Fundamentals of Combustion

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Lecture - 23

Fundamentals of Combustion Kinetics – Part 04

Worked Example

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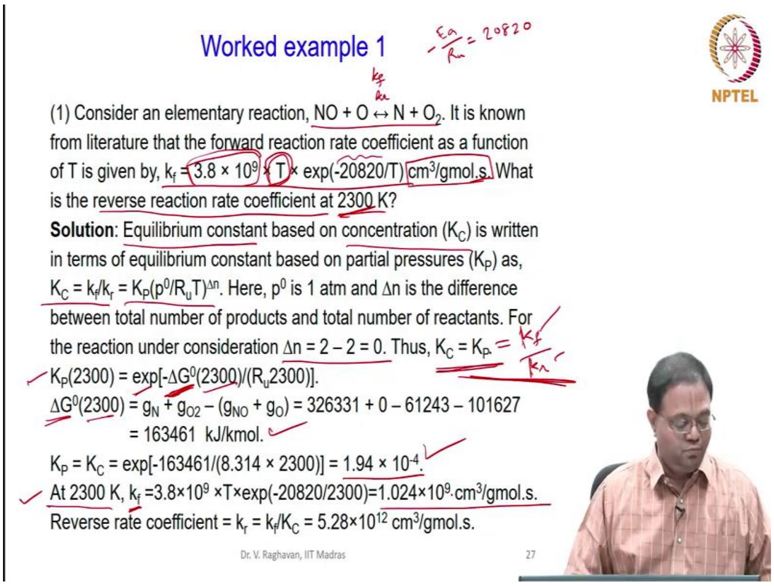

Worked example 1

$-\frac{E_a}{R_u} = 20820$

(1) Consider an elementary reaction, $NO + O \overset{k_f}{\underset{k_r}{\leftrightarrow}} N + O_2$. It is known from literature that the forward reaction rate coefficient as a function of T is given by, $k_f = 3.8 \times 10^9 \times T \times \exp(-20820/T)$ cm^3/gmol.s. What is the reverse reaction rate coefficient at 2300 K?

Solution: Equilibrium constant based on concentration (K_C) is written in terms of equilibrium constant based on partial pressures (K_P) as, $K_C = k_f/k_r = K_P(p^0/R_uT)^{\Delta n}$. Here, p^0 is 1 atm and Δn is the difference between total number of products and total number of reactants. For the reaction under consideration $\Delta n = 2 - 2 = 0$. Thus, $K_C = K_P = \frac{k_f}{k_r}$

$K_P(2300) = \exp[-\Delta G^0(2300)/(R_u 2300)]$.

$\Delta G^0(2300) = g_N + g_{O2} - (g_{NO} + g_O) = 326331 + 0 - 61243 - 101627$

$= 163461$ kJ/kmol.

$K_P = K_C = \exp[-163461/(8.314 \times 2300)] = 1.94 \times 10^{-4}$.

At 2300 K, $k_f = 3.8\times10^9 \times T \times \exp(-20820/2300) = 1.024\times10^9$ cm^3/gmol.s.

Reverse rate coefficient = $k_r = k_f/K_C = 5.28\times10^{12}$ cm^3/gmol.s.

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Now, we will see a couple of worked examples. The worked example one, consider an elementary reaction, so two side reaction $NO + O \leftrightarrow N + O_2$.

So, it is known from literature that the forward reaction rate coefficient as a function of temperature is given. So, this is k_f the forward reaction coefficient, and the reverse reaction coefficient is k_r.

So, from literature we have the value or expression to calculate the forward reaction coefficient k_f. So, what is that? This first term is pre-exponential factor A, and this is T^m where m is one here, $\exp(-E_a/R_uT)$, now, this is nothing but $-E_a/R_u$.

So, this is E_a/R_u, 20820 is nothing but value of E_a/R_uT ok. Now, please see that when I say units are in cm, gram mole etcetera, we have to be careful in selecting our units.

When you want to calculate the reaction rate, you need the concentrations. So, for that you need to take proper units. So, now, your units are in cm^3/gmol-s.

So, now please see this is the pre-exponential factor 3.8×10^9. T^m, where m is equal to 1 here. Now, here $-E_a/R_u = 20820$, so that you have to understand.

So, what is the reverse reaction rate coefficient at a temperature of 2300 K, that is the question asked? Ok, forward reaction rate is given. I want to find the reverse reaction rate.

So, as I told you this curve fit which is obtained from the experiment is highly uncertain; like I said it has higher uncertainties. So, we will implement some thermodynamic based approach to calculate the reverse reaction. So, we will assume equilibrium for this.

So, equilibrium constant based on concentration is calculated for this. So, that is nothing but K_C equal to the forward reaction rate coefficient divided by the reverse reaction rate coefficient.and K_C is connected to K_P by this equation.

$$K_C = k_f/k_r = K_P(p^0/R_uT)^{\Delta n}$$

So, K_C that is the concentration-based equilibrium constant that will be equal to partial pressure-based equilibrium constant $K_P\times p0/(R_uT)^{\Delta n}$, where Δn is nothing but the difference between the number of moles of products and the reactants in this equation.

So, we consider the equation $NO + O \leftrightarrow N + O_2$. The number of molecules in the reactant side is 2; product side also is 2. So, Δn here is 2 - 2 = 0 0. So, we can say that K_C will be equal to K_P.

So, when you calculate K_P, then we can calculate K_C once you know the K_C you know the ratio of k_f/k_r. So, since k_f is known or we can calculate the k_f at temperature of 2300 K, k_r also can be calculated at that temperature. So, I did not measure the value of k_r. Once k_f is known, k_r can be calculated using the equilibrium approach.

Now, K_P at temperature 2300 K is calculated using the standard Gibbs function change ΔG at 2300 K which is nothing but for this reaction so products are $N + O_2$. So, Gibbs free energy of N + Gibbs free energy of O_2 - the reactants Gibbs free energy of NO - Gibbs free energy of O, so that will be the standard Gibbs function change.

$$\Delta G^0(2300) = g_N + g_{O2} - (g_{NO} + g_O) = 326331 + 0 - 61243 - 101627$$
$$= 163461 \text{ kJ/kmol.}$$

So, substituting the value of g_N, g_{O2}, g_{NO} and g_O, etcetera at a temperature of 2300 K I get the value of Δg as here 163461 kJ/kmol.

Now,

$$K_P = K_C = \exp[-163461/(8.314 \times 2300)] = 1.94 \times 10^{-4}$$

So, what is K_P here? $\exp(-\Delta G/R_uT)$, so substituting the value of ΔG here, you get $K_P = K_C = 1.94 \times 10^{-4}$. So, that is the value.

Now, at 2300 K, k_f value is determined. So, wherever T appears, you put 2300 K and get the value of the k_f in cm^3/gmol-s, that is 1.024×10^9 cm^3/gmol-s that is the value for k_f calculated at the given temperature of 2300 K. So, reverse rate coefficient k_r is nothing but k_f/K_C, because K_C is known.

Now, using this equation $k_f/K_C = 5.28\times10^{12}$ cm^3/gmol-s, so that is the way you calculate. So, once the forward reaction rate or reverse reaction rate is known calculate the equilibrium constant K_P and from that, you calculate the value of the equilibrium contract based on concentrations K_C.

Use the definition of K_C which is k_f/k_r, if one of the rate coefficient is known, the other can be calculated, this will improve the inaccuracies. When you experimentally measure, the uncertainties are very high, 40% etcetera.

So, in order to give more accuracy to these calculations, thermodynamics based concepts are used. These thermodynamic based calculation of K_P is very accurate. So, using that and calculating K_P and K_C will be good. So, using the K_C's definition, we can calculate the other reaction rate, so that your overall uncertainty will reduce.

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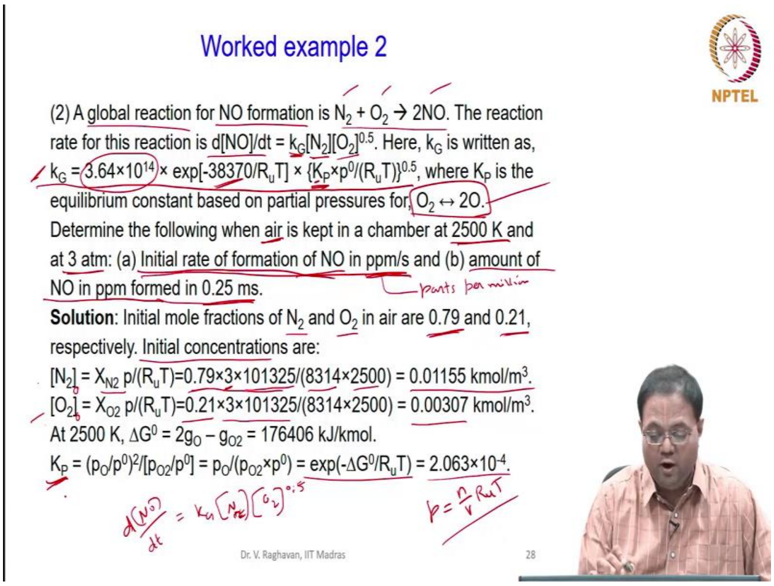

Worked example 2

(2) A global reaction for NO formation is $N_2 + O_2 \rightarrow 2NO$. The reaction rate for this reaction is $d[NO]/dt = k_G[N_2][O_2]^{0.5}$. Here, k_G is written as, $k_G = 3.64\times10^{14} \times \exp[-38370/R_uT] \times \{K_P \times p^0/(R_uT)\}^{0.5}$, where K_P is the equilibrium constant based on partial pressures for $O_2 \leftrightarrow 2O$. Determine the following when air is kept in a chamber at 2500 K and at 3 atm: (a) Initial rate of formation of NO in ppm/s and (b) amount of NO in ppm formed in 0.25 ms.

parts per million

Solution: Initial mole fractions of N_2 and O_2 in air are 0.79 and 0.21, respectively. Initial concentrations are:

$[N_2]_0 = X_{N2}\, p/(R_uT) = 0.79\times3\times101325/(8314\times2500) = 0.01155$ kmol/m^3.

$[O_2]_0 = X_{O2}\, p/(R_uT) = 0.21\times3\times101325/(8314\times2500) = 0.00307$ kmol/m^3.

At 2500 K, $\Delta G^0 = 2g_O - g_{O2} = 176406$ kJ/kmol.

$K_P = (p_O/p^0)^2/[p_{O2}/p^0] = p_O/(p_{O2}\times p^0) = \exp(-\Delta G^0/R_uT) = 2.063\times10^{-4}$.

$\frac{d(NO)}{dt} = k_G[N_2][O_2]^{0.5}$

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

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Second example, here a global reaction for NO formation, global reaction. Please understand this is a global reaction, not elementary reaction; previous are the elementary reaction. This example deals a global reaction where the N_2 and O_2 reacts to form nitric oxide NO, single sided arrow.

$$N_2 + O_2 \rightarrow 2NO$$

It is a global reaction no reversibility is there, and this cannot occur in one step. So, you know that the Zeldovich mechanism what we saw. So, N should react with the O_2 to form NO and O. Similarly, O should react with the N_2 to form NO and N.

So, this cannot occur in one step, and this is the global reaction. The reaction rate of this reaction d[NO]/dt is given as k_G that is the global reaction rate coefficient times the concentration of N_2 power 1 and concentration of O_2 power 0.5.

$$d[NO]/dt = k_G[N_2][O_2]^{0.5}$$

You can see that there is no relationship between the moles there. So, $[N_2]^1$, $[O_2]^{0.5}$ that is the reaction here. So, the concentration of N_2 is raise to power 1, and O_2 is raise to power 0.5, so the overall order of the reaction will be 1.5.

Now, k_G is also given the expression for k_G is also given here like this.

$$k_G = 3.64\times10^{14} \times \exp[-38370/R_uT] \times \{K_P\times p^0/(R_uT)\}^{0.5}$$

You can see that when this approach is made K_P is appearing here. This is because some partial equilibrium has been invoked. So, K_P of this reaction $O_2 \leftrightarrow 2O$ reversibility that is used in this equation. That means, when you do this they have eliminated N and O, and they have given this equation.

$N_2 + O_2 \rightarrow 2NO$. So, k_G now we can see a pre-exponential factor 3.64×10^{14} there is no temperature based term and $\exp[-38370/R_uT]$. So, E_a is -38380 into some factor is given again you can see that K_P appears here. So that the equilibrium constant based on partial pressures of this equation $O_2 \leftrightarrow 2O$ has been used here.

So, you can see K_P atmospheric pressure divided by R_uT total power 0.5. So, some factor is given. So, if we use this, then we can fit the k_G value, get the value of k_G at any temperature. Once that is got, then we can find the reaction rate. So, what is asked is determine the following when air containing N_2 and O_2 is kept in a chamber fixed at 2500 K at 3 atmospheric pressure.

So, if there is a chamber, combustion chamber, where only air is first fed, but the temperature of that chamber is 2500 K and pressure is 3 atm. So, due to the high temperature, N_2 and O_2 will react to form NO. So, what is asked? Initial rate of formation of NO in ppm per second.

What is ppm? parts per million. So, it is actually mole fraction multiplied by some number that is called parts per million. So, mole fraction per second product how much mole fractions of NO is produced per second that by multiplying conversion factor, you can get parts per million per second, initial rate.

So, initially based upon the concentrations of O_2 and N_2 how much NO is produced, the rate of production of NO is what? Second is amount of NO in ppm parts per million formed at the time instant of 0.25 milliseconds, 0.25 milliseconds, what is the amount of NO formed? So, this is the question asked.

Now, solution, initial mole fractions of N_2 and O_2 because air is fed in hot chamber, the volumetric fractions or mole fractions are 0.79 and 0.21 for nitrogen, oxygen respectively. So, concentrations can be now found. Concentrations is nothing but mole fraction into pressure by R_uT. So, $p = (n/V)R_uT$. So, that you use, you get this.

So, partial pressure of N_2 is nothing but $X_{N2}\times p$, partial pressure of N_2 divided by R_uT that is a concentration. So, $0.79\times3\times101325$ that is the pressure in Pa.

So, this will be the partial pressure divided by R_u(8314 J/kmol-K), and temperature is 2500 K, the chambers temperature. So, you get the concentration in kmol/m^3. So, 0.01155 kmol/m^3 of nitrogen.

$$[N_2] = X_{N2}\, p/(R_uT)=0.79\times3\times101325/(8314\times2500) = 0.01155 \text{ kmol/m}^3.$$

$$[O_2] = X_{O2}\, p/(R_uT)=0.21\times3\times101325/(8314\times2500) = 0.00307 \text{ kmol/m}^3$$

Similarly, for oxygen, the concentration is 0.00307 kmol/m^3. You substitute the mole fraction of oxygen as 0.21, and the pressure as 3×101325 in this equation, and you get the concentration as 0.00307 kmol/m^3.

Now, we need the value of K_P. So, we have calculated the concentration in the rate equation here. $d[NO]/dt = k_G[N_2][O_2]^{0.5}$. So, now you need the concentrations, initial concentrations you need because first what is asked is the initial rate of formation of NO. So, the initial concentration is required. So, that is calculated here. This is actually initial concentration I can also put a subscript 0, initial concentration.

Now, for this calculation of k_G, I need the equilibrium constant K_P of this reaction $O_2 \leftrightarrow 2O$. So, for that K_P is calculated like this.

$$K_P = (p_O/p^0)^2/[p_{O2}/p^0] = p_O/(p_{O2}\times p^0) = \exp(-\Delta G^0/R_uT) = 2.063\times10^{-4}$$

So that is the K_P value. Now, you have K_P and you have concentrations.

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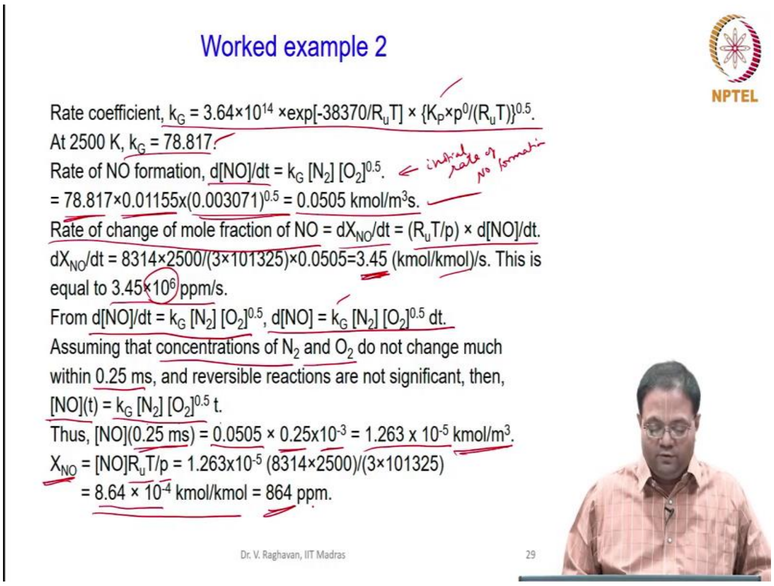

Worked example 2

Rate coefficient, $k_G = 3.64\times10^{14} \times\exp[-38370/R_uT] \times \{K_P\times p^0/(R_uT)\}^{0.5}$.

At 2500 K, $k_G = 78.817$.

Rate of NO formation, $d[NO]/dt = k_G [N_2] [O_2]^{0.5}$. ← initial rate of NO formation

$= 78.817\times0.01155x(0.003071)^{0.5} = 0.0505$ kmol/m^{3}s.

Rate of change of mole fraction of NO = $dX_{NO}/dt = (R_uT/p) \times d[NO]/dt$.

$dX_{NO}/dt = 8314\times2500/(3\times101325)\times0.0505=3.45$ (kmol/kmol)/s. This is equal to 3.45×10^6 ppm/s.

From $d[NO]/dt = k_G [N_2] [O_2]^{0.5}$, $d[NO] = k_G [N_2] [O_2]^{0.5} dt$.

Assuming that concentrations of N_2 and O_2 do not change much within 0.25 ms, and reversible reactions are not significant, then, $[NO](t) = k_G [N_2] [O_2]^{0.5} t$.

Thus, $[NO](0.25 \text{ ms}) = 0.0505 \times 0.25x10^{-3} = 1.263 \times 10^{-5}$ kmol/m^3.

$X_{NO} = [NO]R_uT/p = 1.263x10^{-5} (8314\times2500)/(3\times101325)$

$= 8.64 \times 10^{-4}$ kmol/kmol = 864 ppm.

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So, now k_G is calculated here, k_G value is got. So, substitute here I know K_P, you know p^o, R_uT everything, so just calculate k_G. So, k_G is calculated here. $k_G = 78.817$. Then rate of NO formation, initial rate of NO formation because we are going to substitute the initial concentrations here.

$$d[NO]/dt = k_G [N_2] [O_2]^{0.5}.$$

$$= 78.817\times0.01155x(0.003071)^{0.5} = 0.0505 \text{ kmol/m}^3\text{s}$$

So, this is the initial rate of formation. So, if you substitute here k_G, initial concentration of N_2, initial concentration of O_2 power 0.5. So, this will be the initial rate of NO formation that is 0.0505 kmol/m^{3}s, that is the initial concentration.

Now, rate of change of mole fraction of N. So, this is the rate of change of concentration. d[NO]/dt is the rate of change of concentration of NO now for calculating part per million per second I will calculate now rate of change of mole fraction of NO which is dX_{NO} by dt which is which is nothing, but $R_uT/p\times d[NO]/dt$.

$$dX_{NO}/dt = (R_uT/p) \times d[NO]/dt.$$

$$dX_{NO}/dt = 8314\times2500/(3\times101325)\times0.0505=3.45 \text{ (kmol/kmol)/s}$$

So, when you do that, you get 3.45 kmol of NO/kmol of the mixture. So, kmol/kmol that is the mole fraction. So, kmol/kmol of mixture by time second so it is 3.45.

Now, what is ppm? ppm is this multiplied by 10^6 that is all. So, kmol/kmol, mole fraction multiplied by 10^6 that will give you the ppm. So, in this case, the initial rate of production of NO is 3.45×10^6 ppm - parts per million per second.

Next what is asked is what is the concentration or the amount of NO produced in 0.25 milliseconds in ppm. For that, you take the rate equation again and now you multiply dt to the other side. So, $d[NO] = k_G [N_2] [O_2]^{0.5} dt$.

Now, in order to integrate this equation, I have to assume a given temperature. So, temperature is now maintained at 2500 K. So, at a given temperature, k_G is a constant. If I assume the concentrations of N_2 and O_2 have not changed much within a small time of 0.25 ms, the time is very low.

So, within the time the significant change in the concentration have not occurred. So, this initial concentration itself can be used here. If I assume like that then this is a constant totally. The k_G, concentration of N_2, concentration of O_2 can be held as constants. So, now, I can integrate this. $[NO](t) = k_G \times [N_2][O_2]^{0.5} \times t$.

Now, for 0.25 ms, I can apply this. So, you know this is the rate, $k_G \times [N_2][O_2]^{0.5}$ is the $d[NO]/dt$ that is calculated as 0.0505 $kmol/m^3s$, so that into 0.25 ms, so 0.2×10^{-3} s.

So, you will get 1.263×10^{-5} $kmol/m^3$ that is the concentration of NO at the time of 0.25 ms after the start of reaction. Now, mole fraction of NO is $[NO] \times R_uT/p$. So that will give you a value for this in kmol of NO/kmol of mixture.

Normally, mol/mol we do not write any unit, but it is kmol/kmol, though that is 8.64×10^{-4} kmol/kmol or multiply this by 10^6, you get 864 ppm. So, 864 ppm of nitric oxide is produced in 0.25 milliseconds. So, this is second example.

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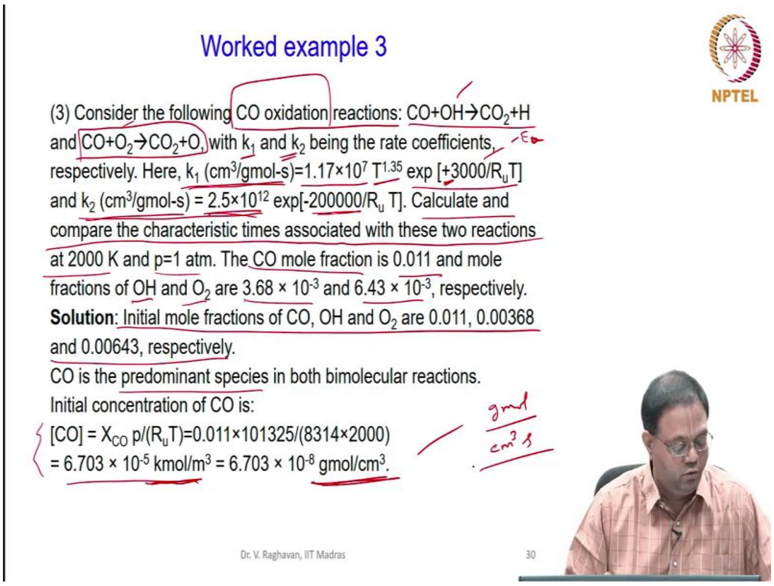

Worked example 3

(3) Consider the following CO oxidation reactions: $CO+OH \rightarrow CO_2+H$ and $CO+O_2 \rightarrow CO_2+O$, with k_1 and k_2 being the rate coefficients, respectively. Here, k_1 ($cm^3/gmol\text{-}s$)$=1.17 \times 10^7 T^{1.35} \exp[+3000/R_uT]$ and k_2 ($cm^3/gmol\text{-}s$) $= 2.5 \times 10^{12} \exp[-200000/R_u T]$. Calculate and compare the characteristic times associated with these two reactions at 2000 K and p=1 atm. The CO mole fraction is 0.011 and mole fractions of OH and O_2 are 3.68×10^{-3} and 6.43×10^{-3}, respectively.

Solution: Initial mole fractions of CO, OH and O_2 are 0.011, 0.00368 and 0.00643, respectively.

CO is the predominant species in both bimolecular reactions.

Initial concentration of CO is:

$[CO] = X_{CO}\, p/(R_uT)=0.011 \times 101325/(8314 \times 2000)$

$= 6.703 \times 10^{-5}\ kmol/m^3 = 6.703 \times 10^{-8}\ gmol/cm^3$.

$-E_a$

$\frac{gmol}{cm^3 s}$

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Third example, you can see, consider CO oxidation reactions. So, CO is oxidized by two species - one is OH and another one is O_2. $CO+OH \rightarrow CO_2+H$. It is a very important reaction and a forward reaction is considered here.

So, we are targeting the consumption of CO, so CO oxidation. So, you are only taking the elementary reaction basically. So, we are taking only the forward reaction to consideration, and determine the time basically that is what we are going to do here.

Similarly, in this reaction also, the forward reaction is taken into account $CO+O_2 \rightarrow CO_2+O$. So, here O_2 is the oxidizer used, in the first reaction OH is the oxidizer used, and the rate coefficients or k_1 and k_2 for these two reactions.

For $CO+OH \rightarrow CO_2+H$, k_1 is the rate coefficient. For $CO+O_2 \rightarrow CO_2+O$, k_2 is the rate coefficient and they are given the expressions also.

Please see the unit is being given cm^3/gmol-s that is the unit of k_1 that is pre-exponential factor of 1.17×10^7, T^m, m is 1.35. Then $\exp(-E_a/R_uT)$. Now, you can see that actually it is plus, you have to remember that. For some equations, it may be so $-E_a/R_uT$.

So, actually the activation energy can be negative, that is what it is here. So, it is only curve fit basically. Based on curve fit you get this. So, $\exp(3000/R_uT)$, so this is E_a, actually this is actually $-E_a/R_uT$. So, this 3000 is -Ea/RuT.

Now, if you see for the k_2 here this is the pre-exponential factor 2.5×10^{12}, you can see that the pre-exponent factor here is 5 orders of magnitude higher than this approximately see its 1.17×10^7, but here it is 2.5×10^{12}. So, the pre-exponent factor is 5 order of the magnitude higher.

Now, activation energy is 2 lakhs it is very high than this. So, you have to keep this in mind. So, which reaction rate is expected to be higher let us see. So, what we have to calculate here is calculate and compare the characteristic times associated with these two reactions at the temperature of 2000 K and 1 atm pressure for which we need the concentrations. The concentration or the mole fraction is given here.

The CO mole fraction is 0.11 and mole fractions of OH and O_2 are very low - 3.68×10^{-3}, and 6.43×10^{-3}, respectively. So, these are the mole fractions.

At this condition these are the mole fractions, temperature is 2000 K, pressure is 1 atm. What is the characteristic reaction timescale?

Now, initial mole fractions are given here. Now, please see that mole fraction of CO is 0.011, and others are low 3.68×10^{-3}. So, keeping that in mind, the CO is the predominant species here, and both are bimolecular reactions.

So, initial concentration of CO is calculated as $X_{CO}\times p/R_uT$. So that you get the concentration as 6.7×10^{-5} $kmol/m^3$. But please see the reaction rate coefficients are having a units of cm/gmol-s.

So, you have to convert this into gmol/cm^3 cube to just use that in the reaction rate. So, concentration of CO which is in kmol/m^3 is now converted into cm^3, 6.703×10^{-8} gmol/ cm^3.

Though based upon the units you have to adjust the units of the concentrations. Then the reaction rate will be in this gmol/cm^3s. Then you can convert it back and so on or you can convert the reaction rate coefficient into kmol/m^3s and so on, that is also possible.

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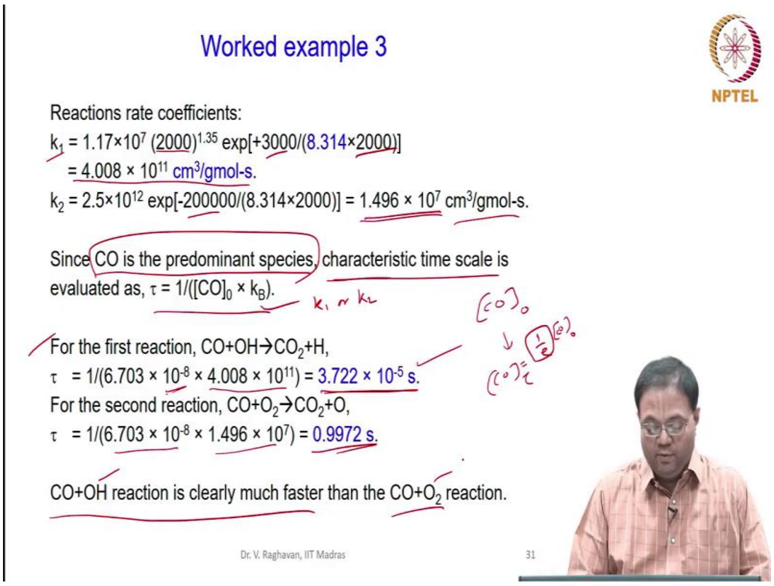

Worked example 3

Reactions rate coefficients:

$k_1 = 1.17\times10^7 (2000)^{1.35} \exp[+3000/(8.314\times2000)]$

$= 4.008 \times 10^{11}$ cm^3/gmol-s.

$k_2 = 2.5\times10^{12} \exp[-200000/(8.314\times2000)] = 1.496 \times 10^7$ cm^3/gmol-s.

Since CO is the predominant species, characteristic time scale is evaluated as, $\tau = 1/([CO]_0 \times k_B)$.

$k_1 \sim k_2$

$[CO]_0$

$\downarrow \frac{1}{e}[CO]_0$

$[CO]_\tau$

For the first reaction, $CO+OH \rightarrow CO_2+H$,

$\tau = 1/(6.703 \times 10^{-8} \times 4.008 \times 10^{11}) = 3.722 \times 10^{-5}$ s.

For the second reaction, $CO+O_2 \rightarrow CO_2+O$,

$\tau = 1/(6.703 \times 10^{-8} \times 1.496 \times 10^7) = 0.9972$ s.

CO+OH reaction is clearly much faster than the $CO+O_2$ reaction.

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Now, the rate coefficients at the temperature of 2000 K is evaluated here.

$$k_1 = 1.17\times10^7 (2000)^{1.35} \exp[+3000/(8.314\times2000)]$$

$$= 4.008 \times 10^{11} \text{ cm}^3\text{/gmol-s.}$$

$$k_2 = 2.5\times10^{12} \exp[-200000/(8.314\times2000)] = 1.496 \times 10^7 \text{ cm}^3\text{/gmol-s.}$$

Just put the temperature there and get the values of rate coefficients. Please see the units, 4.008×10^{11} cm^3/gmol-s for k_1, and for k_2 it is 1.496×10^7 cm^3/gmol-s.

So, even though the pre-exponential factor is 5 orders of magnitude higher, since the activation energy is higher for the second reaction, the overall reaction rate coefficient at the given temperature is 4 orders of magnitude low. That is the important thing you should see. This can be higher the pre-exponential factor can be higher.

But if there is any change in the activation energy that will affect the reaction rate the most. Now, since CO is the predominant species, the characteristic timescale is calculated like this. So, we have already seen bimolecular reaction here a timescale I will just go back and just show you here.

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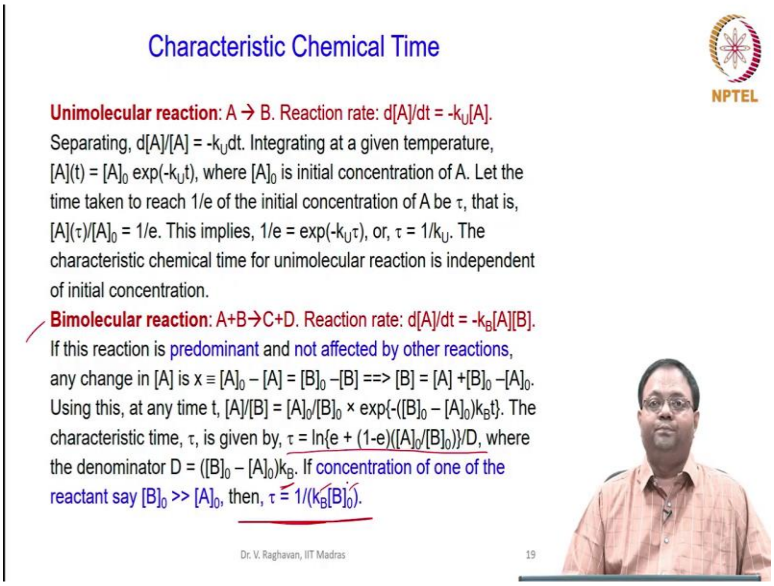

Characteristic Chemical Time

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, $\tau = 1/k_U$. 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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This is the characteristics timescale for the bimolecular reaction what we are considering now. Actually, we have written the characteristic timescale as this involving the concentrations of $[A_o]$, $[B_o]$ etcetera and the rate coefficient. But since one of the species is predominant, we can write the timescale as

$$\tau = 1/([CO]_0 \times k_B).$$

So, in this example CO is the predominant species. The characteristic chemical timescale is nothing but $1/([CO]_0 \times k_B)$. This is k_B can be k_1 or k_2; k_B is bimolecular rate coefficient. In this case, it can be k_1 for the first reaction, k_2 for the second reaction.

So, for the first reaction, τ is 1/[CO] in gmol/cm^3 $6.703\times10^{-8} \times 4.008\times10^{11}$ that will give you this time, 3.722×10^{-5} s. The concentration of CO decreases from the initial concentration of 1/e of the initial concentration within this time τ.

So, this will be equal to 1/e of [CO], initial concentration. So, the initial concentration reducing to 1/e of the initial value, that time is 3.722×10^{-5} for the first reaction.

For second reaction, if we do it, concentration is same, but reaction rate coefficient is substituted here we get almost 1 second. So, the first reaction is very very fast. The consumption of CO by OH is much faster than the consumption of CO by O_2. So, this is very important thing. So, this finishes the worked examples involving the chemical kinetics.