Fundamentals of Combustion (Part 1)
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Lecture – 23
Collision frequency of molecules

Let us start this lecture with a thought process from Sir Cyril Norman Hinshelwood who says that nobody, I suppose, could devote many years to the study of chemical kinetics without being deeply conscious of the fascination of time and change: this is something that goes outside science into poetry; but science, the subject to the rigid necessity of always seeking closer approximation to the truth, itself contains many poetical elements. So, basically he is talking about it is an approximation what we are doing in chemical kinetics and it is approximate to a truth it is not the truth ok. .

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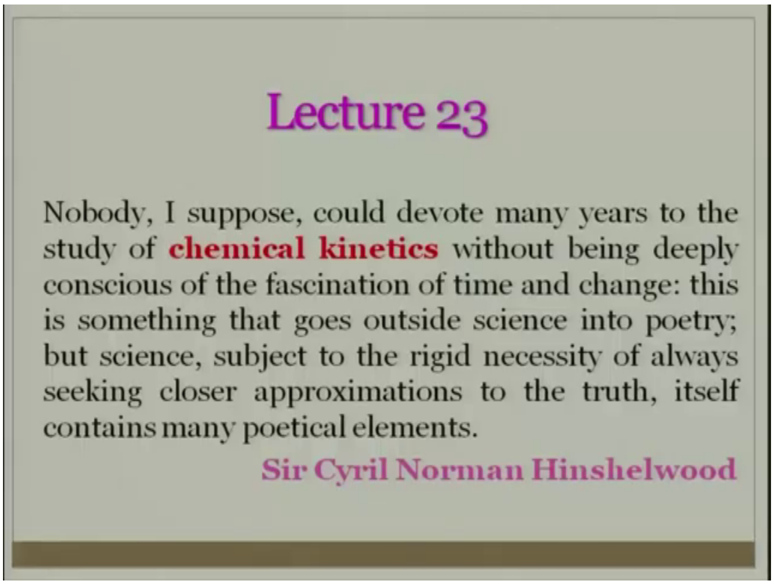

So, anyway we are discussing basically about chemical kinetics and in the last lecture I initiated discussion on collision theory. The collision will be taking place between molecules and even atoms and radicals right. Because these are all moving in a random motion right and even if there is a collision between molecule and a another molecule or a radical then need not to go to the chemical reaction is not it? Will it go to chemical reactions?

Student: Not always.

Not always. So, I will just take one example just to say that why it is not so. Let us say that this is the reaction CH4 is reacting with OH going to CH3 plus water right. If I take the structure C here, let us say H H here right. I will take let us say it is reacting with like OH because this methane molecule is colliding with OH right. OH I can have the like this let us say OH is moving toward that right.

Now will it be any reaction if it is this is the OH, O H and of course, this is your CH4. Now with this H this is going and colliding right. If it is colliding is it leading to the formation of CH3 and water certainly no? This is basically no reaction right. Because each H are similar in nature you know naturally it will be not doing that.

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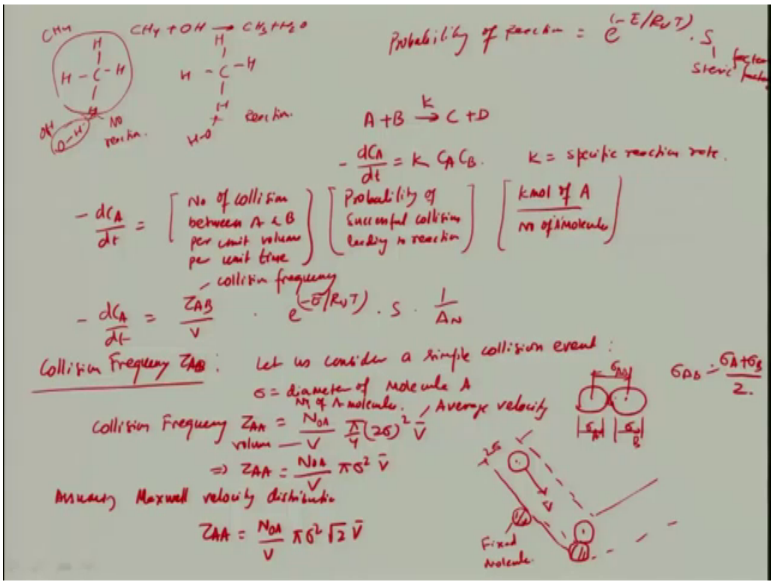

But however, if I take the same example and if it is HO the molecule and it is colliding with here then it will lead to the reaction right. Yes or no? So, this is taken care by what you call a orientation right or you can say geometrically because how it is move getting into. And that is a similar thing we meet several people, but we may not have a good bond right ok. That depends some of the compatibility is important in our relationship. So, that is taken care by a steric factor what we are discussed in the last lecture.

And even if it is oriented properly and it is colliding right of course, the reaction may take place. But we need to look at that it should have a enough energy to break a bond and form a new bond and that energy we call it as a activation energy ok. And we had talked about activated complex leading to that I will be discussing little later on and if you look at and what is the probability of that? That probability of having certain activation energy right leading to a collision what we have looked at is basically probability of you know reaction you can say is what e power to the E by R u T this is one factor and if you compare to your Maxwell function, this is similar terms are there and into steric factor and this is your steric factor.

But why we are talking about it? Why you are talking about it? Because our interest to find out a relationship for the specific reaction rate. For example, if I take the A molecule is reacting with the B going to the product C and D, I want to find out the change of concentration of A with respect to time and keep in mind this is getting consumed therefore, it will be getting negative is equal to k. if I say this is you know forward reaction rate k, then C A and C B. Now our objective is to find out the k is the specific reaction rate and sometime reaction rate coefficient we call right. That is the main objective and if I know this then only I can find out how much concentration of A is changing with respect to time.

Now this will be invoking basically collision theory and then find out. Let us what is that? if I look at from the collision theory of point of view like d C A by d t is nothing but what do you call? Number of collision between molecules A and B right per unit volume and per unit time and then what is the, because not that all collision will be leading to the reaction. There is a probability probability of successful collision leading to reactions. Successful means that, but I am just writing for the clarity. Successful collision means for this case it is only 2 reaction right, otherwise this is not successful. Then kilo mole of molecule A per number of molecules, A molecules I can say A molecules right.

Now if I can say this is basically if you look at number of collisions per unit time means what collision frequency right. That I can write down d C A by d t is equal to Z A B by volume and Z A B is basically collision frequency right into what is that probability we know that is E by R u T into steric factor into this is kilo moles of A per number of molecules A molecules right. What is that? That is nothing but your Avogadro’s number. Yes or no? Kilo moles like per the number of molecules.

That is nothing but Avogadro’s number. So, if you look at now we will have to find out basically collision frequency. For that we will have to go to what you call our molecular theory of gases and find out the, what we did earlier right similar way right. Let us now evaluate collision frequency.

So, let us take a simple molecule collision right. Let us consider simple collision in which molecule A is reacting with another molecule right, with the same diameter right. Let us consider simple molecules right and let us take, let us consider simple collision event. In this event what is happening? The molecule A let us say the molecule A which is moving at a velocity V right average velocity. And it is colliding with another molecules of same diameter keep in mind this is the sigma and this is also sigma. Sigma is the diameter of the molecule right. Sigma is the diameter of molecule A right.

Now when their collision, collision will occur? Only when if you look at when it can happen the collision provided they are of course, touching each other and these diameter will be basically sigma. The center to centre distance between 2 molecules when they are in touch with each other like they are touching each other will be sigma then only if it is more.

Student: Collision.

Collision would not occur right. Now we will consider let us say a case. Let us say there is a molecule here and it is moving right this way right and there is a some other molecule which is similar diameter, but this is fixed. Fixed means is not moving right. Let us say there is a molecule here which is fixed and this molecule has reach here and it has gone with a velocity V average and this is collision occurring here. So, this diameter if you look at this diameter is what this is 2 sigma. This is moving and this is a fixed molecule. We are imagining this not that way. We will go slowly and simplify and just to simplify I am talking about it. .

Now I want to find out collision frequency right collision frequency. I can say Z A A is equal to what will be number of number density right. We know this is number density. What is that? Number of molecules A divided by unit volume right, that is N into if you look at what is this? This is basically I can say alright I can write down A divided by volume right into because I want to find out frequency. So, what I will do there will be collisions right that will be basically this way to volume with which you know the molecules are moving and colliding. Let us say this is between the two mean what you call between two collisions and that distance we call it as a

Student: Mean free.

Mean free path right average distance. And the said volume between two collisions right or the, this thing will be what? Will be pi by 4 2 sigma square right into average velocity. Yes or no? So, that happens to be if I look at this Z A A will be N naught A by V. V is the volume keep in mind this is volume and this is average velocity right. And this is of course, number of molecules A right. This is number of A molecules. Anything I am missing? Sigma is the diameter of the molecule right into pi sigma square V dash. Now keep in mind that this in actual case all molecules will be moving. It is not that fixed it will be moving that molecule this one and this one will be moving right.

Then what will be the average velocity then? If it happens with the same average velocity then it will be root 2. Yes or no? Yes or no? Average velocity will be root 2 V dash. So, for actual right gas in which the molecule is moving assuming of course, the Maxwell relationship velocity distribution Z A A will be N naught A by V pi sigma square root over v dash right. But keep in mind that here what we have assume? The all molecules are having same diameter, but actually it is not.

Let us say that there is a molecule A in this example. There is a molecule B in this example ok. Because I am saying that A is reacting with B. So therefore, the A molecules and B molecules are colliding right. And when this collision will take place? Only when the sigma A plus sigma B divided by 2 will be the diameter right then only for example, if I say this is A right this is B and then sigma A B this will be sigma A B will be sigma A plus sigma B divided by 2, then only collision will occur otherwise, no because if it is far away it would not occur right? Sum of the diameter of A and B divided by 2 that is average diameter right. That distance would be maintained.

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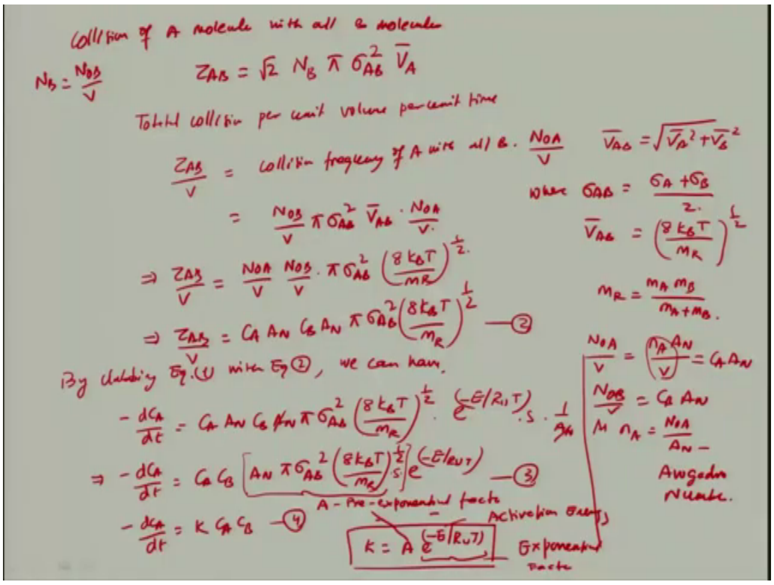

Now if you look at then collision of A molecule with all B molecules right. That will be I can say Z A B will be will be equal to what root 2 into N B and this N B is what N naught B divided by volume ok. N B is nothing but N naught B divided by volume. Yes or no these number densities of the molecule B into pi sigma A B square into V A right. But what we want is basically, basically the collisions of molecule of all A molecule with all B molecules, not A molecule A only not A single molecule of A ok. And what will be that? That will basically total collision for unit volume right. That is total collision per unit volume right per unit time per unit time.

That means, during which all A molecules is reacting with B molecules right, not that only A molecule is reacting with all B molecules. That will be Z A B by volume will be equal to what you call like with equal to what is that? This is collision frequency of A with B with all B into number of molecules for this divided by V right. That means, this is basically N naught B by V pi sigma A B square into V A B average into N naught A by V .

So, what is sigma A B where sigma A B what will be sigma A B? That we have already seen that is sigma A plus sigma B divided by 2. What is V A B from the kinetic theory of gases right. We know that will be 8 k B T divided by relative mass. What is relative mass? Is nothing but mass of A mass of B divided by mass A plus mass B right. So, I can write down here right is equal to Z A B by V is nothing but, N O A by V into N O B by V into pi sigma A B square right into V A B will be what 8 k B T by M R right ok. And keep in mind that this V average A V will be nothing but, root of V A square average plus V V square average right that is the meaning of that is right.

And this we are getting basically from the molecular theory of gases. Keep in mind that what is this N O A? N O A will be what? Can I say this is nothing but your V is equal to what is N O A? N O A is nothing but N A into A N divided by V yes or no? Because number of molecules is equal to we know as N A is equal to N O A divided by A N. A N is your Avogadro's number. This is Avogadro number yes or no number of molecule divided by number of molecules per unit, this thing mole right. So that means, this number of molecule cancel out nothing but mole. Yes or no? So, now what is this one? What is this one concentration right? That is nothing but C A A N. Similarly N O B by V will be C B A N.

So, I can write down right. Z A B is equal to C A A N and C B A N pi sigma A B square 8 k B by T M R. This is relative not I think relative mass half. So, keep in mind that this is the collision frequency per unit volume ok. There will be unit volume. And this is basically provides reasonable good values for A bi molecular reaction. But however, if you look at like tri molecular reactions which is likely to occur the error will be very much it will order of something 10 power to 6 right. Therefore, that is the limitation of this kind of things. Therefore, one has to look at it right and we will have to rely on the experimental values I will be coming to that little later on. .

Now what we will do? Now we will use that thing and then find out a relation for reaction rate right. Let us say this is equation 2, I think I had not told let me get into here. This is equation 1 right. This is equation 1 I am saying I will be using this equation now right. So, by clubbing equation 1 with equation 2 or I could have we can have. So, what I will get d C A by d t is nothing but C A A N C B A N pi sigma A B whole square 8 k B T by M R into e power to the R u T into S into 1 by A N. This A N A N will cancel it out. So, what you will get? You will get d C A by d T is equal to C A C B A N pi sigma A B square 8 k B T by M R e by R u T into S. I am putting S here ok. This is your.

Student: Steric.

Steric factor. And keep in mind that E by R u T is a non dimensional parameter. So, also the steric factor; that means, steric factor is also a non dimensional parameter. And if I consider you know this portion right. These are basically you can say it is a what you call?

Student: Constant.

Constant right now if I will write down this is your let us say equation 3 and then I will write down the what we had done like from the simple the in terms of in terms of the specific reaction constant that is d C A by d T is equal to k C A and C B right. Let us say this I I am saying right now 4. Now if I compare this 3 and 4 what I am getting? I can write down this as A right. A is the pre-exponential factor I am saying. That means, k if you look at I can write down what is k then A R u T. That means, we got a relationship and this is your exponential factor this portion e power is the, is exponential fraction ok. I can say this is exponential factor and keep in mind that this is depend on the temperature and E is the activation energy and A is your pre-exponential factor.

So, with this we will stop over here and we will be discussing more about this specific reaction rate which we have derived from the molecular theory or the considering the collision theory right.

So, thank you very much.