Rate Processes

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Module No. # 01

Lecture No. # 09

Theories of Reaction Rate

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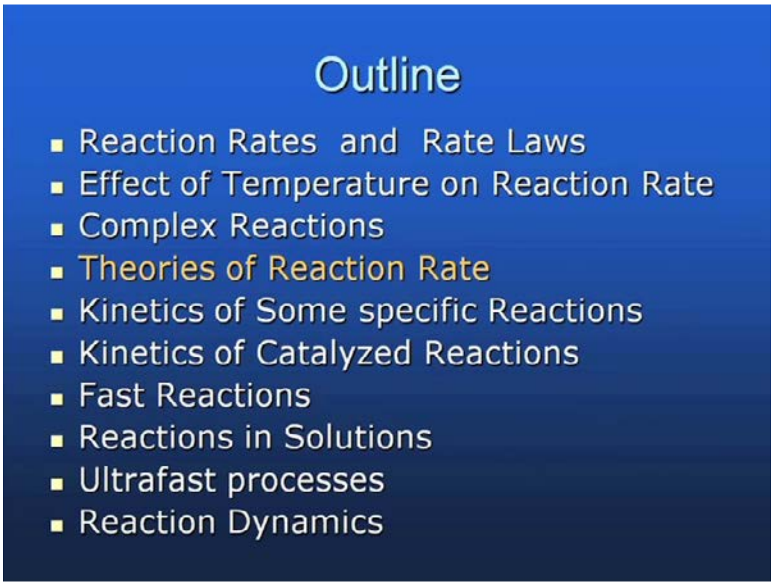

Outline

- Reaction Rates and Rate Laws
- Effect of Temperature on Reaction Rate
- Complex Reactions
- Theories of Reaction Rate
- Kinetics of Some specific Reactions
- Kinetics of Catalyzed Reactions
- Fast Reactions
- Reactions in Solutions
- Ultrafast processes
- Reaction Dynamics

Hello! Good morning everybody. So, today we have come to the fourth topic of our, you know, series of lectures. We have completed reaction rates, rate laws, effect of temperature on reaction rate and then we have completed complex reactions. A great deal of discussion have been made and next is theories of reaction rate. So, we will start this topic from today.

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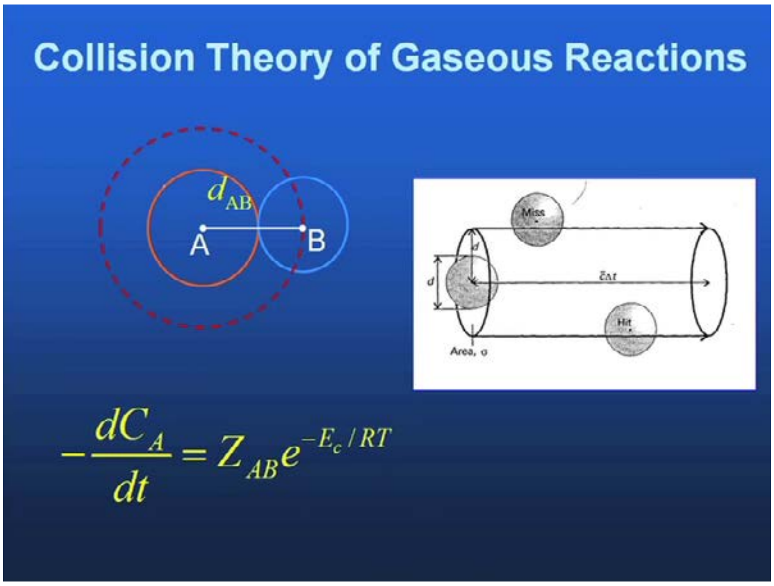

Collision Theory of Gaseous Reactions

$$-\frac{dC_A}{dt} = Z_{AB}e^{-E_c/RT}$$

So, we will start with some elementary idea. So, the celebrated way of, you know what the celebrated theory is the… Or the most elementary theory is the collision theory of gaseous reaction. So, we will start with elementary gas phase reaction, where the mode of the reaction is via collision.

So, all of we…, all of us know that gas molecules, that is, if we confine some gas molecules in a container, then at the given temperature, maybe we are we are confining some volume or some mass of gas molecules. So, what will happen to them is that these molecules will move around. That is, it will move to and fro within the container. And, these molecules are, you know, making collision with the walls of the container. And, this collision is responsible for the pressure that you experience. Ok, gas pressure.

Next is, they are thought according to kinetic molecular theories, these gas molecules are thought to be hard spheres. So, the collisions are thought to be perfectly elastic in nature. And, temperature of gas is a measure of mean random translational kinetic energy.

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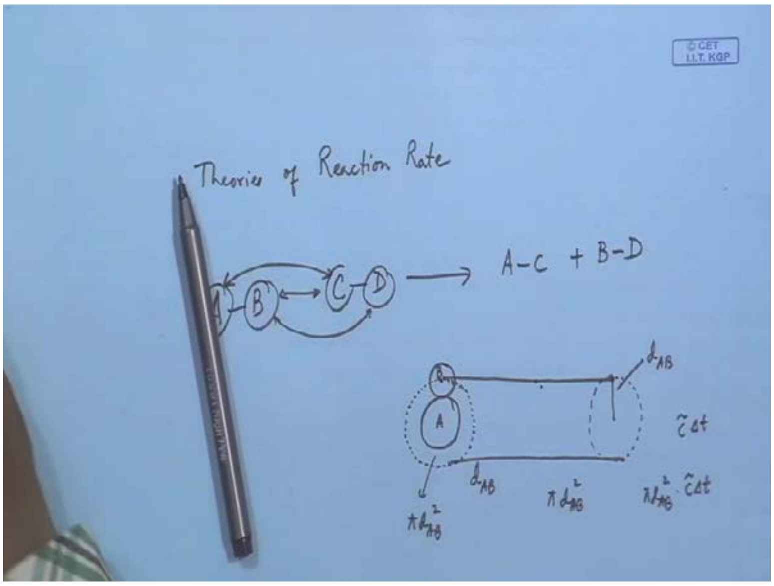

So… and, the thing is that when we consider a simple gas phase reaction; simple gas phase reaction like, say A plus or A-B, there is this set is a molecule. And, it reacts with say C-D. This is another molecule. Giving rise to say A-C plus say B-D. It is a kind of, you know, exchange of portions. Like this portion, these two portions are, you know attached. And, these two portions are attached as a result of, you know, this reaction. So, simplest way; and if this is a gas phase reaction, a simplest way to realize why this is happening is that, if you consider that there is a collision that happened between these two; so, if there is no collision, then there is no chance that, may be this part is coming at a bounding distance to this part.

So, this proximity; that is, they should come; that is, these parts should come close to this part. And, as a result of which, this linkage is established. So, the collision may be regarded as the mode of mechanism that is responsible for this exchange process; exchange of parts of a molecule from one part or from one molecule to another.

So, to have a simplistic idea, we will consider that the molecules or atoms which are undergoing collision with each other. Let us consider that these atoms or molecules are perfectly spherical in nature, may be. All that is difficult assume that a molecule, say it is a… say may be a diatomic or triatomic molecule to be to be spherical. But, for simplicity, let us consider that it is a kind of, you know, hard sphere approximation. That is, sphere is colliding with another sphere and as a result of which we are getting the end product. So, basically collisions are the reason.

So, let us look into this diagram that we have got two molecules. One molecule is A; another molecule is B. And, A is one sphere; B is another sphere. So, and say radius is like this much and the radius for B is this much. So, they will make a collision. If this distance between the centers of A and B is exactly equal to the sum of their two individual radii, and under that condition they will make a collision. So, let us call that this distance to be d AB. So, when d AB is equal to their separation; that is, separation means separation between their between the centers of two nuclei, then there will be a collision.

Now, let us have a sphere like this; say, this is your A sphere and say there is another sphere; say, this is your B sphere. So, if I draw a circle about the center of A with radius d AB d AB. And then, draw a cylinder of this sort. So, this cylinder cylinder is having radius d AB. So, this is d AB d AB. So, what happens is that, if any B molecule is having a position such that, that is in three dimensional space, if B molecule is having a position such that, its center is either within this cylinder, may be here or may be just on this line just on this line, then we can call that there is a chance that this this second molecule B will collide with your A molecule.

So, that means all the molecules of B with their center within this cylinder will suffer the last collision with the molecule of A. That means, with time if this molecule is moving, this A molecule is moving, this molecule is sweeping sweeping, you know, an area which is equal to pi d AB whole square pi d AB square. So, this area is pi d AB square. So, this area, as if this molecule is moving, A molecule is moving, it is sweeping out; swiped out area is pi d AB square. So, volume will be… if it is moving at a, you know, speed say of the order of, if this area is moving at a speed of say C average, then after time delta t delta t, it will make, you know, a cylinder of volume pi d AB square into c average delta t.

So, all the molecules all the B molecules which are within this area, I mean this volume, will suffer the last collision with this A. So, if we if we look into this figure that the center of B molecule is within and here the center of B molecule is outside. So, this is missed and this is hit. Hit means at some point of time, this will make a collision with this one. But, here there is no chance that this will make a collision with this.

So, when there is no collision; that means no question of reaction. But, when there is collision, of course there is an option for the reaction to take place. So, if number density of A molecule is C A; number density means number of molecules of a number of molecules of A in unit volume. If it is C A, then rate of rate of change of concentration of A, rate of change of number density of A with time with a negative sign. Because it is reacting, this A is reacting. We have, you know, the collision rate. That is, number of total number of collisions between A and B into a Boltzmann factor. Why there is a Boltzmann factor? Because not all the collisions are effective or may be, may be you know this represents the… that is the number or the fraction of the total number of molecules having energy. That is the threshold energy, above, either above or just exactly equal to the threshold energy. So, this is the this is the fraction of the total number of molecules having a minimum requisite amount of energy; that is why it E c.

So collision, I mean collision energy you can call that as. So, minus d C A d t is equal to Z AB exponential minus E c by RT. Now, you have to find out this Z AB. That is the collision rate between… I mean the… When you consider the collision between A and B, total number of collisions per unit time. We have to find out.

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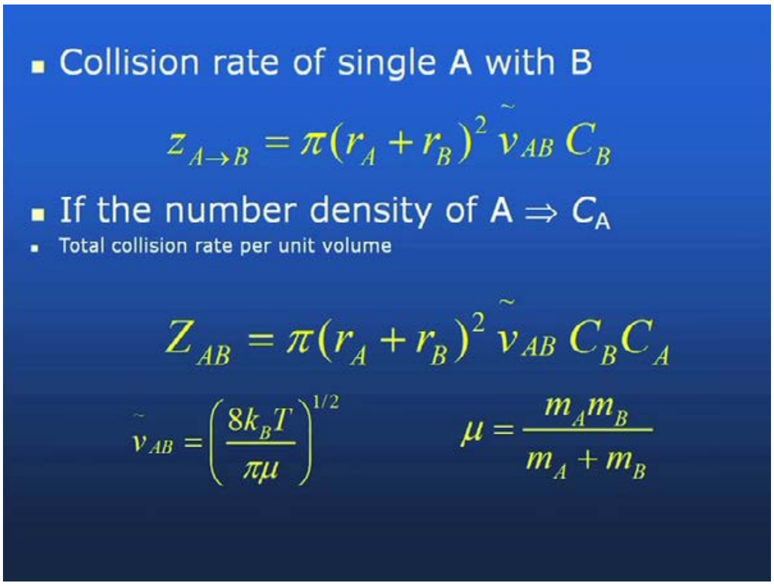

- Collision rate of single A with B

$$z_{A\to B} = \pi(r_A + r_B)^2 \tilde{v}_{AB} C_B$$

- If the number density of A $\Rightarrow C_A$
- Total collision rate per unit volume

$$Z_{AB} = \pi(r_A + r_B)^2 \tilde{v}_{AB} C_B C_A$$

$$\tilde{v}_{AB} = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \qquad \mu = \frac{m_Am_B}{m_A + m_B}$$

So, collision rate; now, you have to concentrate on to the collision rate of a single molecule. Single molecule means, suppose we have got a single molecule of A… which is, suppose by some means we have identified a single molecule which is moving around, and suppose within the continent there is only one molecule of B or or rather A and rest of the molecules are B. So, you would like to know how many collisions are there or how many collisions that this single molecule of A will make with all the molecules of B means per unit time. That That is why it is called a collision rate.

So, let us call this this Z A to B, which is nothing but equal to pi, that is d AB whole square, into v AB average. Why v AB average, I am coming. And, say this is your concentration of B because we have got only one molecule of n, rest are B. So, therefore how many collisions will be, will this single molecule of A will make will depend on the number density of B. If number density of B increases, so this left hand side will increase. So, there is a direct proportionality. There is a direct proportionality between Z A to B and C B. And, of course it will also depend on this v AB. What is this v AB? v AB is the average. You know, the velocity of A B. A B means, suppose this there is a molecule series, say this is A and say this is B. And, see this molecule is static, only this molecule, these molecules are moving. So, what is the relative velocity between A and B? It will be since it is static. So, it will be basically C B or rather I mean because we are using C as concentration. So, let us call this as v B; average velocity of B molecules.

So, in the same way if this is also moving, then the average velocity will be the algebraic sum of this velocity and this velocity. So, the relative velocity will increase if this is moving and that is also moving because that will be an algebraic sum. So, that is why this v AB term has been introduced. If v AB is more; that means, the area swiped out by this circle of d AB in unit time will be more as this average C. This, it may be called as this average relative velocity between A and B, since it is more. So, the volume that it is making because of this movement of this, you know this area pi d AB square will be more. So, more number of molecules, so this will cover more number of B molecules or this will encounter more number of B molecules.

So, that is why Z AB A to B, which is equal to pi r A r B square v AB average into C B is coming. Now, if the number density of A…. Now, you think that we are now putting more of A instead of only single A molecule, putting more than one molecules of A. So, in that case, total collision rate per unit volume. Collision rate means number of collisions per unit time, per unit volume; which is given a notation capital Z AB, which is your pi r A plus r B whole square. Then, of course this because this is the, you know effective volume within which, if some molecule of B is coming, then it will make collision. Time C B, as like the… As it was here. Time C because we have now increased number of molecules of A from a single molecule of A to C A, number density C A.

And from, you know Maxwell distribution of molecular velocities, so average velocity is 8 K T by pi mu. Pi mu means, mu means reduced mass of the system; because now we are considering A and B together because they are moving relative to each other. That is why, you know, this reduced mass and center of mass concept has been introduced. So, that is why v AB v AB is equal to 8 K T by pi mu. So, this v AB at average is equal to square root of 8 K B. of course, this Boltzmann constant by pi mu is the reduced mass, pi is the… constant and mu is mu is m A m B by m A plus m B.

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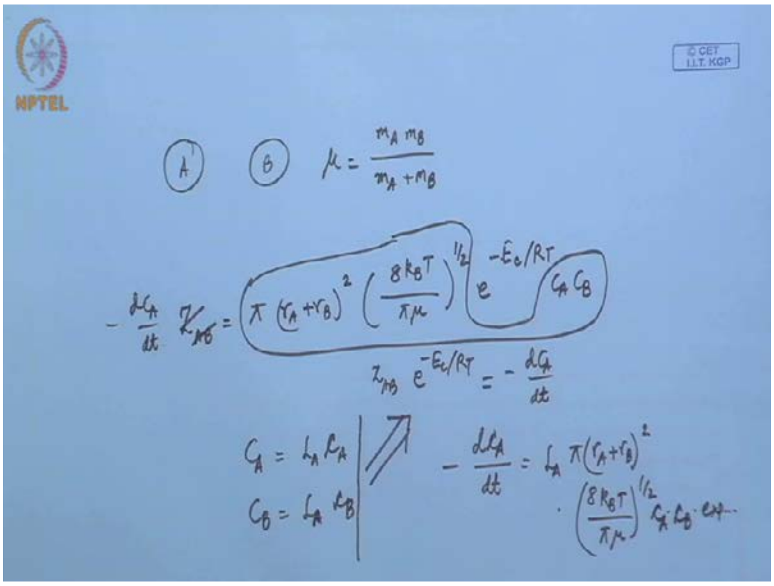

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

$$-\frac{dC_A}{dt} \quad Z_{AB} = \pi (r_A + r_B)^2 \left(\frac{8 k_B T}{\pi \mu}\right)^{1/2} e^{-E_c/RT} C_A C_B$$

$$Z_{AB}\, e^{-E_c/RT} = -\frac{dC_A}{dt}$$

$$C_A = L_A \rho_A$$

$$C_B = L_A \rho_B$$

$$-\frac{dC_A}{dt} = L_A \pi (r_A + r_B)^2 \cdot \left(\frac{8 k_B T}{\pi \mu}\right)^{1/2} C_A \cdot C_B \cdot \exp\ldots$$

So, mu is the reduced mass of the system. That is, as if together say A and B, this mass and that mass together, there is a… This mu means as if this whole system is having a mass mu and which is concentrated at the center of mass of system, of the of this, you know system of masses.

So, mu is equal to m A m B by m A plus m B. So, m A m B, these are the individual masses. So, therefore Z AB is equal to pi r A r B square v AB average C B. So, you can just plug in the expression for V AB and see what we are getting.

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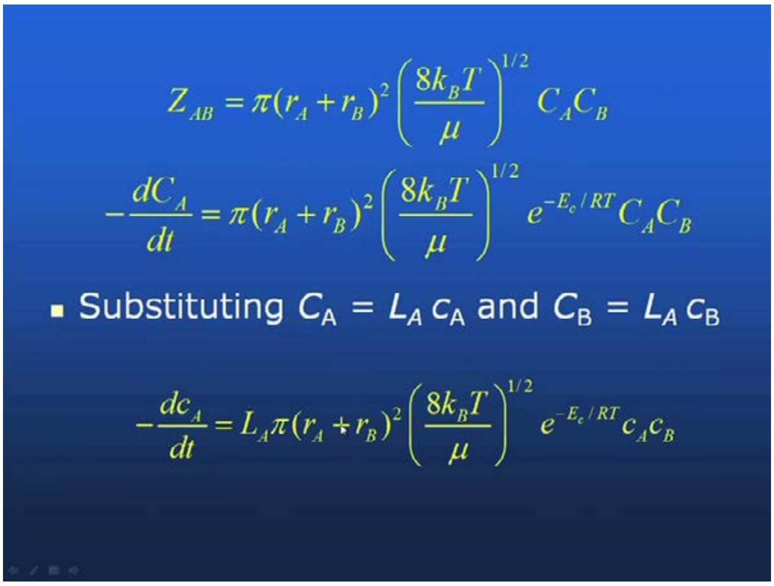

$$Z_{AB} = \pi(r_A + r_B)^2 \left(\frac{8k_BT}{\mu}\right)^{1/2} C_AC_B$$

$$-\frac{dC_A}{dt} = \pi(r_A + r_B)^2 \left(\frac{8k_BT}{\mu}\right)^{1/2} e^{-E_c/RT} C_AC_B$$

- Substituting $C_A = L_A c_A$ and $C_B = L_A c_B$

$$-\frac{dc_A}{dt} = L_A\pi(r_A + r_B)^2 \left(\frac{8k_BT}{\mu}\right)^{1/2} e^{-E_c/RT} c_Ac_B$$

So, capital Z AB which will be equal to pi r A, that is pi d AB square, pi r square; times this is your link that it is covering in unit time, time C A, C B. So, this is the this is the collision rate. That is, total number of collisions that A and B molecules are making in unit time in unit volume. Therefore, if you plug in this on to, in into the original expression, that is this expression, then we get this one; minus d C A d t is equal to pi r A plus r square 8 K B T by mu. Then, of course here there will be there will be a pi because this pi has been somehow it is dropped. In this, so here we have to put pi over here, there should be one pi, there should be pi.

So... So, let me write it over here because there is a little a type anyway. So, Z AB is equal to pi r A plus r B whole square 8 K B T by pi mu to the power half e to the power minus E c by RT C A C B. So, is this the this is the… I mean Z AB, expression for Z AB. So, this Z AB into this will be giving you; left hand side will become, now d C A d t if you multiply, so this is your, this portion is your, basically this one, this portion is your Z AB times e to the power minus E c by RT will furnace you minus d C A d t.

So, this C A is number density per unit volume. If we convert, if you want to convert this to concentration, that is moles per lite; so that will give you, so C A is equal to Avogadro number into C A. In the same way, C B is equal to L B sorry L A into C B. So, in this way, if you plug in this information onto this expression, you will be getting in terms of concentration; that is, moles per liter. It will be d C A d t with a minus sign is equal to L A into pi r A plus r B whole square times 8 K B T by pi mu whole to the power half into C A into C B into exponential term. I am not just writing the exponential, it is basically your e to the power minus E c by RT. So, just make sure that you write here one pi, one pi and one pi over here. This is, there is because of a there is typographical error. So, it was, somehow it was dropped.

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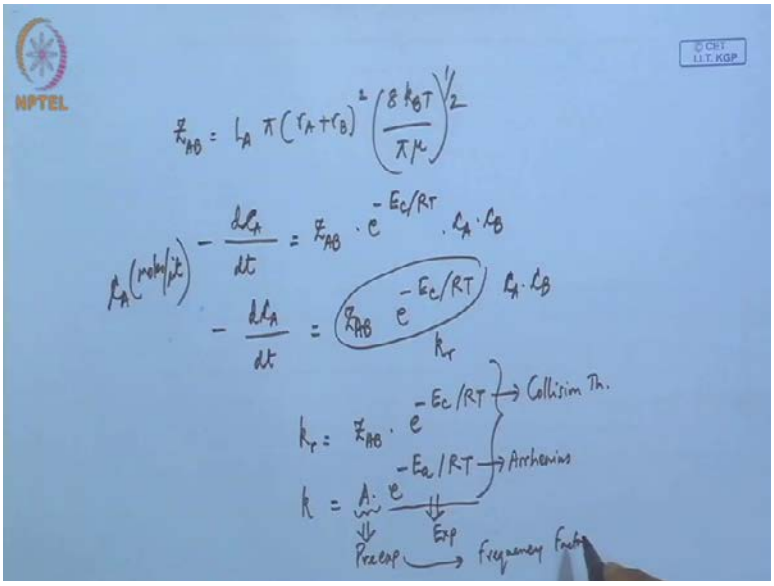

$$z_{AB} = L_A \pi (r_A + r_B)^2 \left(\frac{8 k_B T}{\pi \mu}\right)^{1/2}$$

$$c_A (\text{mol/lit}) \quad -\frac{dc_A}{dt} = z_{AB} \cdot e^{-E_c/RT} \cdot c_A \cdot c_B$$

$$-\frac{dc_A}{dt} = \underbrace{z_{AB}\, e^{-E_c/RT}}_{k_r} c_A \cdot c_B$$

$$k_r = z_{AB} \cdot e^{-E_c/RT} \rightarrow \text{Collision Th.}$$

$$k = A \cdot e^{-E_a/RT} \rightarrow \text{Arrhenius}$$

So, what we are getting then, suppose we are we are, you know writing, we are writing small z AB like this; L A Avogadro number pi r A plus r B whole square 8 K B T by pi mu whole to the power half. So, that will give you minus d C A. Of course, small c d t which is equal to, which is equal to Z AB times e to the power minus E c by RT into C A into C B. So, these are small c not capital. Therefore, therefore, if we compare a general rate equation that minus d C A that is concentration, this in moles per liter. This C A is in moles per liter. d C A d t is equal to small Z AB e to the power minus E c by RT; that means, this is your k into concentration A into concentration of B. So, basically this one is your k reaction rate constant.

So, therefore you can write k r, reaction rate is equal to small z A B into e to the power minus E c by RT. And, if we recall the Arrhenius expression, if we recall the Arrhenius expression, then your k is equal to A into e to the power minus E a by RT. So, now we have got a nice correlation. A nice, you know, analogy between your Arrhenius expression. This is your Arrhenius and this is based on your collision theory.

So, please recall earlier lectures that, I have I have told that this k is equal to A into e to the power minus E a by RT; where this exponential minus E A by RT, this term I called or it is called as the exponential term. And, this is called as the pre exponential term. This is pre exponential, that is a this is exponential. So, this exponential term will, you know, increase with increase of temperature. This we have already discussed. And, this pre exponential term is also termed as your A or the frequency factor frequency factor; that is, it has got some connection with frequency.

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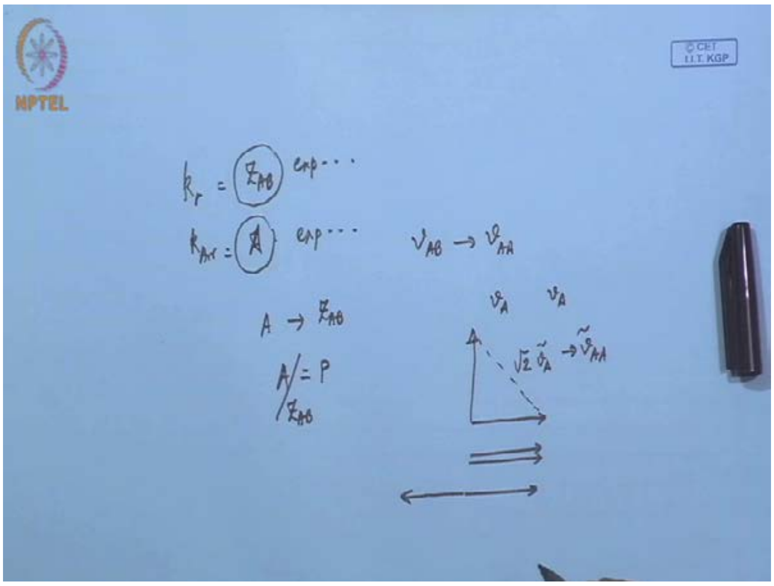

Now frequency factor like, so k r is equal to small z A B into exponential term and your k from Arrhenius. It is I mean A into exponential term. So, this one is your collision frequency; total number of collisions per unit time per unit volume and this is your frequency factor. So, so it has got a good correlation. Therefore, it is… There is a pre exponential term and here also pre exponential term, but in this case collision theory, in collision theory this is your purely, you know, collision term. It may be a little bit complicated, but it has got a close correlation.

Actually, it is found, so therefore therefore A is… We can call that A is basically your Z AB. But, it has been found from various instances, may be after theoretical consideration or may be some experimental findings also tell us that this A is not exactly equal to Z AB for many cases; this small z AB for many cases.

So, it is found that A sometimes is less than your Z AB. So, collision theory may be predicting, is predicting some number as to your rate constant of the reaction at a given temperature. But, when you do the experiment, then it has been found that your pre exponential term is lower than the, predicted by the collision theory. So, in order to account for this apparent, you know, difference between this calculated Z AB and the experimentally obtained A, a new factor has been introduced this way. So, A is equal to, A by Z AB is equal to P, where P is called the probability factor or may be the steady factor also; that means, not all the collisions are effective in making a chemical transformation.

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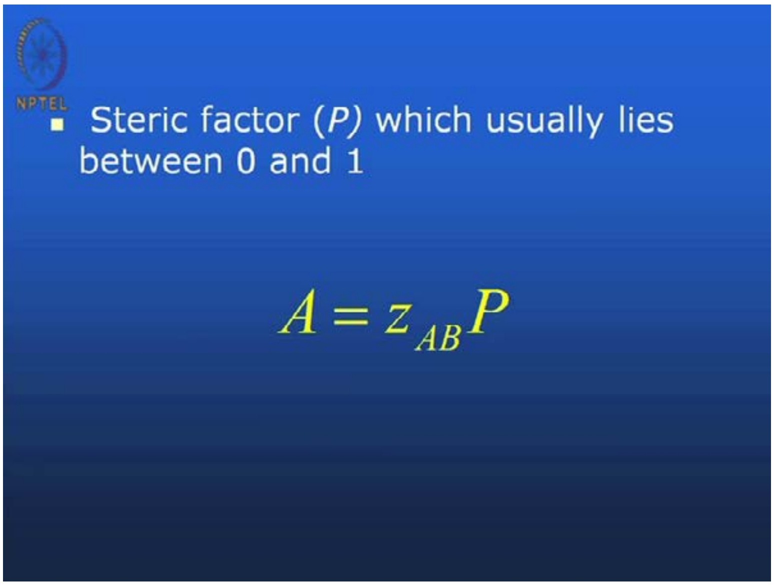

- Steric factor (P) which usually lies between 0 and 1

$$A = z_{AB}P$$

So, probability wise P can be at most one, but it may be less than one. So, it is in between 0 to 1. It may be 0.5, 0.7, may be 0.2, something like that. Now, what is this probability factor? That suppose we have got a molecule of, say we have got these two molecules and suppose that we want to exchange this one with this one. So, in order to exchange this, what do you need? That may be, this will collide this, this one will collide with this molecule, so that there is a direct contact between this molecule with that molecule.

So, this collision may lead to a true exchange of this like, may be after a collision this cover goes to, this cover goes to this one and the cover, this cover goes over to here or may be reserve reverse situation. This collision, so this cover goes to here and the black goes over here. So, this may happen. But, suppose, so this this this is not only the pose in which these two are colliding. Pose may be like this, may be like this or may be in some other way. There is every possibility. That is why only those collisions which are with appropriate orientation, appropriately oriented molecules when undergo collision that may lead to the effective formation of product.

So, may be if collision happens occurs like this, may be this, nothing will nothing will happen. That is why in order to account for this apparent, difference is calculated and the experimentally observed A factor, a new factor has been introduced to take into account of this apparent variation. So, therefore it is called the probability factor. Sometimes it is also related to steric factor. The factor which is arising out of, again with the the system is having a specific orientation, specific geometry or not or maybe, say you have got you have got this, say this molecule and may be this molecule they are colliding, but suppose if this molecule is a little bit complicated one and having some side chains which are covering this head. So, then this molecule, I mean this part of this molecule will not be able to come very close to this part. Therefore, the reaction will not take place.

So, that means, this part may be called as sterically, you know, crowded sterically hindered may be… Commonly used organic, you know, organic terms. So, Organic Chemistry use often use this term. So, this account, this may account for the observed and calculated, you know, number differences.

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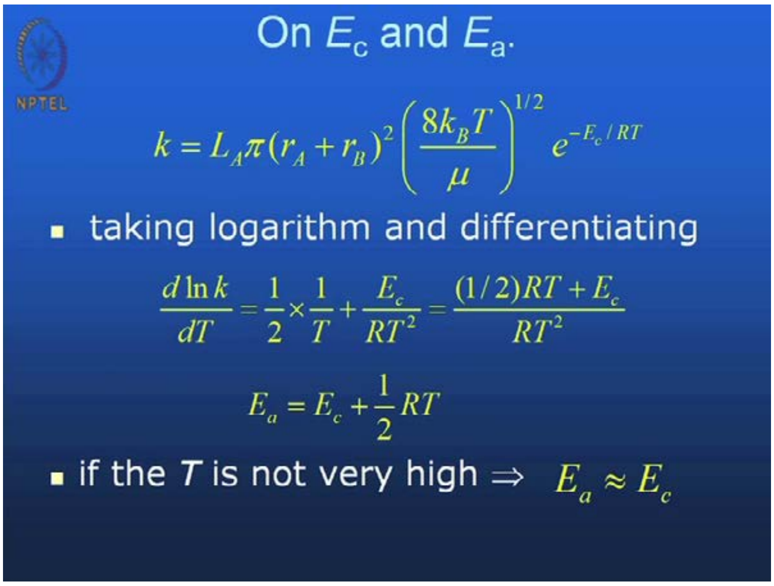

On E_c and E_a.

$$k = L_A \pi (r_A + r_B)^2 \left(\frac{8k_B T}{\mu}\right)^{1/2} e^{-E_c/RT}$$

- taking logarithm and differentiating

$$\frac{d\ln k}{dT} = \frac{1}{2}\times\frac{1}{T} + \frac{E_c}{RT^2} = \frac{(1/2)RT + E_c}{RT^2}$$

$$E_a = E_c + \frac{1}{2}RT$$

- if the T is not very high ⇒ $E_a \approx E_c$

Now, we will we will, you know, talk on E c and E a. Now k is equal to, as I told you, L A pi r A plus r B square 8 k B T by pi, which should be pi mu, you know pi is dropped somehow. I do not know why this happened, anyway, so it should have not dropped, may be some software problem or something, anyway; so, into e to the power minus E c by RT.

Now, you take logarithm and then differentiate. You will be getting d l n k dT is equal to, you know, half RT by E c divided by RT square. So, if you, if you take logarithm and then ln, take ln and differentiate. So, therefore you get activation energy activation energy.

So, basically d l and k dt is equal to E A by RT square. So, this is your E A. So, therefore E a activation energy is equal to E c plus half RT half RT. So, this half RT is coming as a result of may be this term, which is having a square root of temperature dependence. So, k is having one term which is exponential dependence and there is a square root of T dependence. It is coming like this. So, basically E A and E c, they are separated by half r theta half r theta. So, if temperature is not very high, then this term will be small. Therefore, for all practical purposes for all practical purposes we can write E A to be equal to E c. So, this is the, you know, relation between the E c and E a; that is, you know, energy that is collision exponential term which is used in exponential energy term, which is used in collision theory and the term which is used in your regular Arrhenius expression.

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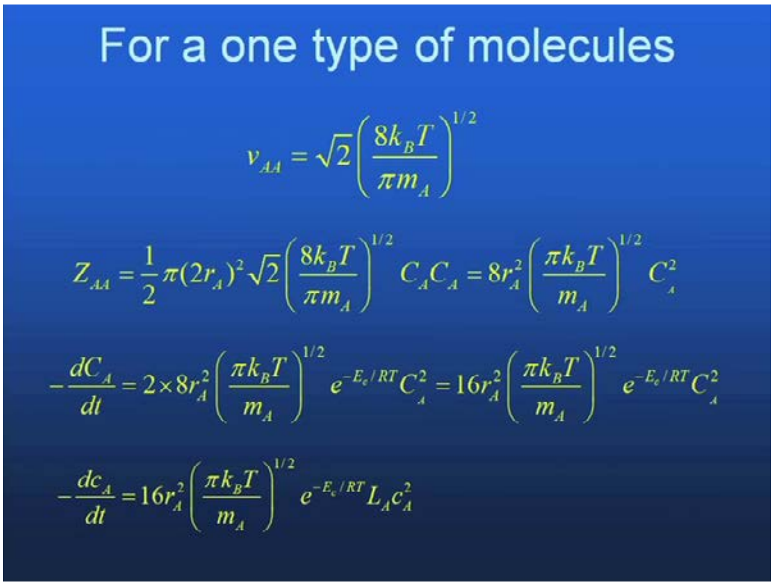

For a one type of molecules

$$v_{AA} = \sqrt{2}\left(\frac{8k_BT}{\pi m_A}\right)^{1/2}$$

$$Z_{AA} = \frac{1}{2}\pi(2r_A)^2\sqrt{2}\left(\frac{8k_BT}{\pi m_A}\right)^{1/2} C_AC_A = 8r_A^2\left(\frac{\pi k_BT}{m_A}\right)^{1/2} C_A^2$$

$$-\frac{dC_A}{dt} = 2\times 8r_A^2\left(\frac{\pi k_BT}{m_A}\right)^{1/2} e^{-E_c/RT}C_A^2 = 16r_A^2\left(\frac{\pi k_BT}{m_A}\right)^{1/2} e^{-E_c/RT}C_A^2$$

$$-\frac{dc_A}{dt} = 16r_A^2\left(\frac{\pi k_BT}{m_A}\right)^{1/2} e^{-E_c/RT}L_Ac_A^2$$

Now for a single type of molecule, these are the corresponding expressions expressions. You can, you can just have a look at it. So, only one type of molecule; so, basically for one type of molecule c A B or v A B should be replaced by a v A A. And, if it is moving at a speed of say v A, another is moving at a speed of v A like this. So, say this one, one is moving this way, another is moving this way. If they are moving in opposite direction their velocity will be 2 A. If they are moving in this direction, on means same direction their relative velocity will be 0.

So, this number is varying from 0 to 2 A. So, what is the average orientation? Average that is, it may have this option or these are other situation is this option. So, average angle, you know, on an average you can call that they are they are at ninety degree. So, this one will be root 2 C A or v A or v average. So, v A A A is your root 2 v A for single type of molecule and the correspondingly you will be getting other expressions. So, for one type of molecule you will have this expression.

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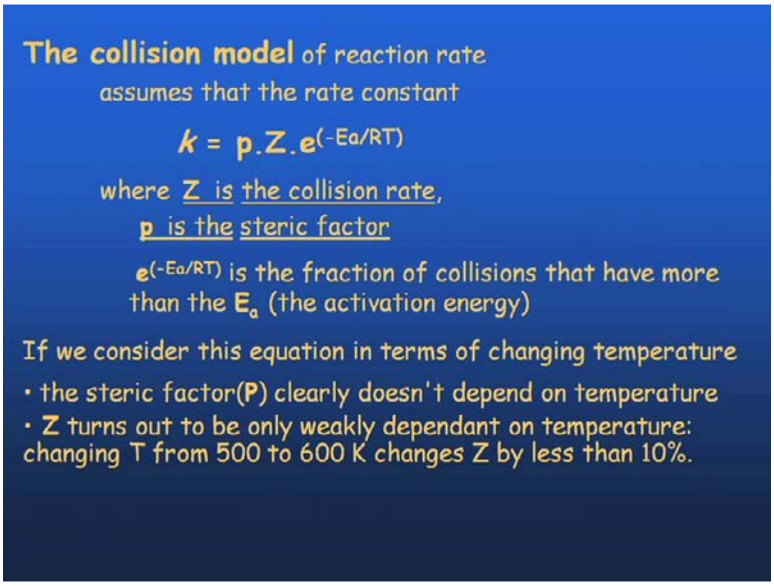

The collision model of reaction rate

assumes that the rate constant

$k = p.Z.e^{(-Ea/RT)}$

where Z is the collision rate,

p is the steric factor

$e^{(-Ea/RT)}$ is the fraction of collisions that have more than the E_a (the activation energy)

If we consider this equation in terms of changing temperature

- the steric factor(P) clearly doesn't depend on temperature
- Z turns out to be only weakly dependant on temperature: changing T from 500 to 600 K changes Z by less than 10%.

So, let us have again this expression. We will start from Arrhenius expression and we will try to, you know, relate this Arrhenius expression with the expression rate; expression for rate constant expression for rate constant after collision theory, which is based on purely collision between molecules. And, this is restricted to gas phase reaction because in solution phase, the situation is, you know, complicated because you know one molecule is moving under the influence of, you know, viscous forces, they are in the solution phase.

So, they are not very free to move around from here to other region of the solution. So, viscous drag is, can complicate can complicate the situation. If we think of the viscous drag that can complicate the situation, so, therefore it is purely, you know, gas phase question. So, it is purely a gas phase description that the collision module of reaction as shows that the rate constant. Rate constant is k which is equal to P is the probability factor. This z means collision rate per unit volume times exponential minus E A by RT. We have just replaced E c by E a because we have just shown that this E c is very close to E a, unless the temperature is very high.

So, and P is the steric factor may be not, which takes into account of the appropriate orientation or appropriate geometry of the molecule with which it is colliding. And, not all the collisions are effective, only those collisions which are with appropriate orientation and having a requisite amount of energy. If the molecule does not have any requisite amount of energy, that is your activation energy, then it will not cross the barrier. So, reaction will not take place.

So... So, this exponential as I as I told this this exponential told you that this, your exponential term e to the power minus E A by RT is the fraction of collisions that have more than the… at least more than or equal to the this requisite amount of energy. So, that is that is called your activation energy. So, if we consider this equation in terms of changing temperature, then, so you should, we should find out. In terms of changing temperature, the steric factor clearly does not depend on temperature and z turns out to be only weakly dependent on temperature. How? You see, it is not exponentially dependent on temperature, this this Z. why? If you come to this expression Z AB, you see this has got a root of RT dependence.

So, it is not very strongly dependent situation. Had this been this been with an exponential dependence, then it would have been a different story. But, it is not the case. So, the steric factor does not depend on temperature. And, Z terms have to be only weakly dependent on temperature. Thing is that, we are giving you an estimate that changing temperature from 500 to 600 kelvin by, that is by a factor, by an amount of 100 kelvin. So, that may change your Z by a factor of ten percent because it has got a root over root over T dependence.

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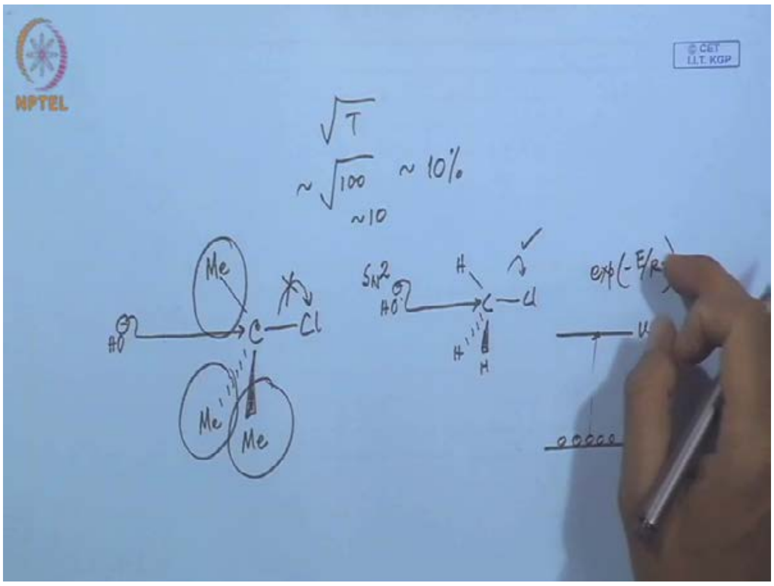

So, difference is about about, you know hundred. So, root over hundred although not exactly, it goes as hundred; will be about 10 percent. That, it it is basically you know ten. So, form 100 to we many may 110 or may be 90. So, it is nothing but a, but a 10 percent change if you move from 500 to 600.

And, steric factor, suppose we have got say a hydrolysis reaction, say tertiary butyl chloride, say like this one, we have got cl and here it is methyl group and you have got OH minus OH minus. So, it will attack from backside. See, this is an this is a celebrated example of hydrolysis of alkyl halide. So, if this had been occurring via SN 2 mechanism, substitution nucleophilic bimolecular, then you will be seeing that it is not a huge; this methyl, these are bulky groups. So, this side of carbon is, you know, this side of carbon is more or less blocked.

So, this OH will not able to approach from this side to displace this one. So, this place. So, this displacement by this backside attack is probably impossible. So, that means, this particular mean, this reaction will not take place in this particular way. That means, this mechanism a mechanism is not a it is not a not an acceptable mechanism for this situation. So, that means, your steric factor says that this reaction will not take place in this mode. But, may be, so in in other case, say you have got methyl chloride CH 3 Cl, in place of three methyl groups you have groups you have got three hydrogen, so what will happen? This OH will, you know, easily attack your carbon from backside and this displacement will take place. This displacement will take place and thereby producing your requisite alcohol in this mode, in this mechanism.

So,... So, this backside attack for this case is not possible, but the backside attack is is possible for this case. So, this proper orientation factor and also this steric factor plays a very… these two play very important role in determining whether some reaction will take place with ease or not. That means your kinetic theory of gas predicts that, that may be this collision, collision between your, may be although it is it is a solution phase reaction. I am just giving you the idea that your collision theory predicts that. If there is a collision between this unit with that unit, then like this, then reaction will take place. But, the thing is that if there is some screening effect that this part cannot come very close to this part, may be there is shielding effect. Therefore, this part may not be able to come very close. So, this part may not be able form a chemical linkage with this part. So that, this this required, some required reaction may take place.

So, that is why steric factor is so important, such an important thing that you should take into an account. And, this is, you know, just to match. The steric factor has been introduced in this expression just to match your experimental result with the theoritically predicted after your collision theory. So, this is just to match your experimental result with your theoretical result. Although, it is very successful in any, many gas phase reaction. This theory predicts react reaction rate quite close to your experimentally observed rate constant. So, in this, you can see that this is the this is the first successful attempt to, you know towards the understanding of a reaction rate, why this reaction is taking place why, you know this reaction rate increases with increase of temperature.

So, so like, if we try to apply Boltzmann distribution, say this is your lower state, say this is you upper state. And, suppose if this molecules, if your molecules do not come to this upper state, it will not be able to proceed for reaction. So, that means you need to put your molecules from here to here by some means; may be by heating that it will acquire energy. And, this molecule will jump from here to here. So that, now these molecules are ready to react. So, Boltzmann distribution says that, the more the energy separation between L and u, the more is the temperature required to, you know, transfer your lower side molecules to upper side molecules; that is, high temperature will tend to increase the reaction rate; low temperature may not be able to do any effect onto the onto the change reaction rate with temperature.

So, that means you are increasing temperature; means you are increasing this factor, exponential factor. This exponential factor, that is, exponential minus e by RT. This factor is a factor; it is your partition factor that how many molecules will be partitioned between these two levels when your energy gap is given, whether more molecules will be here or more molecules will be here. Since, it is higher in energy, so natural tendency is that more molecules will be here. But, as you increase the temperature, some of them will jump from here to here acquiring some requisite amount of energy. And, when this molecules here, then they are ready to ready to you know react. But, again there is a question; becoming ready does not necessarily mean that it will lead to some effective reaction. That means, these are ready, although, but they may collide, they may not collide with requisite orientation.

If they did not collide with requisite orientation, then reaction will have very less probability to proceed further. So, that collision will be ineffective. So, some of the collisions are effective, some of the collisions are ineffective. So, in order to match these two with respect to the total reaction yield, we have to introduce this probability factor. So, this is your Boltzmann factor. That factor if you increase, so more molecules will jump from here. So, more will tend to react. So, it is a, it is a purely collision model and it is purely a, you know classical description that takes into account that this gas phase reactions do occur only by collision only by collision. They will collide and they will they will react. If no collision is there, then you know no reaction.

That means, if you if you radify, I mean if you put some inert gas into reaction mixture, then these molecules will, I mean reacting molecules will get separated from each other. So, separated from each other means, their probability of collision forget about this collision at proper geometry or proper orientation, just the probability of collision will be reduced will be reduced. So, probability of collision reduced means, the reaction rate decreases. So, why this is happening because your rate constant contents two terms, two concentration terms. I mean, number density terms. So, number density terms, you know reduce. Therefore, reaction rate decreases because collision is also reduced.

So, that has a got a very, you know, important consequence. And, this is the first possible way to rationalize reaction rates. And how, why this is happening how you know how temperature can affect your reaction rate. So, that is a very important question. And, that we have been able to, you know, give some justification.

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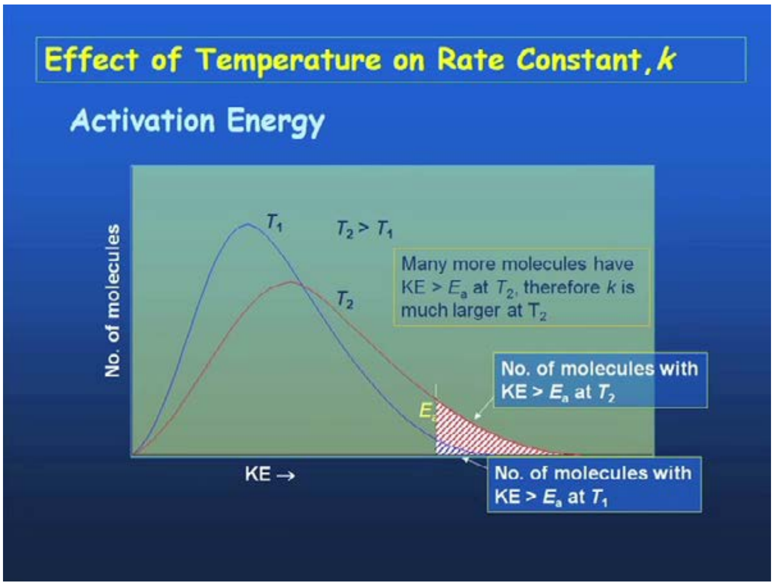

Effect of Temperature on Rate Constant, k

Activation Energy

Many more molecules have KE > E_a at T_2, therefore k is much larger at T_2

No. of molecules with KE > E_a at T_2

No. of molecules with KE > E_a at T_1

In our next slide, we are just trying to understand one point that these two graphs you see that, it is a it is a maximal distribution of molecular velocity. So, it is a number of molecule and this is, you know this way kinetic energy increasing, although this should be plotted. You know, this is your number of molecules and your, this is your number of molecules, I mean number of molecules and this is this is your dnc by n y verses n or. So, what is happening in dnc? So, you are plotting number of molecules as a function of energy may be may be as a function of c also not n, as a function of C.

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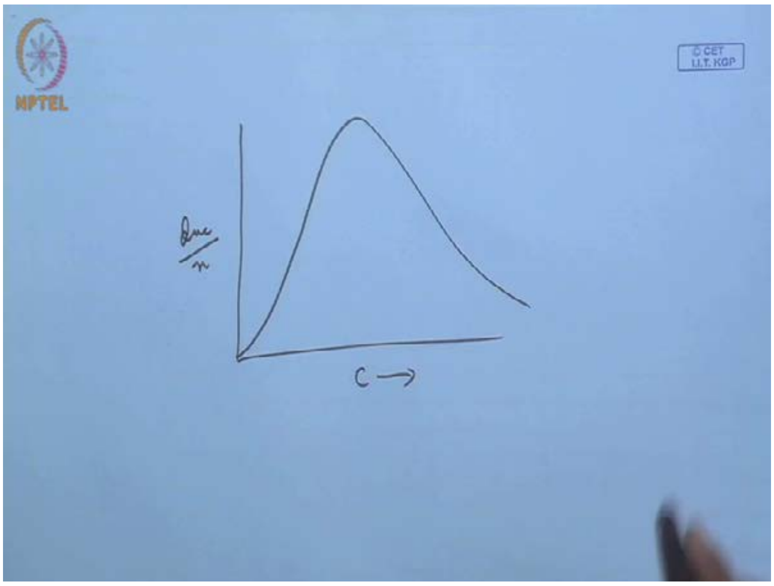

So, it is a, it is plot of number density versus number density verses, it is a plot of number density or dnc by n and your C. This is why it is a C. So, you see that it starts like this and then it is an exponential decaying function.

So, if you if you increase the temperature; so, you see higher temperature, the red graph, it is flattened and your top, this this region is shifted with respect to this term. So, this is your most probable velocity that is, that is a probability of having this velocity, you know, is maximum. It is basically a probability function. So, if you increase the temperature, it is flattened. But, suppose if this is your, this is your line corresponding to energy of activation, actually this plot is the plot of d n c verses C. C means, you know, molecular speed, but this K E with with an arrow means that this way K E is increasing this way k e is increasing. Actually, this is a d n c by n verses, d n c number of molecules with some, with an energy between C and C. I mean, with an energy between C and C mean with a velocity between C and C plus d c… d n c and this is your C this is your C.

So, if you see that this your, this line is corresponding to activation energy. So, this is a graph for lower T and this is a graph for higher T. So, you see that for a lower t, your number of molecules with energy E a or more, is this much. And, if you increase the temperature, this is the total number of molecules it energy equal or more than E a is this much.

So, you see number of molecules increases, as you increase temperature from T 1 to T 2. So, that means you have got more number density with requisite amount of energy, at least requisite amount of energy. So, naturally what will happen? You have got more fraction of molecules, which are capable for doing some chemical transformation. Therefore, increase of temperature leads to an increase in red. That we can successfully explain. And, that is a successful and qualitative explanation. In some cases, it has been found that your, you know calculated one, based on this theory, that is your collision theory, gives you the right estimate for many reactions.

Now, let us sum up. So, in this lecture what we have learnt. So, this is the first attempt to explain your theoretical explanation of your reaction rate, why this reaction is taking place and we have tried to explain and we have tried to understand that collision for a for a homogenous gas phase reaction and collision is the cause of the reaction to take place. So, reaction happens as e result of collision.

So, more the collision, more the reaction. And, somehow if you can increase number of molecules with some requisite amount of energy that is your exponential factor, then you can you can, in principle increase the rate. And, also at a given temperature this depends on this rate constant will depend on not only on this exponential factor that is your partition factor, but also on the factor, that is your collision factor, that is your frequency factor, that is how many number of molecules, how many how many collisions are there in unit time in unit volume; that is, frequency per unit volume. If it increases, then reaction rate increases. And also, in order to account for the fact that in some cases, the predicted number for K has been found to be more than the, than the than your experimentally observed number.

So, in order cope up this, cope with this one, so we have introduced a factor which is called your steric factor, which takes into account that not all the collision are effective. that is, collisions do not means, all the collisions do not take place with the requisite geometry.

So, in this way, we try to have an understanding of this this theory of reaction rates, based on collision theory. It is a purely collisional model and purely based on kinetic theory. and the collisions are thought to be thought to be elastic in nature.

So, in the… in our next lecture, we will talk more on this theories of reaction rate and we will try to try to move on to transition state theory. So, we will have more discussions, more examples to have a complete understanding of theory of reaction rates may be in solution phase, may be in gas phase. So, till then, have nice time. Bye.