Fundamentals of Combustion

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Lecture - 21
Fundamentals of Combustion Kinetics – Part 2
Reaction Rates and Equilibrium Constant

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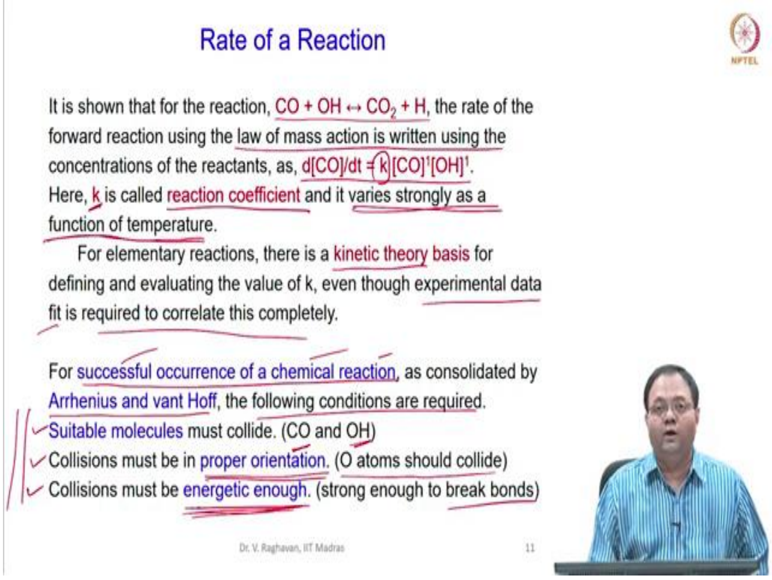

Rate of a Reaction

It is shown that for the reaction, $CO + OH \leftrightarrow CO_2 + H$, the rate of the forward reaction using the law of mass action is written using the concentrations of the reactants, as, $d[CO]/dt = k[CO]^1[OH]^1$. Here, k is called reaction coefficient and it varies strongly as a function of temperature.

For elementary reactions, there is a kinetic theory basis for defining and evaluating the value of k, even though experimental data fit is required to correlate this completely.

For successful occurrence of a chemical reaction, as consolidated by Arrhenius and vant Hoff, the following conditions are required.

- ✓ Suitable molecules must collide. (CO and OH)
- ✓ Collisions must be in proper orientation. (O atoms should collide)
- ✓ Collisions must be energetic enough. (strong enough to break bonds)

Now, rate of a reaction, we will continue with this same reaction $CO + OH \leftrightarrow CO_2 + H$, the rate of the forward reaction using the law of mass action is written using the concentration which we have already seen as $d[CO]/dt = k[CO]^1[OH]^1$ and this is the law of mass action, it says that the reaction rate is proportional to the concentrations raised to appropriate powers. Here, the stoichiometry coefficients itself for the elementary reaction but for global reaction it is not; we will see that later.

The constant of proportionality is not a constant, but it is called rate coefficient k. So, k is called the rate coefficient and it is not a constant, it varies strongly as a function of temperature. The rate coefficient varies very strongly.

So, how to determine the rate coefficient? For elementary reactions, the rate coefficient k can be evaluated with some theoretical basis. So, kinetic theory can be used to have some estimation of k.

Even then you should have some experimental data fit to correlate the value of k completely because k is a strong function of temperature, we need some experimental data also to calculate this.

So, what actually kinetic theory says is to evaluate the value of k; what kinetic theory says? I have not gone into the entire derivation. But what it says I have just put it here. For successful occurrence of a chemical reaction, Arrhenius and vant Hoff have defined the following conditions that are to be satisfied.

What are they? First of all, suitable molecules must collide; for example, here CO and OH should collide. Collisions must be in proper orientation.

So, CO and OH should collide such that the O atoms are going to be involved in the collision, O atom should collide with each other and the collisions must be energetic.

So, proper orientation and energetic, it should have proper energy which is enough to break the bonds, reactant bond should be broken. So, these are the three important criteria for attaining a successful chemical reaction.

So, suitable molecules must collide. So, CO colliding with say CO_2 will not help, OH colliding with H_2O will not help, however, CO and OH they collide properly to result CO_2 and H. So, several molecules are present in this system.

Only appropriate molecules should have to collide with each other. So, CO and OH should collide, that means the concentrations of these two should be sufficient enough for the collision to occur in a proper way.

If the concentration of one of this is very low then this reaction will not trigger. So, the concentrations of CO and concentration of OH should be sufficient enough for triggering this reaction. Suitable molecule should be available at suitable levels of concentrations. Then in proper orientation O atom should collide, that is very important.

Similarly, they should be energetic enough to break the bond; how energy comes? For the moving molecules when temperature increases energy will be higher. So, energy will increase $T^{3/2}$. So, when we have sufficient temperature the molecules will be energetic to collide with each other to break the bonds and form the new bonds which are products.

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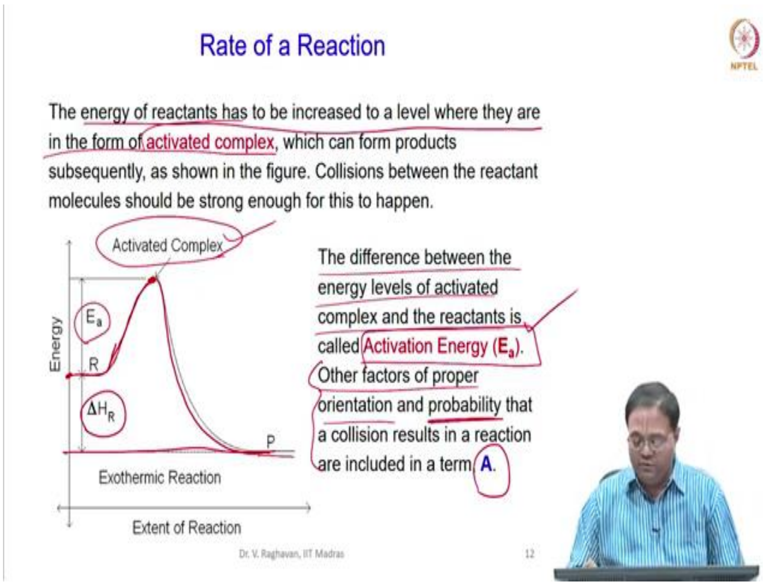

Rate of a Reaction

The energy of reactants has to be increased to a level where they are in the form of activated complex, which can form products subsequently, as shown in the figure. Collisions between the reactant molecules should be strong enough for this to happen.

The difference between the energy levels of activated complex and the reactants is called Activation Energy (E_a). Other factors of proper orientation and probability that a collision results in a reaction are included in a term **A**.

Now, what actually happens is, here the energy of the reactant has to be increased to a level where they form what is called activated complex. Let us see this energy versus the extent of reaction. Now, this is reactant level, reactants are at some energy level. Now, reaction cannot happen.

So, some sources of ignition or some already available flame or hot environment etcetera should be there for the reactants to increase its energy level to a value here which is called activated complex. So, this is attained initially by ignition, then the flame is formed or a hot environment prevails.

The hot environment is sufficient enough for the incoming reactant to get heated up and its energy level increases from a low value to high value like this. Once, it attains the activated complex level then the reactants disintegrate. Then they form products, products go to a low energy level. See this is the product

So, products are formed here, they are at low energy level and this heat is released out; that is the heat of reaction that comes out as heat of combustion. So, this is the exothermic reaction. Reactants are at higher energy level than products, but that is not sufficient for the reaction to occur. The reactant energy level should be increased to a value of that of the activated complex.

So, that you provide energy which is called E_a to increase the reactant from the initial energy level to the activated complex energy level from which products are formed. Now, the energy of the reactant has to be increased to a level where they are in the form of activated complex which can disintegrate to form the product subsequently.

Now, collision between the reactant molecules should be strong enough for this to happen; that is the environment should be hot enough and so on. Stronger collisions are possible by higher temperatures.

The difference between the energy level of the activated complex and the initial reactant is called the activation energy. So, this is the energy part of the equation which is which is going to contribute to the rate coefficient.

So, rate coefficient, for example, in the previous slide there are three things which we told. The energy part is the third one. Collisions must have enough energy so, the energy part comes for the third part. The first two, suitable molecules should collide. So, in a basket of several molecules suitable molecules should collide that some probability is there.

Similarly, they should collide in proper orientation, each collision may not happen at proper orientation. So, the first two actually are some probability dependent factors.

Other factors like proper orientation and the collision between two molecules are probability oriented. So, probability that the collision will result in reaction that means the two proper molecules are going to collide or not.

So, the other two factors will contribute to a term called A in the rate coefficient equation. The rate coefficient which is what we are going to now estimate for that. The energy factor which is the third one is nothing, but the activation energy. First two factors are probabilistic factors which is going to be included in the term called A.

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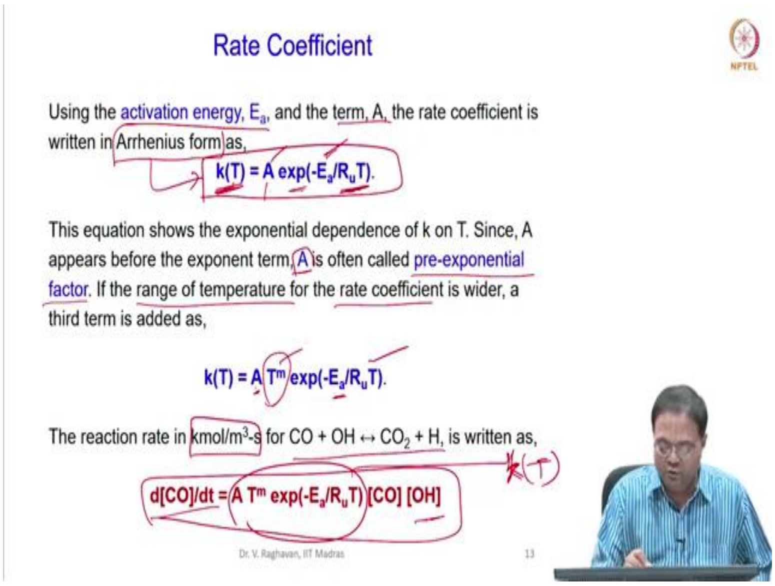

Rate Coefficient

Using the activation energy, E_a, and the term, A, the rate coefficient is written in Arrhenius form as,

$$k(T) = A\exp(-E_a/R_uT).$$

This equation shows the exponential dependence of k on T. Since, A appears before the exponent term, A is often called pre-exponential factor. If the range of temperature for the rate coefficient is wider, a third term is added as,

$$k(T) = A\,T^m\exp(-E_a/R_uT).$$

The reaction rate in kmol/m^3-s for $CO + OH \leftrightarrow CO_2 + H$, is written as,

$$d[CO]/dt = \underbrace{A\,T^m\exp(-E_a/R_uT)}_{}\,[CO]\,[OH] \quad k(T)$$

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Now, if we go to this, the activation energy and the term A, they are used to write the rate coefficient in what this called Arrhenius form. Arrhenius and vant Hoff who told about these factors you know. So, Arrhenius form is nothing but when we write the reaction rate coefficient k which is a strong function of temperature as $A\times\exp(-E_a/R_uT)$.

So, you can see that if you write the rate coefficient in this form, it is called Arrhenius form. This Arrhenius form is very famous. There are two factors in this, one is the A and another one is E_a, activation energy. Now, the exponent term is here. So, the dependent on temperature is very strong due to this term.

Now, since A appears before the exponent term, A is called pre-exponential factor; that is all. Just because it is before the exponential term, it is called pre-exponential factor and this A takes into account of the probability whether the collision will occur between proper molecules or they will occur at proper orientation and they will be successful or not and so on.

These are all probability-based things; that is what I told even though kinetic theory helps us to attain some factors of this. Experiments are going to help us in providing the final data to us.

So, this is where you write the Arrhenius form, pre-exponential factor A into exponent of minus of activation energy divided by R_u universal gas constant into temperature in Kelvin.

Now, if the range of temperature for which the rate coefficient is going to be calculated is wider; then you add a third term like this $AT^m\times\exp(-E_a/R_uT)$. So, this is called three factor Arrhenius equation where the third factor is T^m; some additional contribution by temperature is added.

For example, normally this the reaction rate given in molar basis $kmol/m^3s$. So, for this reaction we can write $d[CO]/dt$ is $AT^m\exp(-E_a/R_uT)\times[CO]^1[OH]^1$. So, this is the way you write this. Now, this is nothing but the rate coefficient k_T.

So, rate coefficient is not a constant, it is a strong function of temperature here. This is calculated by conducting lot of experiments and you have to evaluate the value of A and E_a for set of species. And, you have to fit curves to get these values.

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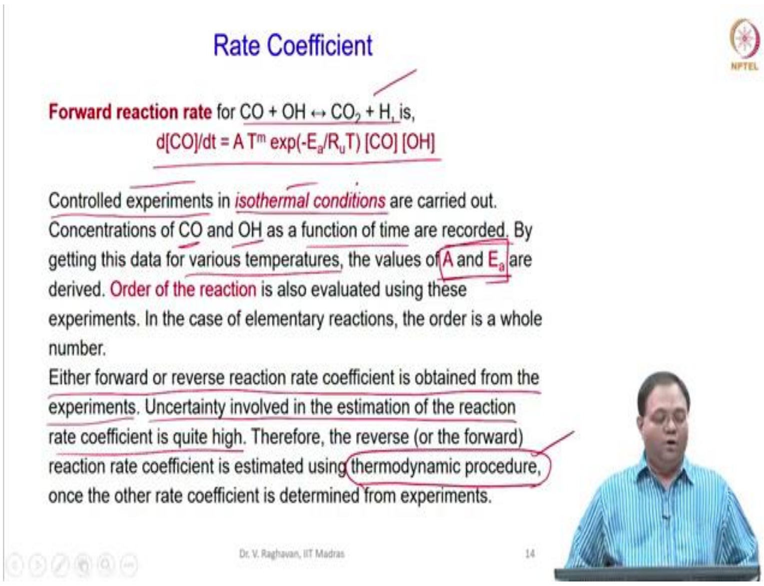

Rate Coefficient

Forward reaction rate for $CO + OH \leftrightarrow CO_2 + H$, is,

$$d[CO]/dt = A\,T^m \exp(-E_a/R_uT)\,[CO]\,[OH]$$

Controlled experiments in *isothermal conditions* are carried out. Concentrations of CO and OH as a function of time are recorded. By getting this data for various temperatures, the values of $\boxed{A \text{ and } E_a}$ are derived. Order of the reaction is also evaluated using these experiments. In the case of elementary reactions, the order is a whole number.

Either forward or reverse reaction rate coefficient is obtained from the experiments. Uncertainty involved in the estimation of the reaction rate coefficient is quite high. Therefore, the reverse (or the forward) reaction rate coefficient is estimated using thermodynamic procedure, once the other rate coefficient is determined from experiments.

Now, forward reaction rate of this is given by this forward reaction. Similarly, we can also calculate the reverse reaction rate. But how we are going to do this? So, we conduct controlled experiments under isothermal conditions. So, we will maintain the combustion chamber at several temperatures starting from say 1000 K or 800 K to say 1500 K or 2000 K and so on.

The concentrations of the reactants are recorded as a function of time. So, we know the rate at which the concentration of CO reduces and concentration of OH reduces with time, any one is enough for us.

By getting the data at various temperatures; now you will conduct experiment at say 800 K, 900 K, till say 2000 K. Once you get this data, you can plot the curve to extract the values of A and E_a. So, this is the way the chemists report.

This is the work which is done by chemist; they conduct lot of experiments like this and report the values of A and E_a for several set of a molecular level reactions. Even global reaction can also be done in it. For example, methane oxygen you put and monitor the concentration of methane as the function of temperature, that is what we are going to see later.

Global reaction also can be done like this. Reaction rate can be found or the rate coefficient can be determined for global reaction also. But the molecular reactions, several reactions have to be done and the chemists do this carefully to extract the values A and E_a and give even the T^m, the m also they will give actually.

By conducting several isothermal experiments and fitting the curves in this. However, the problem here is how accurate these data are. They are not very accurate. The uncertainty when you do experiment every time is high. Every time you do you will get some difference in the values; that is called uncertainty.

This uncertainty should be within some limit, say 5 percent uncertainty. So, once you do the experiment one time and do it second time or third time etcetera and take a mean and standard deviation. If the total variation or standard deviation is within 5 percent or something like that then that is a good experiment. But it is not possible. See all the intension is to get good data, but it is not possible because of several conditions.

So, the uncertainty involved in getting the rate coefficients are not so low, they are very high actually. So, what we do is either the forward or backward reaction rate coefficient is obtained from the experiments. Since, the uncertainty involved in the estimation of the reaction rate coefficient is quite high, it reports 40 percent even you can get 50% uncertainty.

We will not incur the same uncertainty while calculating the reverse reaction also. So, let us say I do careful experiments in isothermal conditions and get the forward reaction rate coefficient A and E_a value. Then, I will not do the same thing for the reverse reaction. I will do something else for that.

So, what I will do is I will find either the forward or reverse reaction rate. And, I will determine the other. If I have measured the forward reaction rate, I will determine the reverse reaction rate using the thermodynamic procedure which is much accurate. So, what is the procedure we will see now.

I will calculate the equilibrium constant and get the value of the reverse reaction rate. So, that is what is the next step what we are going to do. So, once you get the forward reaction rate from careful experiments, but it has higher uncertainty; I will not repeat that for determining the reverse reaction rate. For reverse reaction rate, I will use thermodynamic concepts. How?

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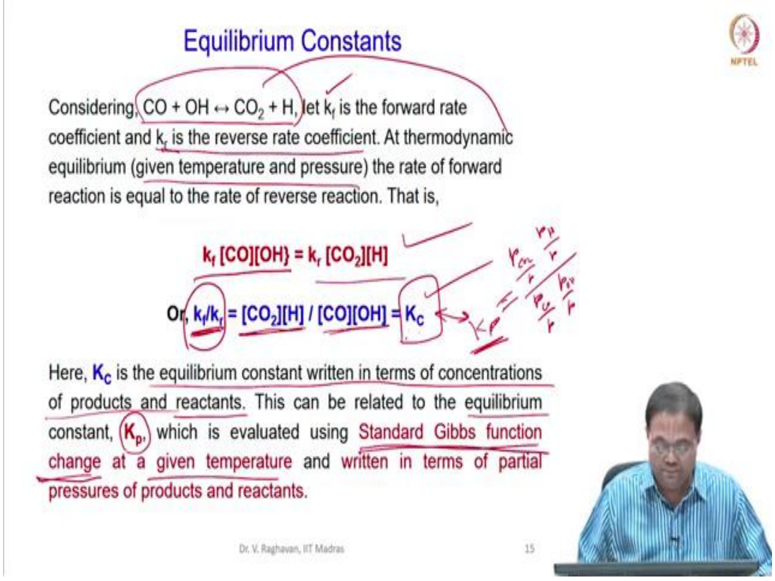

Equilibrium Constants

Considering, $CO + OH \leftrightarrow CO_2 + H$, let k_f is the forward rate coefficient and k_r is the reverse rate coefficient. At thermodynamic equilibrium (given temperature and pressure) the rate of forward reaction is equal to the rate of reverse reaction. That is,

$$k_f [CO][OH] = k_r [CO_2][H]$$

$$\text{Or, } k_f/k_r = [CO_2][H] / [CO][OH] = K_C \leftrightarrow K_P$$

Here, K_C is the equilibrium constant written in terms of concentrations of products and reactants. This can be related to the equilibrium constant, (K_p), which is evaluated using Standard Gibbs function change at a given temperature and written in terms of partial pressures of products and reactants.

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So, now let us consider the same reaction and let k_f be the forward reaction rate coefficient, it is first a strong function of temperature. Similarly, k_r is the reverse reaction rate coefficient. At thermodynamic equilibrium, pressure and temperature equilibrium prevails. At that equilibrium; reverse reaction rate and forward reaction rate are the same. So, $k_f [CO]^1[OH]^1 = k_r[CO_2]^1[H]^1$. These two are same.

The rate at which the forward reaction takes place is same as the rate at which the reverse reaction will take place. So, now the ratio of k_f by k_r that is defined as the equilibrium constant K_c.

This is nothing but the ratio of the products of the concentration of the products divided by the product of the concentration of the reactants. So, when we write the reaction like this, the reactants are CO and OH, products are CO_2 and H.

So, this is the concentration of the products, sum multiplied together. Similarly, this is the concentration of reactants sum multiplied and that ratio the products to the reactants that will be concentration-based equilibrium constant.

So, K_c is nothing but the concentration-based equilibrium constant. That is nothing but the ratio of the forward reaction rate coefficient divided by the reverse reaction rate coefficient. So, K_c is the equilibrium constant written in terms of concentrations of the products and reactants. This can be related to the K_p value.

K_p we have already seen; partial pressure-based equilibrium constant which is evaluated using standard Gibbs function change at a given temperature. So, K_p we know, we can evaluate for any reaction like this.

So, for this reaction actually partial pressure base you can write. $K_p = [(p_{CO2}/p)\times(p_H/p)]/[(p_{CO}/p)\times(p_{OH}/p)]$.

So, based on partial pressure you can write K_p and this K_p can be calculated as a function of temperature alone by using standard Gibbs function change which we have seen already in the equilibrium. Once you know that, if you connect K_p and K_c then I can evaluate one of this, $k_f/k_r = K_c$. So, how will we connect K_p and K_c?

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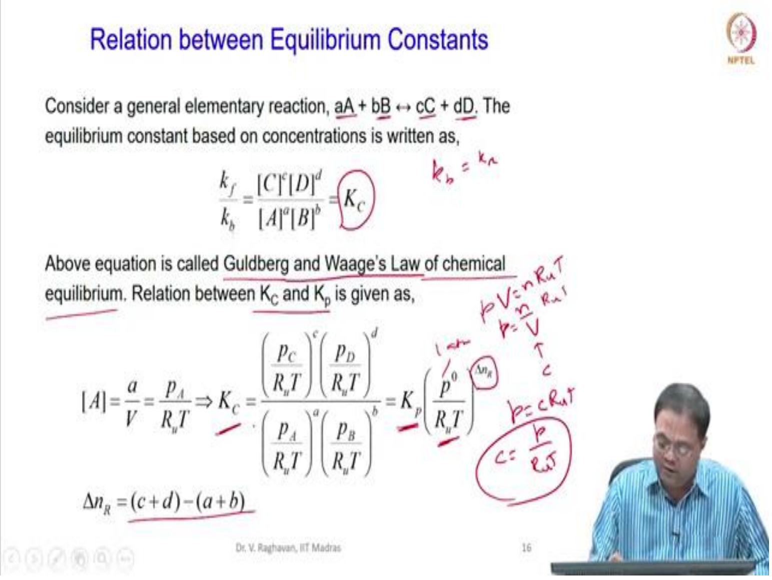

Relation between Equilibrium Constants

Consider a general elementary reaction, aA + bB ↔ cC + dD. The equilibrium constant based on concentrations is written as,

$$\frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_C$$

$k_b = k_r$

Above equation is called Guldberg and Waage's Law of chemical equilibrium. Relation between K_C and K_p is given as,

$$[A] = \frac{a}{V} = \frac{p_A}{R_u T} \Rightarrow K_C = \frac{\left(\frac{p_C}{R_u T}\right)^c \left(\frac{p_D}{R_u T}\right)^d}{\left(\frac{p_A}{R_u T}\right)^a \left(\frac{p_B}{R_u T}\right)^b} = K_p \left(\frac{p^0}{R_u T}\right)^{\Delta n_R}$$

1 atm

$pV = nR_uT$

$p = \frac{n}{V} R_uT$

c

$p = cR_uT$

$c = \frac{p}{R_uT}$

$\Delta n_R = (c + d) - (a + b)$

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So, consider a general reaction capital A, capital B are the reactant species and small a and small b are the stoichiometric coefficients. Similarly, capital C and capital D are the product species and small c and d are the stoichiometric coefficients.

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

For this k_f/k_b, I can write backward reaction or reverse reaction $k_b = k_r$.

Anything you can write that is nothing, but K_c concentration based I am writing.

$$\frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_C$$

Now, this equation is called a Guldberg Waage's law of chemical equilibrium which is written in the concentration terms.

Rate of the forward reaction divided by the rate of the backward or the reverse reaction is nothing, but equilibrium constant based on concentrations K_c. Now, the relation between K_p and K_c, now try to write the partial pressures here. So, what is concentration? $pV = nR_uT$. So, $p = (n/V)\times R_uT$, this is the concentration C.

So, $p = CR_uT$, now $C = p/(R_uT)$, that is the concentration. So, concentration of any species say ‘C’ is nothing but $p_C/(R_uT)^c$. Similarly, for D and A and B, write this.

Now, you also have this definition of partial pressure-based K_p. Now, you can equate this. So that $K_c = K_p(p^0/R_uT)^{\Delta nR}$. So, now, you can write this K_p, p power this is atmospheric pressure.

So, p, 1 atmosphere, divided by R_uT to the power of ΔnR which is the sum of the stoichiometric coefficient of the products minus sum of the stoichiometric coefficient of the reactants. For bimolecular reaction, for example, if A, B, C, D are having values of one each then $\Delta nR = 0$; then, for that case $K_p = K_c$.

So, once you know K_p, you can calculate K_c, K_p can be calculated using Gibbs energy change function change at a particular temperature. Then you can use that to calculate K_c. Once K_c is known, one of this is measured k_f or k_b and one of them is calculated using K_c which is much accurate than the measurement itself.

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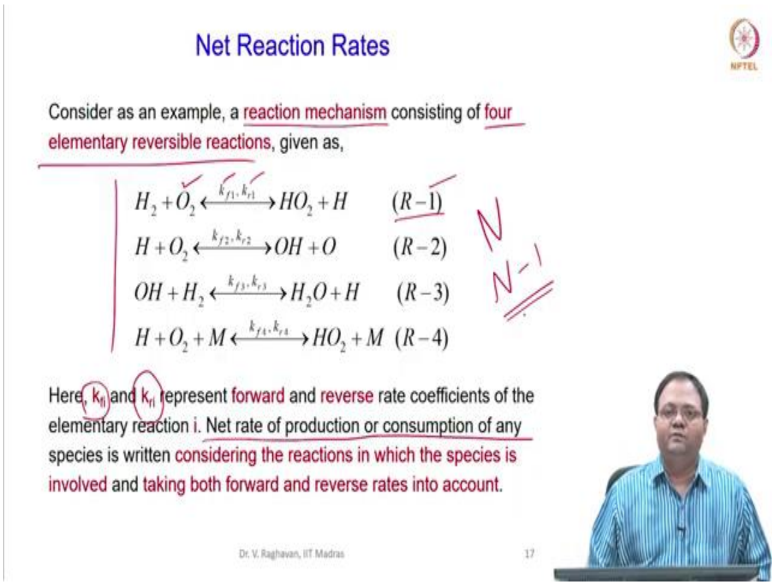

Net Reaction Rates

Consider as an example, a reaction mechanism consisting of four elementary reversible reactions, given as,

$$H_2 + O_2 \xleftrightarrow{k_{f1},k_{r1}} HO_2 + H \qquad (R-1)$$

$$H + O_2 \xleftrightarrow{k_{f2},k_{r2}} OH + O \qquad (R-2)$$

$$OH + H_2 \xleftrightarrow{k_{f3},k_{r3}} H_2O + H \qquad (R-3)$$

$$H + O_2 + M \xleftrightarrow{k_{f4},k_{r4}} HO_2 + M \qquad (R-4)$$

N

N-1

Here, k_{fi} and k_{ri} represent forward and reverse rate coefficients of the elementary reaction i. Net rate of production or consumption of any species is written considering the reactions in which the species is involved and taking both forward and reverse rates into account.

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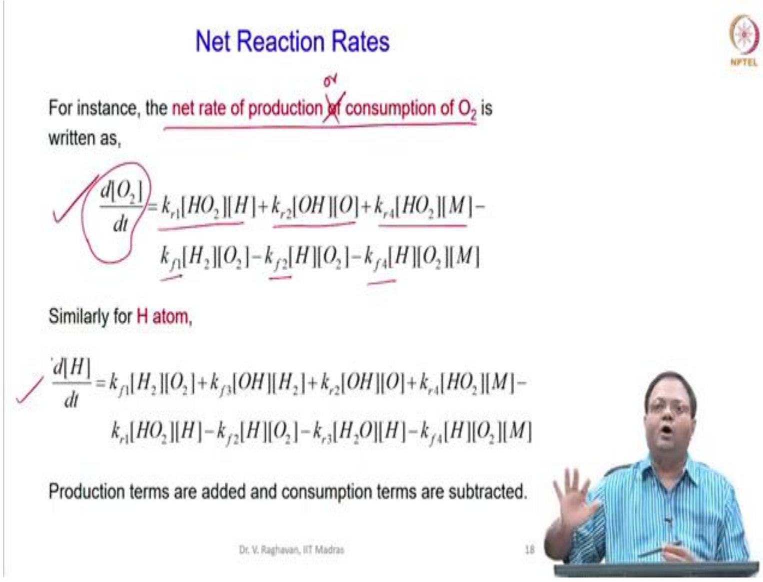
The next topic is net reaction rate. So, when we have several reactions like this $H_2 + O_2$ ←→ $HO_2 + H$. You can see that these are all some of the reactions which is participating in the hydrogen oxidation. So, this mechanism, I am just selecting four elementary reversible reactions in this to demonstrate how you calculate the net reaction rate considering these four reactions. Now, in each of the reaction, the forward rate coefficient, k_f, see for example, the first reaction k_{f1} will be the forward reaction rate and the k_{r1} will be the reverse reaction rate of the equation 1.

So, in general k_{fi} will be the forward reaction rate of the i^{th} reaction 1, 2, 3, 4; i can be 1, 2 or 3 or 4. Similarly, k_{ri} is the reverse rate coefficient of the i^{th} reaction. So, now you know this.

Now, net rate of production or consumption, when there is species in reactant side it will be consumed in the forward reaction but it will be produced in the reverse reaction. So, for example, if I take O_2 here, O_2 is consumed in the forward reaction of R1. Similarly, it is consumed in the forward reaction of reaction 2, R2; it is consumed in the forward reaction of R_4.

So, in three reactions O_2 is consumed. Where it is formed? In the reverse reaction of R1 it is formed, reverse reaction of R2 it is formed and reverse reaction of R4 it is formed. So, the net reaction rate will be, if you add the reactions through which it is formed minus the reaction through which it is consumed. Then you will get the net reaction rate. The net rate of production or consumption of the species you will get.

So, you have to consider all the reactions in which the species is participating and see whether it is consumed or whether it is produced through a forward or reverse reaction suitably. Then you have to add these production terms and subtract to that the sum of the consumption terms. (Refer Slide Time: 23:32)



Net Reaction Rates

For instance, the net rate of production ~~of~~ or consumption of O_2 is written as,

$$\frac{d[O_2]}{dt} = k_{r1}[HO_2][H] + k_{r2}[OH][O] + k_{r4}[HO_2][M] - k_{f1}[H_2][O_2] - k_{f2}[H][O_2] - k_{f4}[H][O_2][M]$$

Similarly for H atom,

$$\frac{d[H]}{dt} = k_{f1}[H_2][O_2] + k_{f3}[OH][H_2] + k_{r2}[OH][O] + k_{r4}[HO_2][M] - k_{r1}[HO_2][H] - k_{f2}[H][O_2] - k_{r3}[H_2O][H] - k_{f4}[H][O_2][M]$$

Production terms are added and consumption terms are subtracted.

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So, the net rate of production or consumption of O_2 is written like this.

So, as I told you, in the reverse reaction of 1, 2 and 4 O_2 is formed. So, add them. The reaction rate of 1, reverse reaction rate of 1 is the reverse rate coefficient into the HO_2

and H are the reactants which is forming O_2. Similarly, O H and O forms O_2, HO_2 and M forms O_2. So, you appropriately add them.

$$k_{r1}[HO_2][H] + k_{r2}[OH][O] + k_{f4}[HO_2][M]$$

Then subtract that to the consumption of the O_2. In the forward reaction of 1, 2 and 4, O_2 is consumed. The reaction rate corresponding to that is $-k_{f1}[H_2][O_2]$ $-k_{f2}[H][O_2]$ $-k_{f4}[H][O_2][M]$, consuming O_2. So, the net reaction rate will be, the chemical equation which will produce O_2 should be added, which will consume O_2 should be subtracted.

This is the net rate of production or consumption; we do not know whether it is positive or negative correct. So, production or consumption of O_2 is given like this. Similarly, for H atom we can write like this. So, we can see this. So, this is only for 4 equations, but actually we will have several number of equations reactions like this.

We have to suitably know where the species is present and in what all reaction species is going to be present, particular species and try to calculate. So, I need this term basically and this term is to be substituted in the species conservation equation. So, the species conservation O_2 can be transported into the combustion chamber and it is going to be consumed.

For example: net rate is negative, it is going to be consumed; then some of that which is not consumed will come out or if it is fully consumed, it will not come out at all. So, based upon this conservation of O_2 if you want to do, I need the net rate of production or consumption of O_2, that is got by this.

Similarly, for every species involved in the multi-component mixture or in the chemical mechanism; we have to do this. So, this is very important to calculate from the mechanism considering a set of equations. We have to find the number of species which are there in the reaction mechanism.

For each of these species, except one (if there are N species), we have to find the net reaction rate whether it is a production rate or consumption rate for N - 1 species. One species we need not even find, because that may be inert species and so on. So, this is what is important to find.

So, you have to accommodate all the reactions which is important, like in which this species is participating and suitably give the positive sign for the reaction which is producing that particular species and negative sign for the reaction which is consuming that species and add them.

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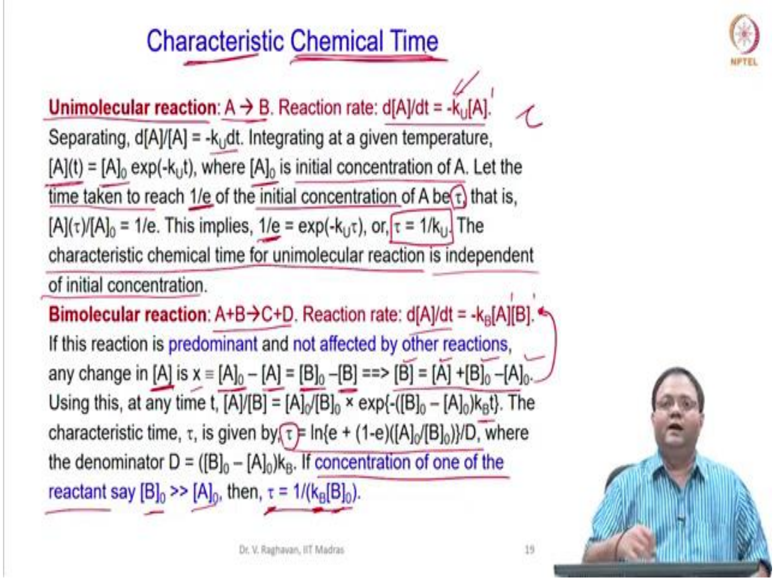

Characteristic Chemical Time

Unimolecular reaction: A → B. Reaction rate: $d[A]/dt = -k_U[A]$.

Separating, $d[A]/[A] = -k_U dt$. Integrating at a given temperature, $[A](t) = [A]_0 \exp(-k_U t)$, where $[A]_0$ is initial concentration of A. Let the time taken to reach 1/e of the initial concentration of A be τ, that is, $[A](\tau)/[A]_0 = 1/e$. This implies, $1/e = \exp(-k_U\tau)$, or, $\boxed{\tau = 1/k_U}$. The characteristic chemical time for unimolecular reaction is independent of initial concentration.

Bimolecular reaction: A+B→C+D. Reaction rate: $d[A]/dt = -k_B[A][B]$.

If this reaction is predominant and not affected by other reactions, any change in [A] is $x \equiv [A]_0 - [A] = [B]_0 - [B] \Longrightarrow [B] = [A] + [B]_0 - [A]_0$. Using this, at any time t, $[A]/[B] = [A]_0/[B]_0 \times \exp\{-([B]_0 - [A]_0)k_B t\}$. The characteristic time, τ, is given by $\tau = \ln\{e + (1-e)([A]_0/[B]_0)\}/D$, where the denominator $D = ([B]_0 - [A]_0)k_B$. If concentration of one of the reactant say $[B]_0 >> [A]_0$, then, $\tau = 1/(k_B[B]_0)$.

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Now, after knowing the rate at which the reaction is take place, we need to know the time; so, that is what we first started with. So, what is the time required for the reaction to complete and whether that is enough for the combustion to complete within the dimension of the combustion chamber?

So, some time scale I want, chemical time. How will you calculate chemical time? So, just I will illustrate with two types of reactions. Let us consider a unimolecular reaction A → B. So, the rate at which the concentration of A changes with time actually A is reactant; so, I put a minus here $-k_U[A]^1$.

Concentration of A, because the only reactant is A. Now, I separate the variable $d[A]/[A] = -k_U \times dt$. Integrate this at a given temperature to get the concentration of A as a function of time. $[A](t) = [A_0]\exp(-k_U t)$. $[A_0]$ is the initial concentration of A.

When I start the reaction at time t = 0, what is the concentration of A? That is $[A_0]$. This k is the unimolecular rate constant; so, unimolecular reaction. So, it is k_U. Again, Arrhenius form terms can be used to evaluate k_U.

So, that is different. This is the function of temperature. That is what you have to understand here. So, when I want to find the time, what is the time I will normally find is the characteristic time. I am talking about time taken to for [A] to reduce to 1/e of the initial concentration, that time let us say is τ.

So, τ is the time when the concentration of A will fall from its initial concentration of $[A_0]$ to 1/e of that value. So, that will be the unimolecular reaction it will be $1/k_U$. So, based upon the temperature alone it will change. If temperature is higher k_U will be higher, so, time taken will be lower.

So, we will have some idea of how the chemical time will change. So, why I am taking 1/e? Why I am not taking $[A_o]$ to 0? Because, normally asymptomatically it will reduce, it will take longer time for it to reach a value of 0. But if you consider this, this is the time we should we should plan for the reaction to be complete.

This is very low time. Based on the temperature, if the temperature is higher enough τ will be low; because k_U will be high at higher temperatures. So, the characteristic chemical time of a unimolecular reaction depends only on the temperature and its independent of the initial concentration. Now, you take bimolecular reactions which are mostly used.

So, we are only talking about these two. So, bimolecular reaction as I told 90 to 95 percent of the elementary reactions are bimolecular in nature. So, how to write reaction rate for this? Take any one of the reactants, $d[A]/dt = -k_B[A]^1[B]^1$ (negative because I know its consumption). So, this we can write through law of mass action.

Now, if this reaction is predominant not affect affected by the reactions; then we can say that. For example, why I am saying this because, see B, if a set of reactions are there and this reaction is predominant in that set. That means, the major consumption of A or B will occur only due to this reaction.

If that is so, major consumption of A or B is going to occur only by this reaction; other reactions are not majorly going to affect this reaction. Then the change in the concentration of A, let us say it is x, it is nothing but initial concentration minus the concentration at a particular time instant t that is [A].

So, $[A_0] - [A]$ that will be same as the difference in the initial concentration of B to the concentration of B at the particular time same time ($[B_0] - [B]$). So, now this equation can be used to write the concentration of B at any time as concentration of A at that particular time plus the initial concentration of B minus initial concentration of A.

$$[B]=[A] + [B_0] - [A_0]$$

Now, substitute this in this equation, for any time t you substitute this. You can write at any time t, the concentration of A divided by the concentration of B will be equal to initial concentration of A divided by the initial concentration of B times exponent of this minus of B_o minus A_o times the molecular rate coefficient k_B into t.

$$[A]/[B] = [A]_0/[B]_0 \times \exp\{-([B]_0 - [A]_0)k_B t\}.$$

Now, again the time required to reduce the concentration of A from initial to the 1/e of the initial value, that if you take as τ; then τ is evaluated like this.

$$\tau = \ln\{e + (1-e)([A]_0/[B]_0)\}/D, \ D = ([B]_0 - [A]_0)k_B$$

Now, here the denominator D is B_o minus A_o into k_B. So, this is the equation, you can just work it out it is a very simple separation and integration. So, just work it out, then you get this value.

Now, one important factor here is if the concentration of the one of the reactants say B_o is very high than A_o out of the two A and B the concentration of one may be very high than when compared to the other. In that case, then we can write the τ as this.

$$\tau = 1/(k_B[B]_0)$$

We are estimating the characteristic time, characteristic time is the typical time of a reaction to complete. So, that time will be dependent on the higher concentration reactant species. So, k_B is also present in the denominator, B_o also is present. So, if k_B is higher which is because at high temperature k_B is higher, then τ will reduce. Similarly, the initial concentration dependence on the τ has come here.

If the initial concentration is higher, then the time taken is low, if this B_o reduces, then the time will be higher. So, some characteristic chemical time can be calculated using these analyses.