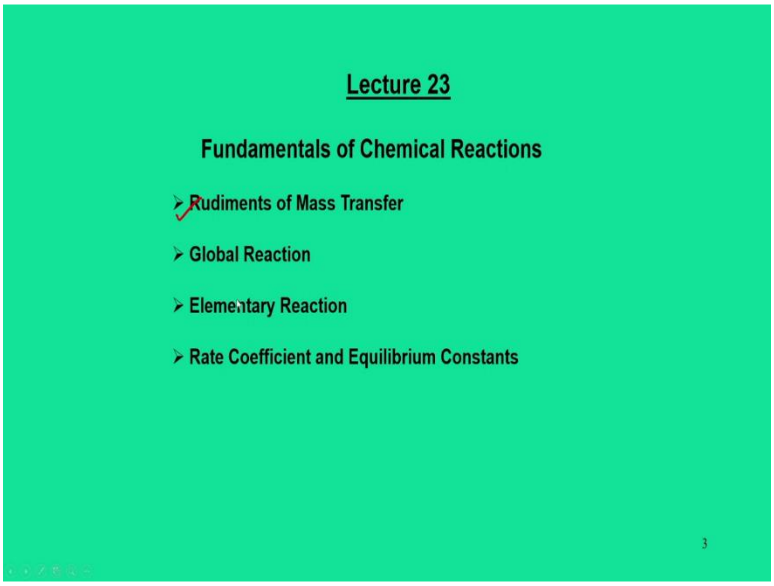

Lecture 23

Fundamentals of Chemical Reactions

- Rudiments of Mass Transfer
- Global Reaction
- Elementary Reaction
- Rate Coefficient and Equilibrium Constants

In the study of fundamental sub chemical reactions that is lecture number 23, we will discuss some elementary topics of mass transfer then we will discuss about global reactions and elementary reactions. These two reactions are very vital to study the parameters that governs the reaction mechanisms.

And such parameters are known as rate coefficient and equilibrium constants. In fact, the dominance of this parameter will decide whether the reaction will proceed in the forward directions or in the backward directions.

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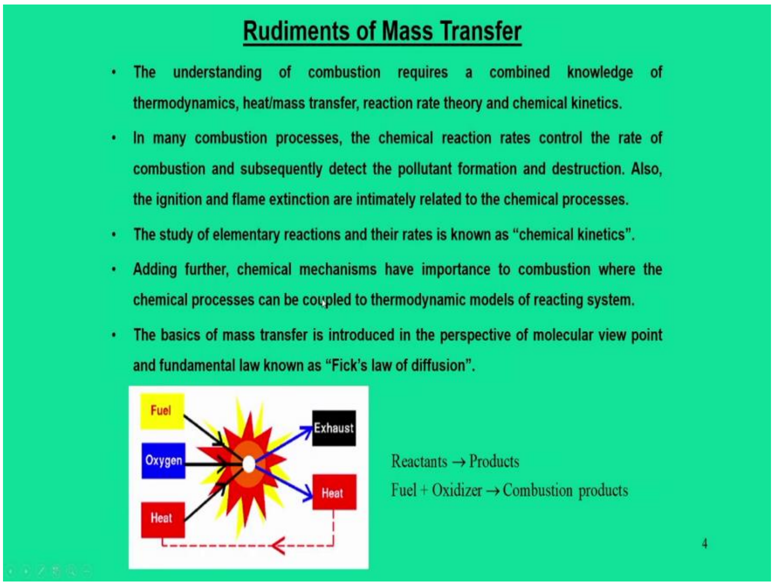

Rudiments of Mass Transfer

- The understanding of combustion requires a combined knowledge of thermodynamics, heat/mass transfer, reaction rate theory and chemical kinetics.
- In many combustion processes, the chemical reaction rates control the rate of combustion and subsequently detect the pollutant formation and destruction. Also, the ignition and flame extinction are intimately related to the chemical processes.
- The study of elementary reactions and their rates is known as "chemical kinetics".
- Adding further, chemical mechanisms have importance to combustion where the chemical processes can be coupled to thermodynamic models of reacting system.
- The basics of mass transfer is introduced in the perspective of molecular view point and fundamental law known as "Fick's law of diffusion".

Reactants → Products

Fuel + Oxidizer → Combustion products

So, let me start the first segment of this today's lecture that is Rudiments of Heat Mass Transfer that is basically the fundamentals of mass transfer. Why this mass transfer is required? Because the study of chemical kinetics is mainly dealt with the concentration gradients and these concentration gradients can be quantified by a law what is called as Fick's law of diffusion.

And this Fick's law of diffusion is nothing but in general it tells us how the diffusion parameters play a vital role in transferring mass from one point to another in a gaseous medium. So, that we call this as a rudiments of mass transfer. So, the mechanism of mass transfer is something similar to heat transfer.

Because the driving potential for heat transfer is normally temperatures because heat flows from high temperature to low temperature. In same sense, when you talk about mass transfer the driving factor is the concentration gradient or change in the concentration. And through this change in the concentrations when there is a transfer of mass.

So, that method we call it as a diffusion. Now to quantify this amount of mass that gets transferred, we require the fundamental law that is Fick's law of diffusion. So, this is all about the rudiments of mass transfers which we are going to discuss. Just to give emphasize the importance of mass transfer. Let me tell that in the combustion system, the reaction rates control the rate of combustions and subsequently detect the pollutant formation and destruction.

So, basically there are two aspects one is the concentration aspect, other is the chemical kinetics aspects. Now this chemical kinetics is governed through some fundamental parameters. Adding further the chemical mechanisms have also importance to combustion where chemical processes can be coupled to thermodynamic models of reacting systems.

So, now, if you want to study this mass transfer. So, the basics of mass transfer is introduced with a molecular view point and with the fundamental law which is known as Fick’s law of diffusion. Now, the this is one aspect other aspect when you deal with the chemical kinetics, when the fuel and oxidizer gives the combustion products ideally, we expect that the reaction should proceed in the forward directions; that means, fuel and oxidizer must react to produce to the combustion products.

And that we see as a end results, but in between when the fuel and oxidizer they form the combustion products, this does not happen in a single go. So, there are sequential processes or sequential events in which the fuel and oxidizer reacts; that means, there is a formation of intermediate species, intermediate molecules and these intermediate molecules can have other reactions which you have not seen in the global reactions.

But they can have either direction, either in the forward directions or reverse direction. But globally what you see that fuel and oxygen when it mixes, we get heat out of it and as a result we get the combustion products in the form of exhaust.

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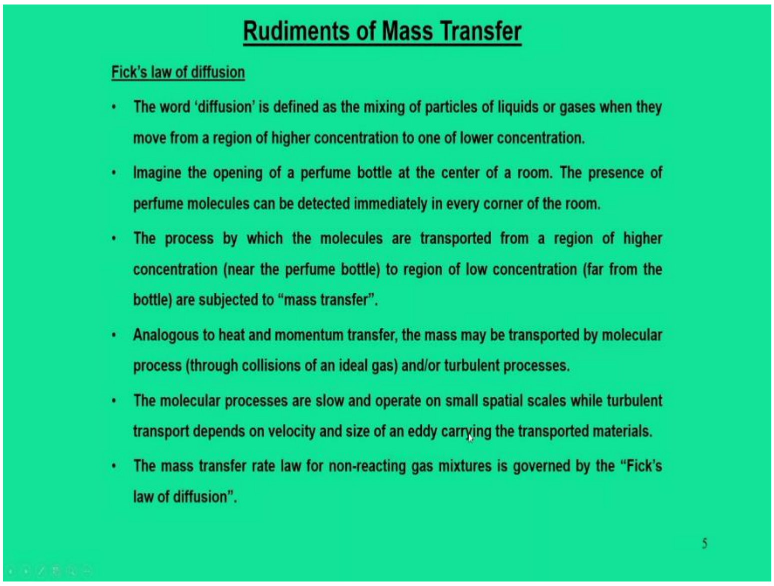

Rudiments of Mass Transfer

Fick's law of diffusion

- The word 'diffusion' is defined as the mixing of particles of liquids or gases when they move from a region of higher concentration to one of lower concentration.
- Imagine the opening of a perfume bottle at the center of a room. The presence of perfume molecules can be detected immediately in every corner of the room.
- The process by which the molecules are transported from a region of higher concentration (near the perfume bottle) to region of low concentration (far from the bottle) are subjected to "mass transfer".
- Analogous to heat and momentum transfer, the mass may be transported by molecular process (through collisions of an ideal gas) and/or turbulent processes.
- The molecular processes are slow and operate on small spatial scales while turbulent transport depends on velocity and size of an eddy carrying the transported materials.
- The mass transfer rate law for non-reacting gas mixtures is governed by the "Fick's law of diffusion".

Before you discuss all those aspects, let me discuss about the Fick's law of diffusion. So, the word diffusion is defined as the mixing of particles and that is liquids or gases when they move from one region of higher concentration to other region of lower concentrations.

So, in our day-to-day life this we can realize that when a perfume bottle is opened in a room. So, its smell spreads everywhere in the room. So, basically what happens is that concentration in the vicinity of perfume bottle is higher and the concentration at other parts of the room is less. And by virtue of this concentration difference, there is a transfer of mass and this process is known as diffusion process.

So, analogous to heat and momentum transfer the mass also may be transferred and this diffusion process is a molecular phenomenon. And in fact, we can enhance this diffusion process by the turbulent mechanisms or mixing. So, for example, when the perfume bottle is opened and if there is a fan running in the room, then the chances of mass transfer or the spreading of mass transfer gets enhanced.

So, this is accelerated mainly due to the turbulence or mixing of the molecular gases and in fact many a times this is modeled through the collision processes. Normally the molecular processes are slow and basically this is analogous to heat and mass transfer.

But this process is a very slow process and operate in a very small spatial scales whereas, turbulent transport properties they are related with respect to velocity and the size of the system. The mass transfer rate law for non-reacting gases is generally governed by the Fick's law of diffusion.

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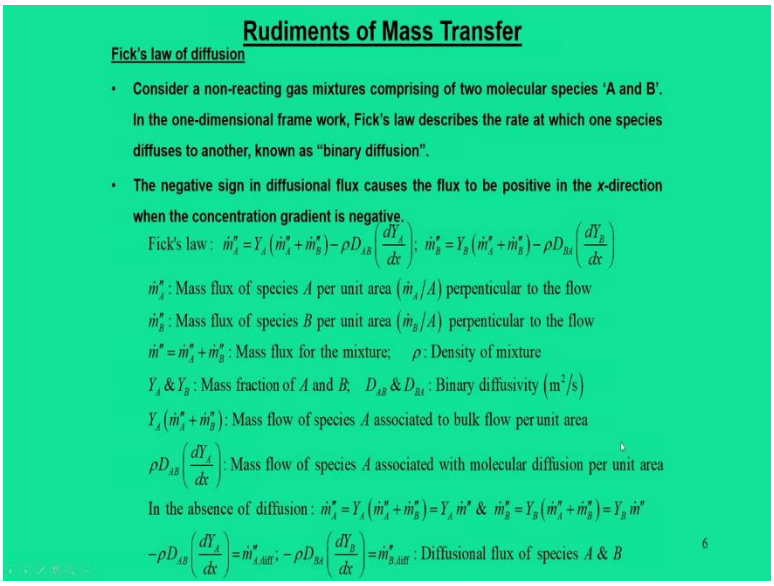

Rudiments of Mass Transfer

Fick's law of diffusion

- Consider a non-reacting gas mixtures comprising of two molecular species 'A and B'. In the one-dimensional frame work, Fick's law describes the rate at which one species diffuses to another, known as "binary diffusion".
- The negative sign in diffusional flux causes the flux to be positive in the *x*-direction when the concentration gradient is negative.

Fick's law: $\dot{m}''_A = Y_A\left(\dot{m}''_A + \dot{m}''_B\right) - \rho D_{AB}\left(\frac{dY_A}{dx}\right)$; $\dot{m}''_B = Y_B\left(\dot{m}''_A + \dot{m}''_B\right) - \rho D_{BA}\left(\frac{dY_B}{dx}\right)$

$\dot{m}''_A$: Mass flux of species A per unit area $\left(\dot{m}_A/A\right)$ perpenticular to the flow

$\dot{m}''_B$: Mass flux of species B per unit area $\left(\dot{m}_B/A\right)$ perpenticular to the flow

$\dot{m}'' = \dot{m}''_A + \dot{m}''_B$: Mass flux for the mixture; ρ : Density of mixture

Y_A & Y_B : Mass fraction of A and B; D_{AB} & D_{BA} : Binary diffusivity $\left(\mathrm{m^2/s}\right)$

$Y_A\left(\dot{m}''_A + \dot{m}''_B\right)$: Mass flow of species A associated to bulk flow per unit area

$\rho D_{AB}\left(\frac{dY_A}{dx}\right)$: Mass flow of species A associated with molecular diffusion per unit area

In the absence of diffusion: $\dot{m}''_A = Y_A\left(\dot{m}''_A + \dot{m}''_B\right) = Y_A\dot{m}''$ & $\dot{m}''_B = Y_B\left(\dot{m}''_A + \dot{m}''_B\right) = Y_B\dot{m}''$

$-\rho D_{AB}\left(\frac{dY_A}{dx}\right) = \dot{m}''_{A,\mathrm{diff}}$; $-\rho D_{BA}\left(\frac{dY_B}{dx}\right) = \dot{m}''_{B,\mathrm{diff}}$: Diffusional flux of species A & B

So, mathematically how do you quantify this Fick's law of diffusions? So, consider a non-reacting gas mixtures that comprises of at least two molecules molecular species A and B. So, basically when we say diffusion process, we try to say that rate at which one species diffuses in the other. So, for example, perfume bottle is opened in a room and before it is opened, air is the content that can be considered as one of the gasses.

But when the perfume bottle opens, the species or the concentration or the gas or whatever contents is there that can be considered as another gas or liquid and when it spreads. So, basically perfume diffuses into air and that term we call this as a binary diffusion because there are only two species.

And in fact, there are multiple species, if there are three species A B C. So, the species A can diffuse in species B at certain rate, species A can diffuse in species C in certain rate. So, the diffusion coefficient normally decides what rate it will diffuse into other. And this term we define is as a binary diffusion.

Now let us say through this diffusion process how much mass is going to diffuse into other. Now if you look at this Fick's law it says that mass flux of species A per unit area which is perpendicular to the flow consists of two parts one is $Y_A(\dot{m}''_A + \dot{m}''_B)$.

$$\dot{m}_A'' = Y_A(\dot{m}_A'' + \dot{m}_B'') - \rho D_{AB}\left(\frac{dY_A}{dx}\right)$$

So, which will give you the mass flow of species A associated to bulk flow per unit area. The other is minus. Negative sign tells that diffusion has to start from higher concentration to lower concentration.

And that part you call this as a mass flow of species A associated with molecular diffusion per unit area. That is by Fick's law that you do the mass balance and there are two parts one part we call this as flow of species A associated to the bulk flow, other part is the mass flow of species A associated with the molecular diffusion.

Now, similarly one can find out the mass flux species B as well. $\dot{m}_B'' = Y_B(\dot{m}_A'' + \dot{m}_B'') - \rho D_{BA}\left(\frac{dY_B}{dx}\right)$. So, diffusion coefficients will be just reverse that is D_{BA}. So, binary diffusion coefficient will be represented by D_{BA}. So, BA stands for species B diffuses into species A and here also you have to take the mole fraction for species B.

Now, if this is your mass balance. So, if there is no diffusion, the second component will be 0 and in the absence of diffusions, we have the mass balance and the presence of diffusions we come across with two fluxes and these fluxes are called diffusion fluxes. So, diffusion fluxes $\dot{m}_{A,diff}'' = -\rho D_{AB}\left(\frac{dY_A}{dx}\right)$. Similarly, $\dot{m}_{B,diff}'' = -\rho D_{BA}\left(\frac{dY_B}{dx}\right)$.

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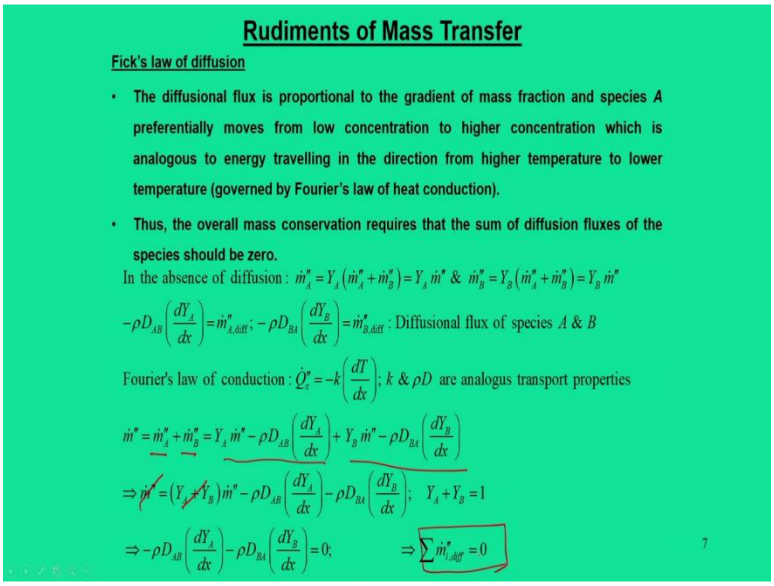

Rudiments of Mass Transfer

Fick's law of diffusion

- The diffusional flux is proportional to the gradient of mass fraction and species *A* preferentially moves from low concentration to higher concentration which is analogous to energy travelling in the direction from higher temperature to lower temperature (governed by Fourier's law of heat conduction).
- Thus, the overall mass conservation requires that the sum of diffusion fluxes of the species should be zero.

In the absence of diffusion : $\dot{m}_A'' = Y_A\left(\dot{m}_A'' + \dot{m}_B''\right) = Y_A\dot{m}''$ & $\dot{m}_B'' = Y_B\left(\dot{m}_A'' + \dot{m}_B''\right) = Y_B\dot{m}''$

$-\rho D_{AB}\left(\frac{dY_A}{dx}\right) = \dot{m}_{A,\text{diff}}''$; $-\rho D_{BA}\left(\frac{dY_B}{dx}\right) = \dot{m}_{B,\text{diff}}''$: Diffusional flux of species *A* & *B*

Fourier's law of conduction : $\dot{Q}_x'' = -k\left(\frac{dT}{dx}\right)$; k & ρD are analogus transport properties

$$\dot{m}'' = \underline{\dot{m}_A''} + \underline{\dot{m}_B''} = \underline{Y_A\dot{m}'' - \rho D_{AB}\left(\frac{dY_A}{dx}\right)} + \underline{Y_B\dot{m}'' - \rho D_{BA}\left(\frac{dY_B}{dx}\right)}$$

$$\Rightarrow \cancel{\dot{m}''} = \left(\cancel{Y_A + Y_B}\right)\dot{m}'' - \rho D_{AB}\left(\frac{dY_A}{dx}\right) - \rho D_{BA}\left(\frac{dY_B}{dx}\right); \quad Y_A + Y_B = 1$$

$$\Rightarrow -\rho D_{AB}\left(\frac{dY_A}{dx}\right) - \rho D_{BA}\left(\frac{dY_B}{dx}\right) = 0; \qquad \Rightarrow \boxed{\sum \dot{m}_{i,\text{diff}}'' = 0}$$

Now, a close look between these two we can say that if you only consider the diffusion fluxes. And side by side we consider the Fourier law. We can say there is a strong resemblance between the heat transfer and the mass transfer through this diffusion process.

And the analogous $\frac{dY_A}{dx}$ is nothing but the concentration gradient and whereas, in the Fourier law $\frac{dT}{dx}$ refers to the temperature gradient. And the analogous term that is ρD_{AB} basically it is for mass transfer and for Fourier law it is the thermal conductivity, they have closely resemblance and they are treated to be transfer properties.

Because it transfers the information of the parameters in a medium. Now when you do the closed loop; that means, if you make a total mass balance for A species A and species B then we can sum it the together. And by summing it, and rearranging the term we can say that $Y_A + Y_B = 1$ that is mole fraction of A and B that is 1 by the fundamental law.

So, if this is case and this term will get cancelled and ultimately what we get is $-\rho D_{AB}\left(\frac{dY_A}{dx}\right) - \rho D_{BA}\left(\frac{dY_B}{dx}\right) = 0$. So, in other words we write a simplified expression the summation of all diffusion fluxes must be 0; $\sum \dot{m}''_{i,diff} = 0$. So, the mass transfer analysis says that the overall mass conservations require the sum of diffusion fluxes should be equal to 0. So, this we call as a fundamental law and which is governed through Fourier law of diffusions.

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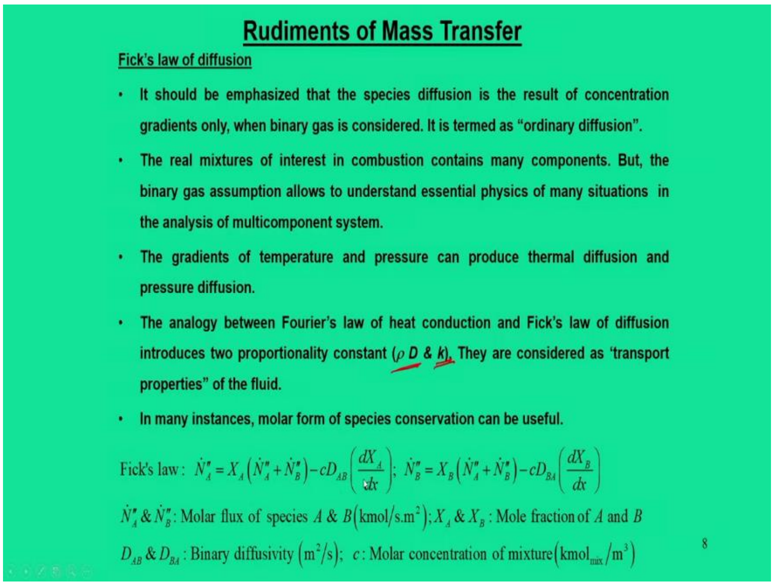

Rudiments of Mass Transfer

Fick's law of diffusion

- It should be emphasized that the species diffusion is the result of concentration gradients only, when binary gas is considered. It is termed as "ordinary diffusion".
- The real mixtures of interest in combustion contains many components. But, the binary gas assumption allows to understand essential physics of many situations in the analysis of multicomponent system.
- The gradients of temperature and pressure can produce thermal diffusion and pressure diffusion.
- The analogy between Fourier's law of heat conduction and Fick's law of diffusion introduces two proportionality constant (ρD & k). They are considered as 'transport properties" of the fluid.
- In many instances, molar form of species conservation can be useful.

Fick's law: $\dot{N}''_A = X_A\left(\dot{N}''_A + \dot{N}''_B\right) - cD_{AB}\left(\frac{dX_A}{dx}\right)$; $\dot{N}''_B = X_B\left(\dot{N}''_A + \dot{N}''_B\right) - cD_{BA}\left(\frac{dX_B}{dx}\right)$

$\dot{N}''_A$ & $\dot{N}''_B$: Molar flux of species A & $B\left(\text{kmol/s.m}^2\right)$; X_A & X_B : Mole fraction of A and B

D_{AB} & D_{BA} : Binary diffusivity $\left(\text{m}^2/\text{s}\right)$; c : Molar concentration of mixture $\left(\text{kmol}_{\text{mix}}/\text{m}^3\right)$

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Now, some of the important information that can be derived here that whatever you discussed so far, it should be emphasized that the species diffusion is the result of concentration gradient only when the binary diffusion is considered and this is called as ordinary diffusion.

But the real mixtures of interest in a combustion contains many components and but entire flow physics or entire physics is mainly governed through the concept of binary gas assumptions. May be in a sense that similar concepts can be extended when we have a multi component systems.

The gradients of temperature and pressure can produce thermal diffusion and pressure diffusion and one can find the analogy between the Fourier law of heat conduction and Fick's law of diffusion. Through this proportionality constant that is ρD from the Fick's law and k thermal conductivity for Fourier law and they are treated as a transport properties.

So, prior to this you must have aware of thermodynamic properties, fluid properties and now through this mass transfer study and heat transfer two properties were introduced that is called as transport properties. So, all that we have discussed today discussed far is the Fick's law of diffusions and there many a times we also express this Fick's law in terms of molar concentrations.

So, basically mass is shifted to number of moles and accordingly c is introduced. So, we say molar concentration of the mixtures. So, unit of mass was kg per meters cube here we will call it as a kilo mole of the mixture per meter cube. So, similar expressions can be also found out.

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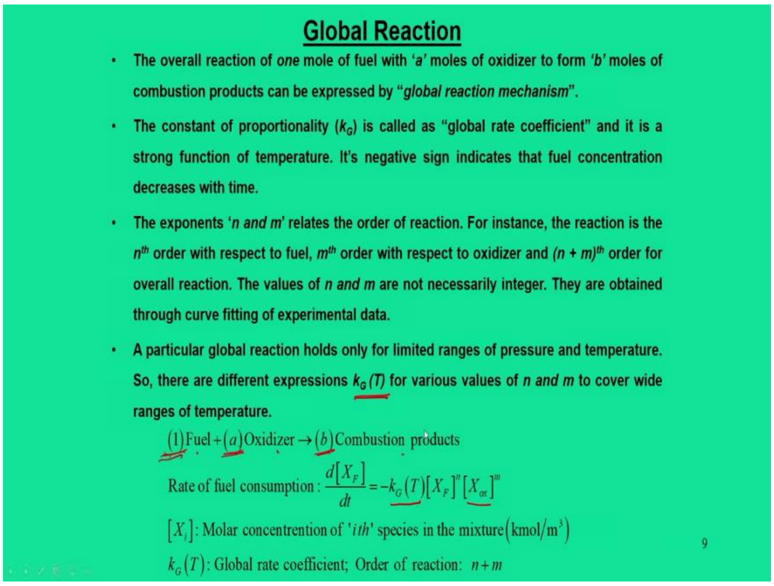

Global Reaction

- The overall reaction of *one* mole of fuel with '*a*' moles of oxidizer to form '*b*' moles of combustion products can be expressed by "*global reaction mechanism*".
- The constant of proportionality (k_G) is called as "global rate coefficient" and it is a strong function of temperature. It's negative sign indicates that fuel concentration decreases with time.
- The exponents '*n and m*' relates the order of reaction. For instance, the reaction is the n^{th} order with respect to fuel, m^{th} order with respect to oxidizer and $(n + m)^{th}$ order for overall reaction. The values of *n and m* are not necessarily integer. They are obtained through curve fitting of experimental data.
- A particular global reaction holds only for limited ranges of pressure and temperature. So, there are different expressions $\underline{k_G(T)}$ for various values of *n and m* to cover wide ranges of temperature.

$$\underline{(1)}\text{Fuel}+\underline{(a)}\text{Oxidizer}\rightarrow\underline{(b)}\text{Combustion products}$$

$$\text{Rate of fuel consumption}: \frac{d[X_F]}{dt}=-\underline{k_G(T)}[X_F]^n\underline{[X_{ox}]}^m$$

$[X_i]$: Molar concentrention of 'ith' species in the mixture$\left(\text{kmol/m}^3\right)$

$k_G(T)$: Global rate coefficient; Order of reaction: $n+m$

The next segment that we are going to discuss is the global reactions. So, the overall reaction of one mole of fuel with a mole of oxidizer to form b mole of combustion products is expressed by global reaction mechanisms.

So, if you look at here, we have fuel plus oxidizer gives combustion products, to quantify this and all the entire analysis is governed per one mole of fuel. When we say one mole of fuel, we need to find out the corresponding requirement for oxidizer and corresponding formation of the combustion products.

So, here it is a and it is b. And here when the reaction proceeds, we can define how the concentration of the fuel varies; that means, mainly for fuel that is called as X_F. Now when the reaction proceeds; that means, fuel burns out and the concentration of combustion product goes up; that means, we can say rate of fuel consumptions for this reaction can be expressed by this equations and that equation is called as a global reaction equations.

And this equation is in the form of $-k_G(T)[X_F]^n[X_{ox}]^m$. So, basically n and m are nothing but the stoichiometric coefficients and this m plus n will be defined as the order of reactions.

So, exponent m and n relates the order of reaction. For instance, the reaction of nth order of the fuel with respect to mth order of oxidizer will have m plus nth order of overall reactions.

The values of m and a n are not necessarily integers and they are obtained through power fitting techniques and this global reaction is mainly expressed by the parameter which is called as global rate coefficient $k_G(T)$. Finding this rate coefficient is very vital to know the reaction or chemical kinetics of overall systems.

Now, when fuel and oxidizer gives the combustion product we really do not know what happens in between. So, effectively if you want to study the physics of formation of this combustion product, it is essentially the collision of molecular collision among the fuel and oxidizer particles and through this collision process, there are many intermediate species that are formed. And once they get settled down, we get this combustion products.

But we are not really worried about what are those intermediate products. So, many a times the overall reaction does not give the entire information, what happens within the reaction period? What are the intermediate species that are formed? Whether there is really a collision or not?

So, there may be some species which are not seen in the global form, but they may have their presence during that intermediate species reactions and not in the global reactions. So, such things has to be analyzed to study and to study this particular parameter which is called as rate coefficient. And this rate coefficient is essentially determined by those individual reaction mechanisms.

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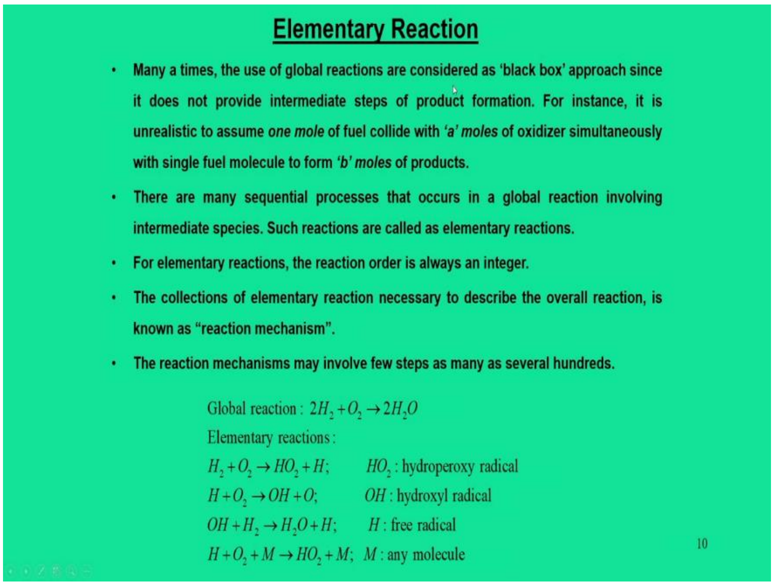

Elementary Reaction

- **Many a times, the use of global reactions are considered as 'black box' approach since it does not provide intermediate steps of product formation. For instance, it is unrealistic to assume *one mole* of fuel collide with *'a' moles* of oxidizer simultaneously with single fuel molecule to form *'b' moles* of products.**
- **There are many sequential processes that occurs in a global reaction involving intermediate species. Such reactions are called as elementary reactions.**
- **For elementary reactions, the reaction order is always an integer.**
- **The collections of elementary reaction necessary to describe the overall reaction, is known as "reaction mechanism".**
- **The reaction mechanisms may involve few steps as many as several hundreds.**

Global reaction : $2H_2 + O_2 \rightarrow 2H_2O$

Elementary reactions :

$H_2 + O_2 \rightarrow HO_2 + H$; HO_2 : hydroperoxy radical

$H + O_2 \rightarrow OH + O$; OH : hydroxyl radical

$OH + H_2 \rightarrow H_2O + H$; H : free radical

$H + O_2 + M \rightarrow HO_2 + M$; M : any molecule

So, for that reasons we have to study Elementary Reactions. So, many a times the use of global reactions are considered as a black box approach because they do not provide the intermediate steps or the product formations. For example, it is a very unrealistic to assume that one mole of fuel collides with one mole of oxidizer simultaneously with single fuel to form b moles of products.

So, this is very unrealistic. So, a possible approach to thought is that there are many sequential processes that occurs in a global reactions which involves many intermediate species and these reactions are called elementary reactions. And for elementary reactions the reaction order is always an integer.

So, this is another point that need to be emphasized that when you take m and n for global reactions, they need not be an integer. But when you study the elementary reactions which essentially form this final global reaction, reaction order is always an integer. And the collection of all such elementary reactions are necessary to describe the overall reaction and known as reaction mechanisms.

So, our study is mainly focused on the kinetic parts and this reaction mechanism parts. We will study those things in this model. The reaction mechanisms may involve a few steps, there may be hundreds of elementary reactions, but a single global reactions.

For example, if you say that mixing of hydrogen and oxygen to form water, we can write the global reactions can be $2H_2 + O_2 \rightarrow 2H_2O$. But while doing so we are not really bothered that during this formation process what other elementary reactions would have occurred and they are normally do not show up their face in the global reactions.

So, such elementary reactions for this could be $H_2 + O_2 \rightarrow HO_2 + H$. And $H + O_2 \rightarrow OH + O$. And again $OH + H_2 \rightarrow H_2O + H$.

H_2O does not take part in any of the reactions, but H and O_2 plus there may be any other molecule or intermediate species that may have formed. So, and these are called as elementary reactions.

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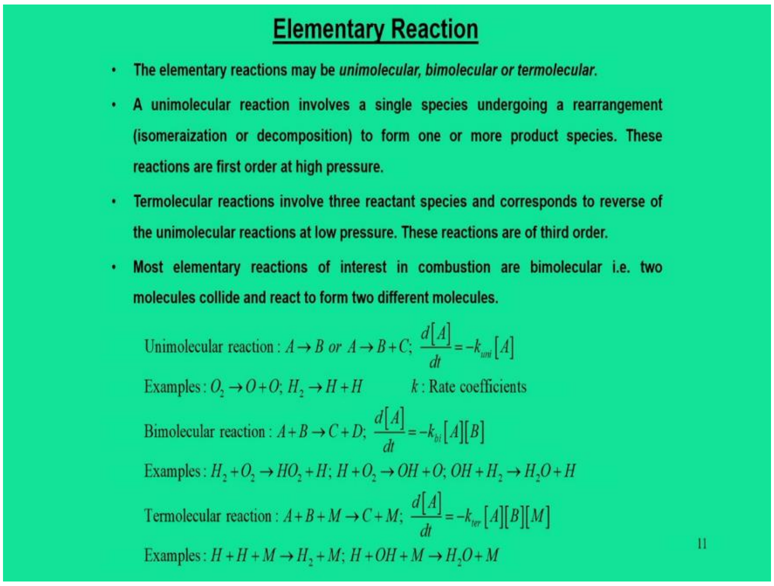

Elementary Reaction

- The elementary reactions may be *unimolecular, bimolecular or termolecular.*
- A unimolecular reaction involves a single species undergoing a rearrangement (isomeraization or decomposition) to form one or more product species. These reactions are first order at high pressure.
- Termolecular reactions involve three reactant species and corresponds to reverse of the unimolecular reactions at low pressure. These reactions are of third order.
- Most elementary reactions of interest in combustion are bimolecular i.e. two molecules collide and react to form two different molecules.

Unimolecular reaction : $A \rightarrow B \; or \; A \rightarrow B + C; \; \frac{d[A]}{dt} = -k_{uni}[A]$

Examples : $O_2 \rightarrow O + O; \; H_2 \rightarrow H + H$ k : Rate coefficients

Bimolecular reaction : $A + B \rightarrow C + D; \; \frac{d[A]}{dt} = -k_{bi}[A][B]$

Examples : $H_2 + O_2 \rightarrow HO_2 + H; \; H + O_2 \rightarrow OH + O; \; OH + H_2 \rightarrow H_2O + H$

Termolecular reaction : $A + B + M \rightarrow C + M; \; \frac{d[A]}{dt} = -k_{ter}[A][B][M]$

Examples : $H + H + M \rightarrow H_2 + M; \; H + OH + M \rightarrow H_2O + M$

So, in this case there are only four to five elementary reactions for a given one global reactions, but there are certain situations that may be hundreds of elementary reactions for one global reactions. Now looking at the elementary reactions they can be unimolecular, bimolecular, tertiary molecular or simply term molecular is used. So, unimolecular reaction involves single species undergoing a rearrangement.

So, this word rearrangement is like chemical structure changes or decompositions and this structural changes we call as isomerization or decompositions and so that they form products and these are reactions of first order at high pressures. So, a unimolecular reaction can be considered that $A \rightarrow BorA \rightarrow B + C$ and its rate coefficient is treated as k_{uni} that is rate coefficient for unimolecular reactions.

$O_2 \rightarrow O + O;$ it is a unimolecular reactions. And the other last one is termolecular reactions where there are three reactant species and that corresponds to reverse of unimolecular reactions; that means, if I say the reverse of unimolecular reactions two or more species $A + B + M \rightarrow C + M.$

So, this is something like a reverse of unimolecular reaction, but except there is a part that is intermediate molecule M which is comes into picture when we have termolecular reactions and these reactions are of third order. However, there is another reaction what we call as bimolecular reactions.

In fact, most elementary reaction of interest what we have used in the combustions they are bimolecular in nature. And that is two molecules collide and react to form different molecules. So, $A + B \rightarrow C + D$. So, accordingly rate coefficients are defined as $\frac{d[A]}{dt} = -k_{bi}[A][B]$. Typical example could be $H_2 + O_2 \rightarrow HO_2 + H; H + O_2 \rightarrow OH + O$.

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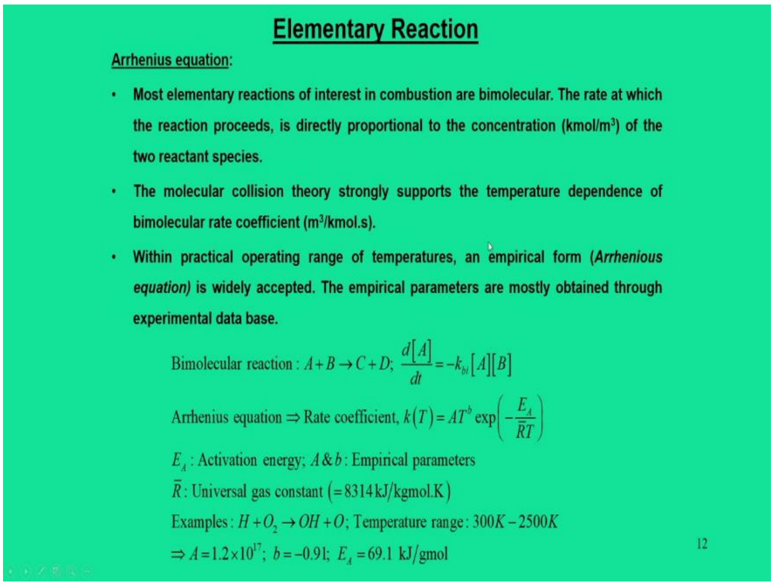

Elementary Reaction

Arrhenius equation:

- **Most elementary reactions of interest in combustion are bimolecular. The rate at which the reaction proceeds, is directly proportional to the concentration (kmol/m³) of the two reactant species.**
- **The molecular collision theory strongly supports the temperature dependence of bimolecular rate coefficient (m³/kmol.s).**
- **Within practical operating range of temperatures, an empirical form (*Arrhenious equation)* is widely accepted. The empirical parameters are mostly obtained through experimental data base.**

Bimolecular reaction : $A + B \rightarrow C + D;\ \frac{d[A]}{dt} = -k_{bi}[A][B]$

Arrhenius equation $\Rightarrow$ Rate coefficient, $k(T) = AT^b \exp\left(-\frac{E_A}{\bar{R}T}\right)$

E_A : Activation energy; $A \,\&\, b$: Empirical parameters

$\bar{R}$: Universal gas constant $(=8314\,\text{kJ/kgmol.K})$

Examples : $H + O_2 \rightarrow OH + O$; Temperature range : $300K - 2500K$

$\Rightarrow A = 1.2 \times 10^{17};\ b = -0.91;\ E_A = 69.1\ \text{kJ/gmol}$

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Now, once you know this unimolecular, bimolecular and termolecular reactions and we have said that most of the reactions are bimolecular. Now how to quantify this rate coefficients? There are many techniques that are involved through experimental measurements.

And in particular when you deal with bimolecular reaction and that too in the combustion process one of the important empirical form of equation that is essentially governs and in fact, it is simple and becomes highly useful that is called as Arrhenius equations.

Arrhenius is the name of the scientist; he formulated one empirical equation that essentially governs almost all bimolecular reactions and this will help you to calculate the rate coefficients. And in fact, typically if you find this rate coefficient reactions people use molecular collision theory or kinetic theory of gases to find the rate coefficients.

But that becomes a very critical part or maybe not scope of this course rather we will focus on the calculating the rate coefficient through Arrhenius form of equation. So, what it says is that $A + B \rightarrow C + D$ and we write concentration $\frac{d[A]}{dt} = -k_{bi}[A][B]$. Because A and B order for this reaction order is two and this stoichiometric coefficient are also one and one.

And what it says is that you define this rate coefficient in a functional form and he claimed that this rate coefficient is mainly a function of temperatures and that is expressed as $k(T) = AT^b \exp\left(-\frac{E_A}{\bar{R}T}\right)$. So, T the temperature is known, A and b are some empirical parameters and he introduced E_A which is called as activation energy and of course, we know $\bar{R}$ is the universal gas constant. So, for example, $H + O_2 \rightarrow OH + O$.

If you use this Arrhenius equations in the temperature range for 300-2500 K, we can find out that $A = 1.2 \times 10^{17}; b = -0.91; E_A = 69.1\frac{\text{kJ}}{\text{gmol}}$. So, this is one example when data will be given, temperature is known to us and activation energy one can find out. Activation energy also can be found out from the tabular data.

So, the strong advantage for this fact is that we can easily get the rate coefficient through this empirical form. And here we have to use this rate coefficient in a with a unit meter cube per kilo mole into second or gram mole into second.

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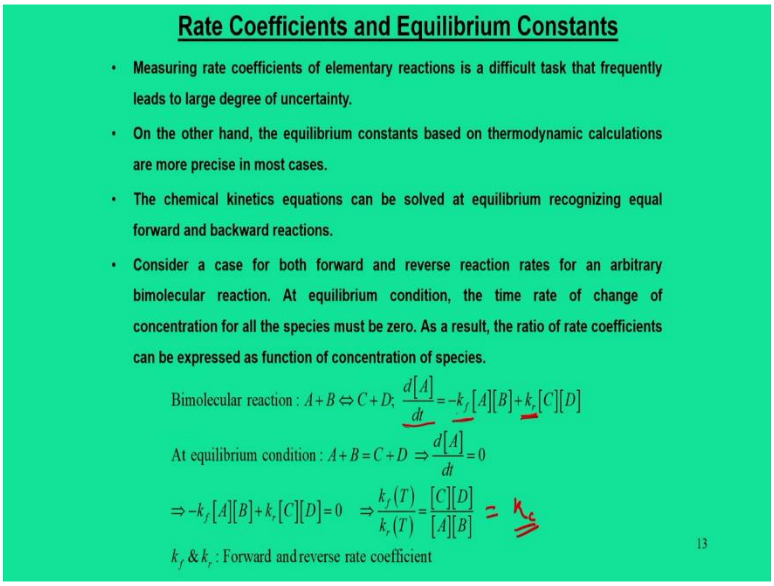

Rate Coefficients and Equilibrium Constants

- Measuring rate coefficients of elementary reactions is a difficult task that frequently leads to large degree of uncertainty.
- On the other hand, the equilibrium constants based on thermodynamic calculations are more precise in most cases.
- The chemical kinetics equations can be solved at equilibrium recognizing equal forward and backward reactions.
- Consider a case for both forward and reverse reaction rates for an arbitrary bimolecular reaction. At equilibrium condition, the time rate of change of concentration for all the species must be zero. As a result, the ratio of rate coefficients can be expressed as function of concentration of species.

Bimolecular reaction : $A+B \Leftrightarrow C+D;\ \underline{\frac{d[A]}{dt}} = \underline{-k_f}[A][B]+\underline{k_r}[C][D]$

At equilibrium condition : $A+B=C+D \Rightarrow \frac{d[A]}{dt}=0$

$\Rightarrow -k_f[A][B]+k_r[C][D]=0 \quad \Rightarrow \frac{k_f(T)}{k_r(T)}=\frac{[C][D]}{[A][B]} = \underline{\underline{K_c}}$

$k_f \,\&\, k_r$: Forward and reverse rate coefficient

Now, next component that we are going to discuss is the comparison between rate coefficient and equilibrium constant. So, prior to this we have introduced the term equilibrium constant in our previous model and here we introduce the term rate coefficients.

So, let us see what is the resemblance between these two parameters. So, as you have emphasized that measuring rate coefficients of elementary reaction is a very difficult task and it gives lot of uncertainty. So, one way is to find out the equilibrium constants. So, people used to find equilibrium constant like we did whether the mixture is lean or rich through this equilibrium constant.

Because they are thermodynamic estimates and more precise in many cases. Because it is very easy to measure the concentration of species or molar mass or actual mass of the species. So, by knowing this and if there is a link between the equilibrium constant and rate coefficient. By doing so, we find there is a definite link and that will take as an advantage to correlate these two parameters. So, that is the essential feature of this chemical kinetics. So, this chemical kinetics equations can be solved at equilibrium recognizing equal forward and backward reactions.

Now to do that we consider a case for a forward and reverse reactions in an arbitrary bimolecular situation. We say $A + B \Leftrightarrow C + D$ and you can imagine that reaction can proceed as well forward direction and backward directions. Like this again happens in many biomolecular reactions, concentration of one is a dominance term sometimes concentration of a C is dominant.

So, the reaction can proceed in either direction. To justify this fact, we have to find out in what way the reaction should proceed. So, for example, like formation of water, we have seen that many intermediate species are formed. Now when they form whether those reactions can be in a forward direction or backward directions that is governed through the rate coefficients.

So, for that what you introduce is that while calculating concentration of A with respect to t, if the reaction has to happen in a forward directions, we say it is a forward rate coefficient k_f and that is negative. Now, when the reaction has to do in the backward directions the concentration of C and D becomes dominance. So, we define this rate coefficient as k_r and it has to be positive. So, at equilibrium both concentration is 0. So, when you look at the equilibrium concentration both equal to 0.

So, what we can say that ratio of forward rate coefficient and reverse rate coefficient which is a function of concentrations number, this concentration numbers can be easily measured, $\frac{k_f(T)}{k_r(T)} = \frac{[C][D]}{[A][B]}$. And that number we have already told that that is K_c or we say equilibrium constant based on concentration.

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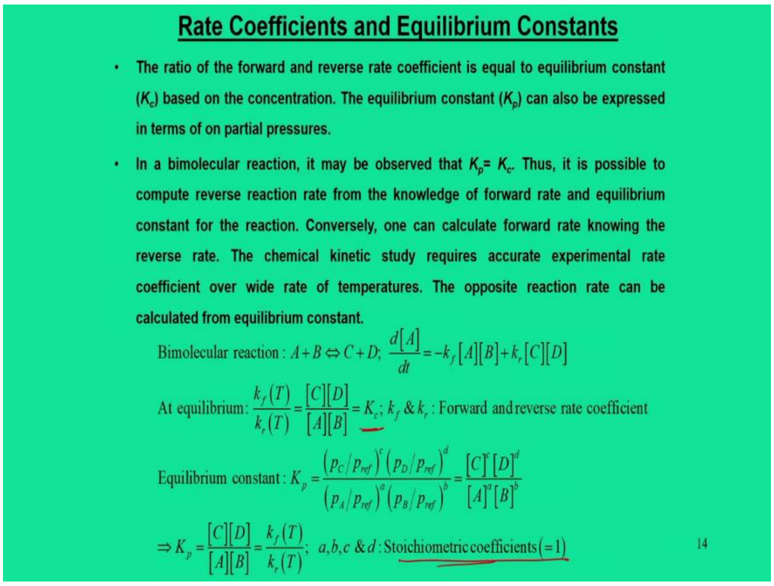

Rate Coefficients and Equilibrium Constants

- The ratio of the forward and reverse rate coefficient is equal to equilibrium constant (K_c) based on the concentration. The equilibrium constant (K_p) can also be expressed in terms of on partial pressures.
- In a bimolecular reaction, it may be observed that $K_p = K_c$. Thus, it is possible to compute reverse reaction rate from the knowledge of forward rate and equilibrium constant for the reaction. Conversely, one can calculate forward rate knowing the reverse rate. The chemical kinetic study requires accurate experimental rate coefficient over wide rate of temperatures. The opposite reaction rate can be calculated from equilibrium constant.

$$\text{Bimolecular reaction}: A+B \Leftrightarrow C+D;\ \frac{d[A]}{dt} = -k_f[A][B] + k_r[C][D]$$

$$\text{At equilibrium}: \frac{k_f(T)}{k_r(T)} = \frac{[C][D]}{[A][B]} = \underline{K_c};\ k_f \,\&\, k_r: \text{Forward and reverse rate coefficient}$$

$$\text{Equilibrium constant}: K_p = \frac{(p_C/p_{ref})^c (p_D/p_{ref})^d}{(p_A/p_{ref})^a (p_B/p_{ref})^b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$\Rightarrow K_p = \frac{[C][D]}{[A][B]} = \frac{k_f(T)}{k_r(T)};\ a,b,c \,\&\, d: \underline{\text{Stoichiometric coefficients}(=1)}$$

Now, same expression we look at in a different way. So, we say Kc is your equilibrium concentration and. But when you define this equilibrium constant Kp, it is expressed in the form of partial pressure. So, equilibrium constant, one way we find the concentration other way we find this in terms of its partial pressure for each species concentrations; for C, D, A and B and they have raised to the stoichiometric coefficient for their reaction.

$$K_p = \frac{\left(\frac{p_C}{p_{ref}}\right)^c \left(\frac{p_D}{p_{ref}}\right)^d}{\left(\frac{p_A}{p_{ref}}\right)^a \left(\frac{p_B}{p_{ref}}\right)^b}$$

Now, when I say C and D, because when the stoichiometric coefficients are equal then it takes the form of K p in this form. So, Kp becomes Kc. So, when the stoichiometric coefficients becomes 1, we say Kc is equal to Kp. So, if you have a provision to find out the Kp, then we can control the ratio of forward rate coefficient and reverse rate coefficients and which are mainly function of temperatures.

So, the ratio of forward and reverse rate coefficient is equal to equilibrium constant based on the concentration and the equilibrium constant Kp also can be expressed in terms of partial pressure. So, it has been seen that in a bimolecular reaction both are equal which means it is possible to compute reverse reaction rate from the knowledge of forward rate and the equilibrium constant for the reaction, conversely one can calculate the forward rate by knowing the reverse rate.

In other words, we can say the chemical kinetic study can provide accurate experimental rate coefficients over a wide range of temperatures. So, these two things, rate coefficient and equilibrium constant will govern all the parameters during all the elementary reactions.

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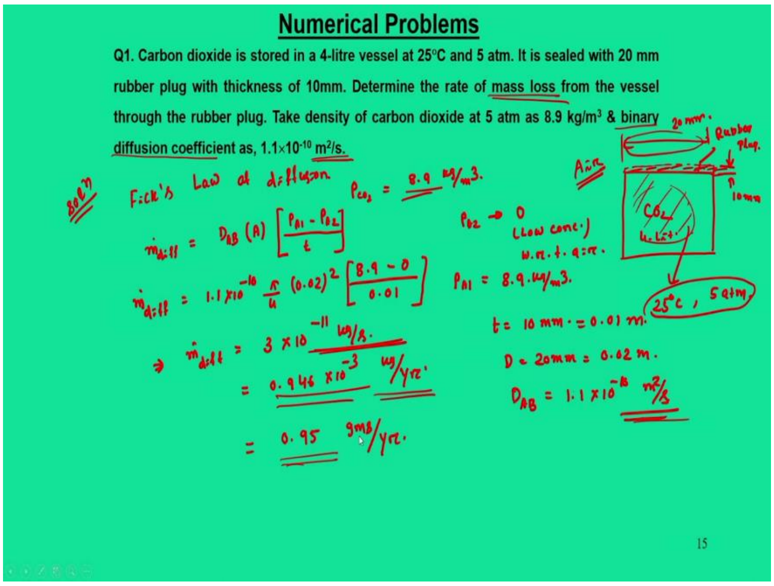

Numerical Problems

Q1. Carbon dioxide is stored in a 4-litre vessel at 25°C and 5 atm. It is sealed with 20 mm rubber plug with thickness of 10mm. Determine the rate of mass loss from the vessel through the rubber plug. Take density of carbon dioxide at 5 atm as 8.9 kg/m³ & binary diffusion coefficient as, 1.1×10^{-10} m²/s.

Sol^n

Fick's Law of diffusion

$\rho_{CO_2} = 8.9$ kg/m³.

$\dot{m}_{diff} = D_{AB}(A)\left[\frac{\rho_{A1}-\rho_{A2}}{t}\right]$

$\rho_{A2} \rightarrow 0$ (Low conc.) w.r.t. air.

$\dot{m}_{diff} = 1.1\times10^{-10}\,\frac{\pi}{4}(0.02)^2\left[\frac{8.9-0}{0.01}\right]$

$\rho_{A1} = 8.9$ kg/m³.

t = 10 mm = 0.01 m.

$\Rightarrow \dot{m}_{diff} = 3\times10^{-11}$ kg/s.

D = 20mm = 0.02 m.

$= 0.946\times10^{-3}$ kg/yr

$D_{AB} = 1.1\times10^{-10}$ m²/s

$= 0.95$ gms/yr.

So, with this I come to the end of this lecture, but before you leave, we will try to solve some numerical problems based on the fundamental concept discussed in this lecture. So, the first problem is based on Fick’s law of diffusion. We say that we have a closed container which consists of CO_2 and it is 4-litre capacity and it is sealed with a rubber plug on the top and this has some thickness of 10 mm and its diameter is 20 mm. So, this is what you say rubber plug.

This CO_2 is kept at 25 C and 5 atmosphere pressure. So, 5 atmosphere pressure means very high pressure as well; that means, compressed CO_2 has been kept at very high pressures. What the question is that we have to find what is the mass loss. So, here the mass loss is basically the leak that we are going to calculate.

And when you say leak, you have entire things CO_2 here that means, CO_2 is going to diffuse into the other medium and other medium is say if it is air; that means, we need to find out the binary coefficient of CO_2 with respect to air. So, if it is going to diffuse we need to quantify what is the mass loss.

So, data that is given is that rho density at rho CO_2 that is at 5 atmosphere, it is given 8.9 kg per meter cube. So, let us recall the expressions for rate of mass loss. So, we can say $\dot{m}_{diff} = D_{AB}(A)[(\rho_{A1} - \rho_{A2})/t\,]$.

So, here we have to find leak through this thickness. So, we can say ρ_{A2} which we can assume to be 0 because it is low concentration that concentration has to be calculated with respect to air. And ρ_{A1} you can write in terms of density its density you can write it is very high, 8.9 kg per meter cube and thickness is 10 mm that is 0.01 meter, diameter 20 mm that is 0.02 meter.

So, and $D_{AB} = 1.1 \times 10^{-10} m^2/s$ and remember always the unit of binary diffusion coefficient is m^2/s because it is a transport property. Then we can calculate t$\dot{m}_{diff} = D_{AB}\left(\frac{\pi}{4}0.02^2\right)[(\rho_{A1} - \rho_{A2})/t\,] = 3 \times 10^{-11} kg/s$.

So, hardly there is any leak or if you can calculate that even if you are storing this vessel for years, it to be effective. So, this number would be about $0.946 \times 10^{-3} kg/year$; that means, we can say this just to give a realistic number, this is about 0.95 grams of per year.

So, diffusion of mass loss from the vessel is almost negligible through this diffusion process and that also we said very rightly the molecular diffusion process is a very slow process and this problem demonstrates the same concept. But in some sense if you want to find the concentration of CO_2 and the mass loss in some situations, if it is a very costly gas which needs to be carried or need to be kept for long time, then this loss can be a very vital task.

For example, when you carry a liquid oxygen in a satellite to higher altitude or higher space or deep space. So, we expect that should not be any loss because the importance of oxygen is realized during the during combustion process in the deep space where availability of oxygen is not there. So, in a such scenario this loss has to be judiciously taken into account.

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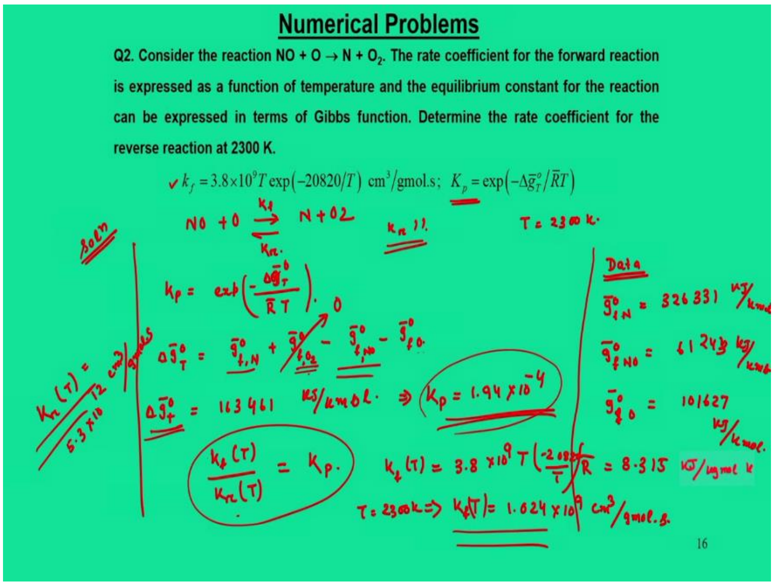

Numerical Problems

Q2. Consider the reaction NO + O → N + O_2. The rate coefficient for the forward reaction is expressed as a function of temperature and the equilibrium constant for the reaction can be expressed in terms of Gibbs function. Determine the rate coefficient for the reverse reaction at 2300 K.

✓ $k_f = 3.8\times10^9 T \exp(-20820/T)$ $cm^3/gmol.s$; $K_p = \exp\left(-\Delta\bar{g}_T^o/\bar{R}T\right)$

Soln

$NO + O \underset{K_r}{\overset{K_f}{\rightleftarrows}} N + O_2$ K_r ??   T = 2300 K.

$K_p = \exp\left(-\frac{\Delta\bar{g}_T^0}{\bar{R}T}\right)$.

$\Delta\bar{g}_T^0 = \bar{g}^0_{f,N} + \cancel{\bar{g}^0_{f,O_2}} - \bar{g}^0_{f,NO} - \bar{g}^0_{f,O}$ 0

$\Delta\bar{g}_T^0 = 163461$ kJ/kmol. $\Rightarrow K_p = 1.94\times10^{-4}$

$\frac{k_f(T)}{K_r(T)} = K_p$.

$k_f(T) = 3.8\times10^9\, T\left(\frac{-2.08}{T}\right)$ $\bar{R} = 8.315$ kJ/kgmol K

T = 2300 K ⇒ $k_f(T) = 1.624\times10^9$ $cm^3/gmol.s$

$K_r(T) = 5.3\times10^{12}$ $cm^3/gmol s$

Data

$\bar{g}^0_{f,N} = 326331$ kJ/kmol

$\bar{g}^0_{f,NO} = 61243$ kJ/kmol

$\bar{g}^0_{f,O} = 101627$ kJ/kmol.

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So, next problem we are going to discussed in terms of the rate coefficient versus equilibrium constants. So, we consider a bimolecular reaction $NO + O \rightarrow N + O_2$, the rate coefficient in the forward directions is expressed as a function of temperature and equilibrium constant also is given in the form of Gibbs function. So, we need to find out the reverse rate coefficients.

So, when I say $NO + O \rightarrow N + O_2$ and we say in the forward directions it is k_f and in the reverse direction it is k_r that is rate coefficients. What is given is kf and what is not known is kr, we need to find out. But this kr to be found out, we have to use the Kp and temperature is given as 2300 kelvin.

So, the first step that we need to find out what is Kp? So, Kp can be calculated as $K_p = \exp\left(-\frac{\Delta\bar{g}_T^0}{\bar{R}T}\right)$. And we need data for this Gibbs function calculation. Now this $\Delta\bar{g}_T^0$, for this reaction we can write $\Delta\bar{g}_T^0 = \bar{g}^0_{f,N} + \bar{g}^0_{f,O_2} - \bar{g}^0_{f,NO} - \bar{g}^0_{f,O}$.

Now, here it is a stable gas, $\bar{g}^0_{f,O_2}$ will be 0 and these three data is required. So, you have to take the data from thermodynamics books and this number I can write as for nitrogen it is 326331 kilo joule per kilo mole. For NO this number is 61243 kilo joule per kilo mole, for oxygen it is an atom, is not a stable gas. So, we have to find its Gibbs function, this number is 101627 kilo joule per kilo mole.

And we have R bar is equal to 8.315 kilo joule per kg mole per kelvin. Then by inserting this value we say $\Delta\bar{g}_T^0$ change is 163461 kilo joule per kilo mole. So, once you know this we can find. So, by inserting this number $K_p = 1.94 \times 10^{-4}$.

And its unit less because it is the ratio of partial pressures. $K_p = \frac{k_f(T)}{k_r(T)} = \frac{3.8\times10^9 T \exp(-20820/T)}{k_r(T)}$. This will give you reverse reaction $k_r(T) = 5.3 \times 10^{12} cm^3/gmol.s$. So, this expression demonstrates that knowing the equilibrium constant and rate coefficient in the forward directions, one can calculate the rate coefficient for the reverse directions. So, with this I conclude.

Thank you for your attention.