Rate Processes

Prof. M. Halder

Department of Chemistry

Indian Institute of Technology, Kharagpur

Module No. # 01

Lecture No. # 32

Reaction Dynamics (contd.)

Hi, good morning everybody. Welcome back to the class of rate processes and we were in reaction dynamics, molecular reaction dynamics. So, in our last lecture, we started our discussion with molecular reaction dynamics and we started with elementary collision process between structureless reactants like hard spheres. So, basically molecular dynamics is the dynamics of molecular collision. So, dynamics of molecular collision is the study of molecular level mechanism of elementary chemical and physical rate processes. Process maybe elementary chemical or may be elementary physical. Physical means no chemical reaction is taking place. It seeks to understand what actually takes place when a net change that is maybe a physical or maybe chemical is occurring.

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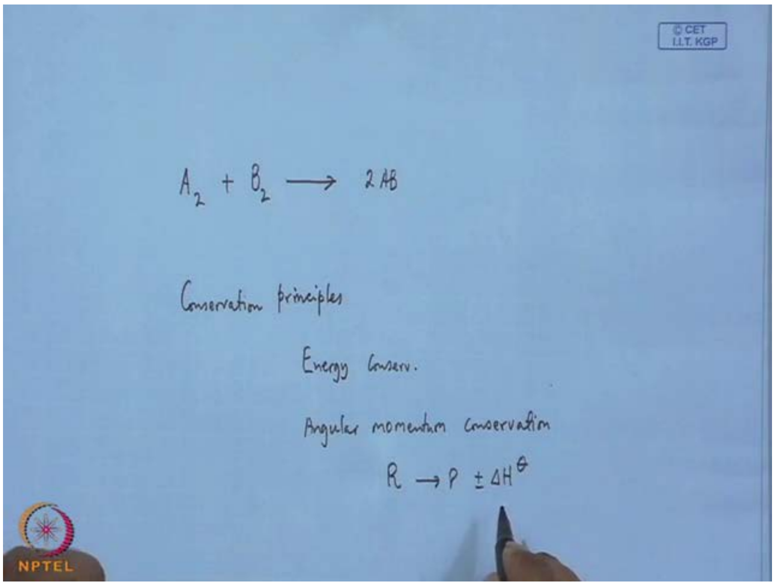

$A_2 + B_2 \longrightarrow 2AB$

Conservation principles

Energy Conserv.

Angular momentum conservation

$R \rightarrow P \pm \Delta H^{\theta}$

Suppose two gases are its like A2 plus B2, I mean diatomic gas, one A2 another B2 is introduced in a container and maybe what is seen is that no reaction is taking place. We are expecting maybe 2AB but reaction is not taking place. Collision occurs between A2 and B2, but no exchange of atom is there. So, we would like to study possibility of such elementary reactions, and like we want to probe, and we want to promote maybe. So, this is what we are going to elaborate, this particular point.

Now, in our last lecture, we have been discussing these conservation principles. Conservation principles, that is, energy conservation and angular momentum conservation, maybe rotational angular momentum and maybe orbital angular momentum or a combination of that. That is in between your reactant to product. There has to be conservation of energy. Suppose, this reaction leads to a change in enthalpy of this much, so maybe plus minus whatever, so left hand side total energy and the right hand side total energy. That should be conserved in the same way left hand side total angular momentum and right hand side total angular momentum must be conserved.

Now, next are the forces and potential energy factors. Now, forces like molecular forces are operative like that is the we would like to understand the forces which control the interaction forces that control the interaction.

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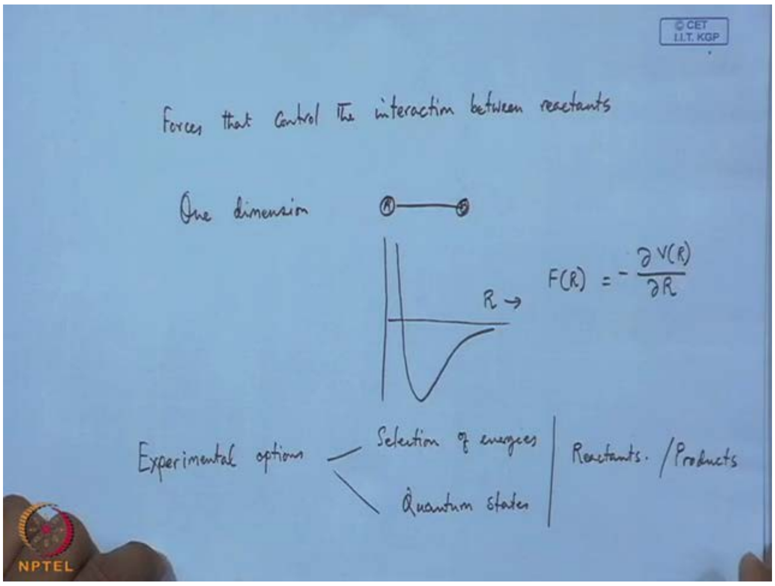
Forces that Control the interaction between reactants

One dimension

$F(R) = -\frac{\partial V(R)}{\partial R}$

Experimental options — Selection of energies / Quantum states | Reactants. / Products

Interaction between reactants in one dimension for a diatomic system like AB diatomic system, the potential energy curve looks like something like this with separation, where FR force is minus del v R del R. So, it is in one dimension, but suppose, two reactant molecules are interacting like this, then it no longer remains confined in one dimension. Rather a three dimensional description of this potential is needed which is called the potential energy surface. In that case, I mean a multi-dimensional description is required like in that case only this coordinate is not sufficient; maybe another coordinate has to be introduced in order to account for the approach of another reactant from all possible directions.

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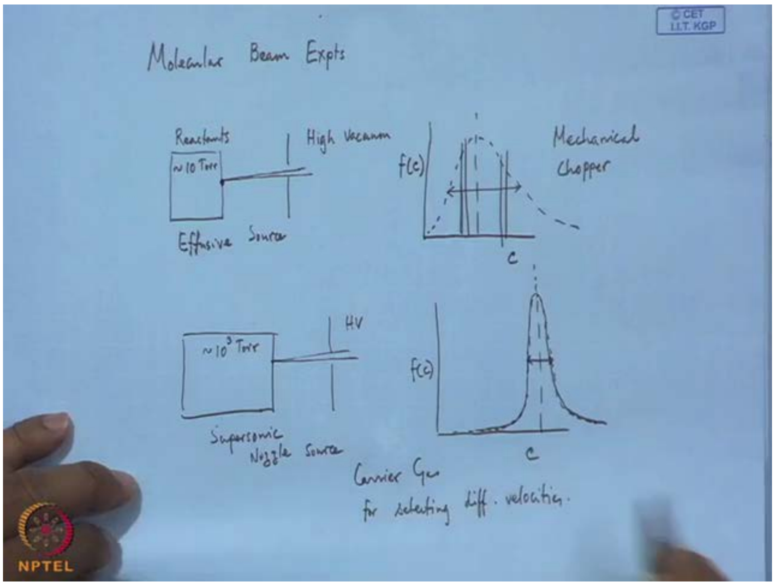

Now, next we will move onto experimental options that is, we have to select the energy and quantum states of reactants. So, selection of energies and quantum states for reactants and also in the same way we have to probe the energies and population and quantum state populations in the product as well, that is the product which is created, which is formed because of reactants, so reactants and also products. We have to ensure that when there is a distribution distribution in different quantum states for the reactants and also for the products, then that should not be scrambled due to collisional exchange of energy. So, that has to be ensured. So, that is why we have to adapt a very specific technique.

One technique could be Molecular beam. Molecular beam experiments, what is that? That you have got a container in which your reactants are there, so gaseous reactants and there is a small orifice. Maybe it is pressure is of the order of several torr, maybe of the order of 10 torr and this side there is high vacuum. So, from the source, this reactant will effuse like this, so this source will act as effusive source and the distribution of various speeds will be fc will be something like this. It is like this distribution of speed and average energy will be in the lower side.

Now, another situation could be created like that you have another source where I mean, where the pressure is very high. Pressure is very high means of the order of 10 to the power 3 torr and of course, this side is high vacuum. So, the molecules will come from higher pressure to lower pressure side high vacuum and this source will act as a supersonic nozzle source. Your distribution fc versus c will be more shifted in this region and it will be narrower but you see this one and that one, it is more shifted to this direction. So, it is a supersonic source where you are getting a narrower distribution but here it is a wider distribution and this is more wide compared to this one, this is less.

So, velocities can be selected with here, in this case, we use a mechanical chopper. Chopper can be used to select different velocities, I mean like you can select maybe this portion, maybe this portion with the help of a mechanical chopper but what will happen for this. In this case, you have to use a different carrier gas different carrier gas to select velocities. I mean velocities can be tuned with the help of various carrier gas, maybe carrier gas means maybe nitrogen maybe like argon means the gas which are not reactive. You can select with the help of carrier gases you can select various velocities.

Next, what we can measure from this from such an arrangement, I mean molecular beam experiment, what we can measure? What is the net in using such molecular rearrangement, that in one case you use an effusive source, in another case you use supersonic nozzle source. So, here you have to use carrier gas for selecting different velocities.

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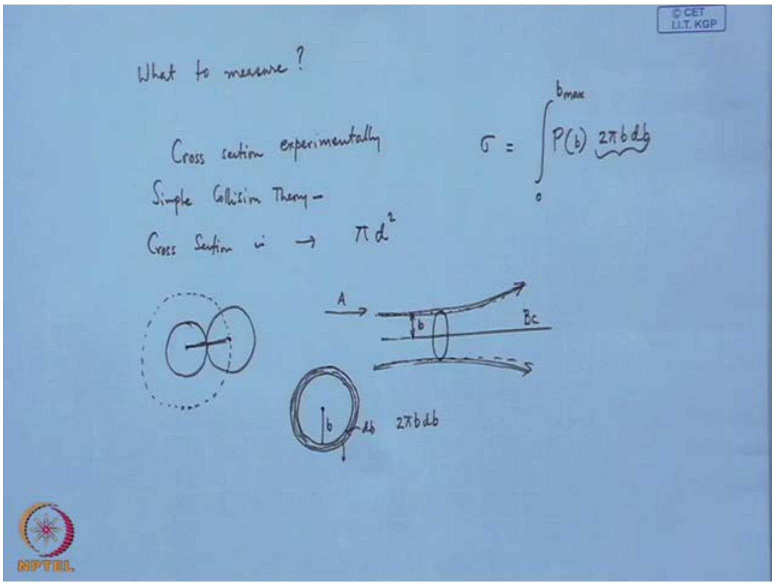

What to measure?

Cross section experimentally

Simple Collision Theory –

Cross Section is → πd^2

$$\sigma = \int_0^{b_{max}} P(b)\, 2\pi b\, db$$

So, what are you going to measure? What can be measured? So, what to measure what to measure what to measure? Now, we want to measure cross section experimentally reaction cross section. So, reactions cross section experimental. Now, reaction cross section maybe regarded as an effective target target area for the reaction to occur. It is the effective target area. Target area means, suppose you have got a dartboard and you want to throw the magnet on it. So, your dartboard is the effective area and suppose those situations where magnet gets stuck onto the dartboard corresponds to an effective collision and reaction. So, that means within that particular area if you can throw if you can keep your target and if you can hit that, then reaction will take place. You can think in that way.

So, it is the effective target area for the reaction to occur. Now, in simple collision theory we started with collision theory that it is an elementary process. That is if you go back to our earlier one of our earlier lectures that if you think of reaction mechanism, you will be finding that sometime it is complicated and it is composed of a number of elementary reactions. It is not that simple A and B combining aa plus bc giving rise to ab plus c. It is not simple reaction something happens suppose the mechanism is such that say bc disassociates to form b and c and then a plus b producing ab. It may happen; it may so happen or maybe in some other way. So, basically it is composed of a number of elementary reactions and each elementary reaction can be considered to be like means if it is gas phase reaction like is occurring maybe via collisional mode. So, using elementary collision mechanism where collision is the means by which reaction is taking place. If it is an atom exchange reaction, say if the collision is effective, then atom is exchanged from one entity to another entity giving rise to a product. So, that is why we started with simple collision theory.

The number of collision is very much important, I mean it is an important factor but not all collisions are effective. Only certain fraction of the total collisions is effective in bringing a chemical change. So, in simple collision theory you know this cross section is defined as pi cross section. So, simple collision theory cross section is defined as is basically pi d square where d is the sum of the radii of two spheres like this is one sphere and this is another sphere. So, maybe some of the radii so, this is your cross section, so this plus that this is your d. So, basically suppose we have got say Bc like this, this is your Bc and its cross section is like this and say A is approaching this way, so maybe it will approach it may do something like this. So, it moves this way, it is approaching from this side, so A is going this way so what is this? So, if you think in this way that you have got a two concentric circles.

So, this is say b and this will be say db, say this is db. So, this area between the two concentric circles this area will be 2 pi b db. Now, what is this b? Say this is b, now if we think of simple collision theory thinking in terms of collision theory that b is the b can be regarded, so you see that this is the closest approach I mean the closest that A reactant can approach this Bc. It can be maybe more than that but that is the closest approach because that will give some effective collision. So, the distance of closest approach of two particles in absence of any external force. If there is any other force then it may be different but in absence of any external force, this could be the closest approach, so b may be regarded as the distance of closest approach and it is a measure of closeness of collision. If b is small collision is more, if b is bigger than collision probability will be less.

Now, in classical physics, now the cross section is defined in this fashion that sigma is the cross section which is nothing but equal to a function. A function which you know represents the reaction probability, so Pb that is probability with b value Pb into 2 pi b db. So, 2 pi b db is this, then it is a probability factor which is called the probability reaction probability or it is called the opacity function and you have to integrate from 0 to say b max. So, maximum value of b that one can reach.

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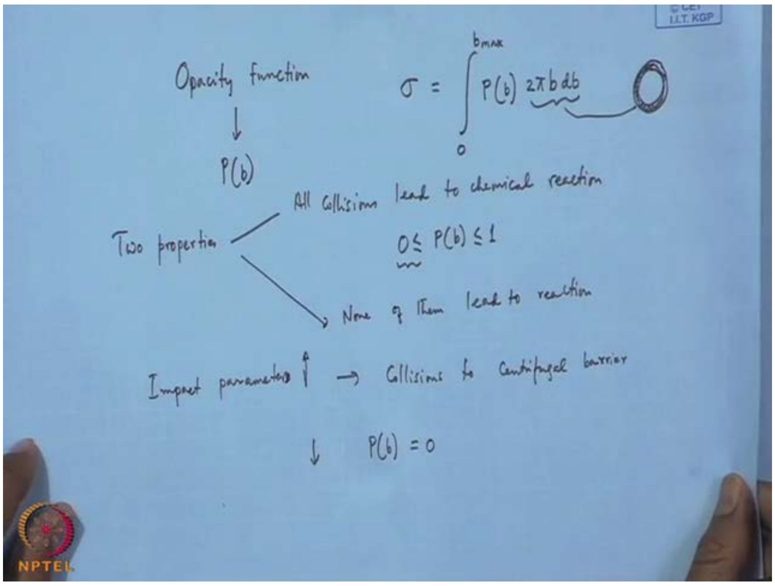

Opacity function

$\downarrow$

$P(b)$

$$\sigma = \int_{0}^{b_{max}} P(b)\, 2\pi b\, db$$

Two properties

All Collisions lead to chemical reaction

$0 \leq P(b) \leq 1$

None of them lead to reaction

Impact parameter $\uparrow$ $\rightarrow$ Collisions to Centrifugal barrier

$\downarrow$ $P(b) = 0$

What is this Pb? Pb is the opacity function and it represents the fraction of the collisions with impact parameter b that gives rise to chemical reaction. What is this opacity function or reaction probability function? Let us try to understand, what is this opacity function? So, remember the expression cross section sigma is equal to integral 0 to b max Pb into 2 pi b db, so 2 pi b db is coming from this area, so 2 pi b db is this.

Now, this reaction cross section governs the rate of those collisions that lead to a chemical reaction. Now, it is a measure of the effective size of the molecule as determined by their ability to reaction and it is necessarily smaller than the total collision cross section which governs the rate of all collision. As the reactant collide at a given energy when there is a collision, then we characterize the initial approach in terms of the impact parameter and we define in terms of this opacity function Pb and it is the fraction of the collisions with impact parameter b that leads to chemical reaction. This opacity function has two properties; one is at most all collisions lead to reaction, so Pb could be unity, so all collisions lead to chemical reaction. So, that means this value I mean it will be 0 less than equal to Pb less than equal to 1. I mean when this is 0, that means other possibility is all will lead to chemical reaction and none of them lead to reaction, so that is why this range. So, P b will range from 0 to 1 in between 0 to 1.

So, if it is 100 percent, then P b will tend to be 1. If it is nothing, then P b will be very close to 0 and for a chemical reaction to occur, it is necessary that atoms or reactants to approach closely, so that chemical forces will operate and necessary atomic re-arrangement may be possible. For high impact parameter collisions, I mean when impact parameter is high, the collisions occurring at the centrifugal barrier, so collisions to centrifugal barrier and this will act to keep molecules apart. So, since it is centrifugal barrier means it is a repulsive barrier, so this will tend to make them apart.

So, when impact parameter b is high collisions to centrifugal barrier and leading to less reaction, therefore expect that reaction will only take place when b is small. That is when impact parameter is less that is of the order of range of impact parameter, I mean order of range of intermolecular forces then reaction will take place.

So, if Pb is 0, then reaction does not take place and that corresponds to high value of b. So, in terms of opacity function Pb what can we write? So, thing is that if the impact parameter b is high that is it is a measure of closeness. So, impact parameter high means collisions to the centrifugal barrier and if impact parameter less, then intermolecular force are operative and a reaction may take place that is when b is small that is of the order of range of intermolecular forces, then the reaction is expected to occur.

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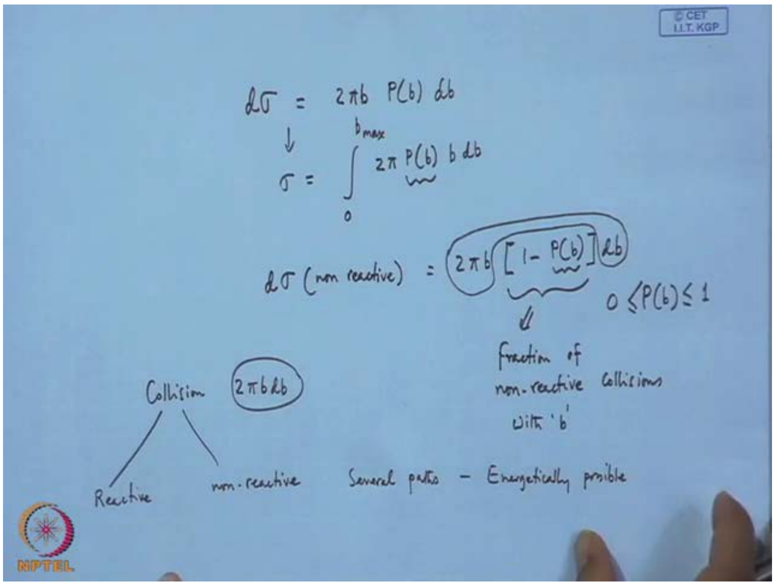

$$d\sigma = 2\pi b\ P(b)\ db$$

$$\downarrow$$

$$\sigma = \int_0^{b_{max}} 2\pi\ \underset{\sim}{P(b)}\ b\ db$$

$$d\sigma\ (\text{non reactive}) = \boxed{2\pi b\ \underbrace{\boxed{[1 - \underset{\sim}{P(b)}]}}_{\Downarrow}\ db}$$

$$0 \leq P(b) \leq 1$$

Fraction of non-reactive collisions with 'b'

Collision $\boxed{2\pi b\, db}$

Reactive

non-reactive

Several paths - Energetically possible

Now, in terms of opacity function again we can write the reaction cross section sigma or rather d sigma which is equal to twice pi b pb db. Then if you integrate, then you will be getting sigma upon integration you will be getting sigma is equal to integration from 0 to some b max 2 pi Pb bdb. This way you can express sigma. Now, here 2 pi b Pb db is the element of total collision cross section and Pb is the fraction of effective collision.

Now, what happens is that total cross section, I mean cross section for the reaction, may be it is divided into effective and non-effective that is reactive cross section and non-reactive cross section. You can subdivide into two. So, in that way for non-reactive cross section you can write d sigma non-reactive which is equal to twice pi b into 1 minus Pb into db. So, Pb is the effective and as I told you that P b will range from Pb will range like this. It is a measure of effective I mean probability of reaction to occur. So, that means this represents the probability of reaction that is not I mean means probability that reaction will not occur. I mean the collisions which are ineffective, so non-reactive cross section may be retained in this fashion non-reactive cross section. So, this is the total cross section, I mean reactive cross section and this is the non-reactive cross section.

So, that is this factor, this factor is the fraction of collisions that are non-reactive with impact parameter b. So, impact parameter may have some value but may be this means with given impact parameter this is the fraction of the collisions that are not reactive, so fraction of non-reactive, reactive, non-reactive collisions when of course, with impact parameter b.

So, we have to remember one point that while we are distributing, we are partitioning you know the impact parameter, I mean partitioning the cross section into reactive and non-reactive one. So, collisions reactive and non-reactive, so while partitioning in between this you note that while we are partitioning between these two that some of the cross sections will have always means we have to partition in such way that the sum of the cross sections will have to be like total will be like this. Sum of the total we have to partition in such a way that it will be 2 pi b db irrespective of whatever it is.

That means, if the reaction has several different paths, then what is needed? Now, suppose if the reaction has several paths which are energetically possible of course energy. If energy does not permit, then it will not happen, so energetically possible, then if out of many paths suppose one path is promoted I mean one cross section of one path is if it is increased, then that has to affect the other. I mean that should increase at this expense of the reduction of the order path, so that is very important.

So, that means the cross section of other path which is energetically possible, the increase of cross section can happen at the expense of the decrease decrease of another, that is or the at the expense of non-reactive cross section. That is maybe non-reactive cross section will be reduced and that will be transferred to a that will be converted to a reactive cross section but it will never be more than 2 pi b db when the impact parameter is b. So, that is the limit that is 2 pi b d b is the limit and final outcome of collision with b in the range b to b plus db, I mean you have to think of that b is ranging from b 2 b plus db, so that this value becomes 2 pi b db. So, reaction cross section I mean you can think in this fashion.

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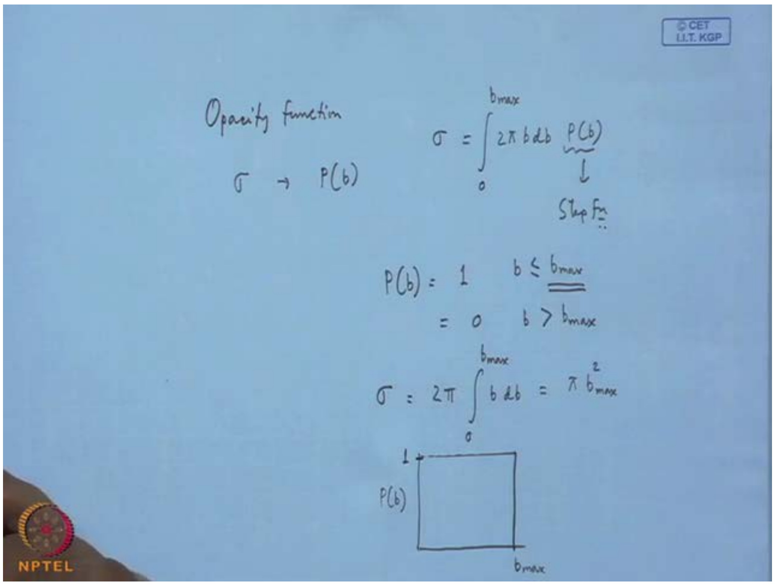

Opacity function

$\sigma \rightarrow P(b)$

$$\sigma = \int_0^{b_{max}} 2\pi\, b\, db\, \underbrace{P(b)}_{\downarrow}$$

Step Fn

$$P(b) = 1 \quad b \le b_{max}$$
$$= 0 \quad b > b_{max}$$

$$\sigma = 2\pi \int_0^{b_{max}} b\, db = \pi b_{max}^2$$

Next, let us look into a simple opacity function. Now, determination of reaction cross section cannot uniquely specify Pb. So, if you determine reaction cross section sigma it cannot uniquely determine Pb but it determines its b weighted value, I mean basically it is integration between 0 to b max, so it is cross section 2 pi b db into Pb. Since, P is dependent on b so when you determine this you will be getting the b weighted magnitude. Let us rather than trying to find out this Pb, let us assume some simple functional form with view with very few parameters to understand it.

Now, let us think in this way that we have a step function of kind I mean let us have its functional form like a step function such that Pb, let us think in this way Pb is equal to 1 when b is less than or equal to b max and is equal to 0 when impact parameter b is greater than b max. So, this will be just like a step function that it remains flat for certain situation and then it becomes 0. So, this is the cut-off value means somehow if b is a little more than b max, it will give you 0, so it has to be within b max then it will be 1. So, it is a step function, that is the b max is the highest b with which the reaction can only occur and beyond that it will be 0. So, in that case what will happen is that your sigma will be equal to twice pi integration from 0 to b max, b max your b db.

In that case, it will be giving you pi into b square max. So, this way you can think of. So, you have got your Pb 1 for certain value that means you say its representation is I mean graphical presentation is Pb. It is say 1, which remains this much and this is your say b max, so this is 1. So, beyond you know b max the value it is just like a step function, it is a square pulse kind of thing, so it is 1. So, in that way you will be assuming some specific functional form means rather than rigorously trying to determine the determine Pb, consider some simple case and then you should be able to find out the sigma.

So, this is about impact parameter and the opacity function that is the reaction probability function. So, where are we at? Now, Pb is the opacity function is the reaction probability function which is also termed as the opacity function and the it represents the fraction of collisions with impact parameter b that will lead to chemical reaction. Therefore, cross section, so cross section can be thought of as something that is averaged like as I told you that the dartboard description so it is thought of as dartboard average of reaction probability.

So, sometime opacity function is difficult to determine, so that is why using some simple functional form I mean simple as I use this step function, you should be able to find out the cross-section because opacity function could be a complex description.

So, next we will move onto types of encounter. So, it is an encounter process as I told you that simple collision theory we have started with simple collision theory that collision occurs between reactants and as I told you reactants are structureless maybe atomic collision. Importantly, that is your impact parameter b as I told you that first we have to think that impact parameter for the description of the impact parameter as if there is no attractive or repulsive force operative. Then we think that means we introduce that there is some attractive or repulsive force which is operative between reactants and then that operative force I mean repulsive or attractive will be determining the effective collision whether the collision will be effective or not. So, that is why when as I told you that impact parameter, if it is low value or if it is high value, then the situation will be like you know Pb that is the opacity function will be in one case will be very low, in another case it will be it will be high. That is reaction probability will be less, maybe reaction probability will be high that is when your collision occurs at the centrifugal barrier, then possibility of reaction is less. So, high impact less reaction but low impact possibility of reaction may be more that I already have told you

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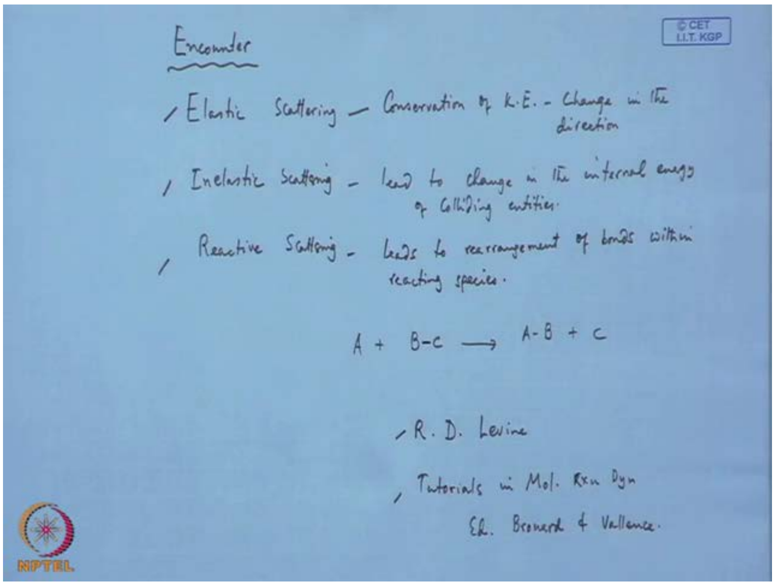

Encounter

Elastic Scattering – Conservation of K.E. – Change in the direction

Inelastic Scattering – lead to change in the internal energy of colliding entities.

Reactive Scattering – leads to rearrangement of bonds within reacting species.

$$A + B-C \longrightarrow A-B + C$$

R. D. Levine

Tutorials in Mol. Rxn Dyn

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So, next is type of encounter that is here the most important thing is encounter. Encounter is important. So, it can have categories, it can be categorized. So, one is elastic scattering, another is inelastic scattering and third is reactive scattering. So, what is this elastic scattering? It conserves the kinetic energy and lead to change in the direction, so conservation of kinetic energy but that will lead to maybe change in the direction change in the direction. It is elastic inelastic means that will lead to change in the internal energy of colliding entities.

So, that means basically what is happening that they are means entities are colliding. So, if it is elastic that means perfectly this momentum is transferred here, this momentum is transferred over here and this momentum is transferred over here, so exchange of momentum. So, this was initially this one was initially moving in this direction and that one was initially moving in this direction. The moment they are colliding, their direction has been reversed. So, that is why there is a change in direction for your elastic scattering.

Inelastic scattering collisions maybe because of certain degrees of softness that may happen because say your atoms may have some finite volume. So, when they collide, then maybe there is some kind of initially they were bigger, the moment they are colliding there is a squeezing or something some kind of it happening. So, that exactly the translation to translation is not occurring, translation degrees of freedom to translation degrees of freedom maybe other modes are activated and as a result of which internal energy is increasing. Not the translational but the internal energy of one is changing, maybe this one is also has suffered from change in internal energy.

So, therefore that leads to change in internal energy of the colliding entity which is called inelastic scattering. The third category is the reactive scattering that leads to the re-arrangement of bond, so reactive scattering leads to leads to leads to re-arrangement of bonds bonds within reacting species. So, that means say you have got A plus B c giving rise to AB plus c, so as if this bond is migrated in between this and c is freed. So, that is this scattering has led to led to effective chemical reaction. So, this reaction I mean this scattering has led to effective chemical reaction ok.

So, these are the types of encounter that we have to consider. So, what we have told so far, now the important point is while considering chemical reaction I mean in chemical dynamics I mean reaction dynamics, we have to we should focus on the reactive collision because reactive collisions are important for chemical reaction to take place.

These are very important for the chemical reaction to take place. Now, again I would like to mention one point that the book that we should means you may consult is the is the book by Raphael D. Levine. Levine that is also book on chemical, I mean molecular reaction dynamics and another newly published book that is by tutorials in molecular reaction dynamics by Broward; it is edited by Broward and Vallence. These two are the books or maybe other books are also there.

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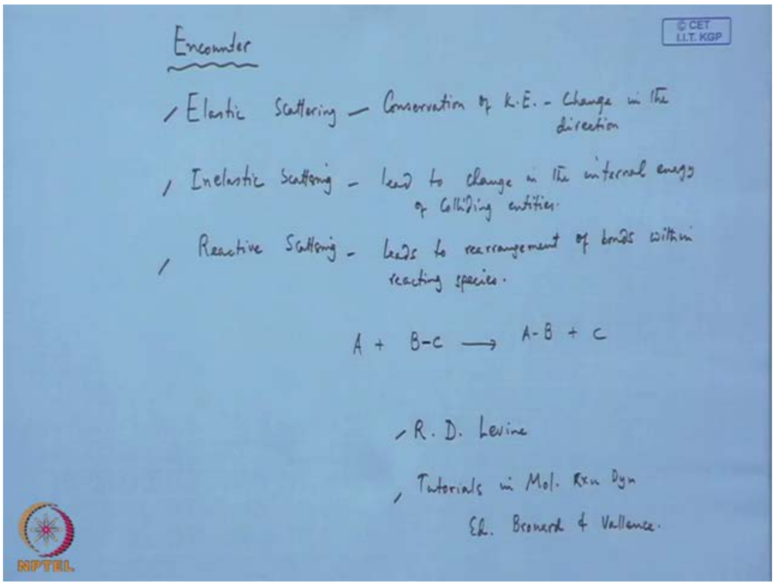

Encounter

- Elastic Scattering – Conservation of K.E. – Change in the direction
- Inelastic Scattering – lead to change in the internal energy of colliding entities.
- Reactive Scattering – leads to rearrangement of bonds within reacting species.

$$A + B{-}C \longrightarrow A{-}B + C$$

- R. D. Levine
- Tutorials in Mol. Rxn Dyn Ed. Broward & Vallence.

Now, today we have we focused on forces, I mean potential energy and forces. Then we have talked a little about one dimensional case and then maybe later on we will we will come to potential energy surface that is a multi-dimensional energy landscape. Now, we also talked about experimental requirement for selecting velocities. One is this effusive source we may have to use, maybe in other case it is supersonic nozzle. So, with supersonic nozzle we can select different velocities using various carrier gases and then we talked about reaction cross section which may be regarded as the effective target for the concerned reaction.

We also have introduced the opacity function that is a reaction probability function and also we have introduced this d factor that is the impact parameter parameter factor. As a typical case, we have considered a step function for this Pb that is opacity function and tried to find out this sigma that is reaction cross section. We also talked little about types of encounter that are responsible for that may be important and specially reactive scattering which we will take up maybe later on.

So, I guess that is all for today. Now, in the next lecture will take up experimental measurement of cross section and maybe we will talk about crossed beam experiment. So, till then have a nice time. Thank you.