Rate Processes
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Module No. # 01
Lecture No. # 33
Reaction Dynamics (contd)

Hi, good morning. Welcome back to rate processes.

We were discussing reaction dynamics in the last series of, I mean, last lecture, we talked about this opacity function and reaction cross section, and we ended our discussion with encounter and it is elastic collision or maybe, I mean, we just have given ideas about elastic scattering, inelastic scattering and reactive scattering that is the scattering which leads to chemical reaction. Now, still one aspect that we have not talked about so far that is the steric requirement.

That is we have to consider this the factor which is called the steric factor. We have talked about this opacity function and we tried to find out using some functional form, that is, a step function for p b; so p b means your opacity function.

So, now, in that case, we have found out that sigma reactive, I mean, cross section reaction cross section and that can be divided into this sigma can be divided into reactive and nonreactive, but the total will be we have some value, I mean, it cannot exceed some number. So, if in one case for certain energetically favorable reaction, if it is increased, then it must be surmounted from the other reaction.

So, 2 pi b d b, so that is the maximum, I mean, that is the sum that you we will be looking into. So, another factor that, I mean, this b factor, so b factor is a which is a measure of, I mean, measure of closeness of collision. So, usually there are usually other requirements besides the closeness, besides the b factor, that closeness of approach for the reaction to take place, besides that besides this closeness factor, still another factor is important, I mean, another factor is important. means I mean, if two reactants come close to each other, reaction may take place, but the point is, I mean, the question is that the situation that if this I mean entity is interacting, I mean, colliding with this b c, do you think that any orientation in any orientation if this collides with b c, there will be any favorable reaction that is the question? That whether every orientation is a favorable orientation and the and with I means collision with every orientation is it corresponding to does it correspond to reactive collision that is the question.

So, in particular, there is a possibility that steric requirement, I mean, the specific geometric requirement is important, that is, some specific in some specific configuration, maybe the reaction is taking place.

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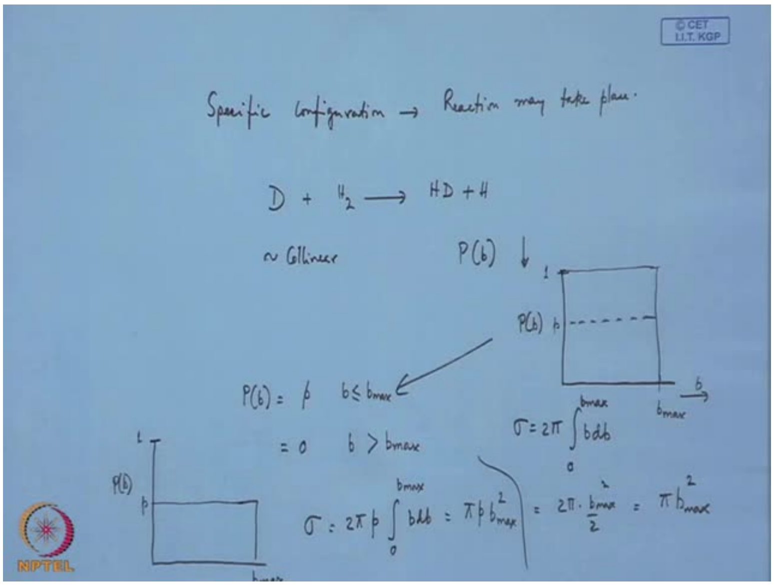

Specific Configuration → Reaction may take place.

$D + H_2 \longrightarrow HD + H$

~ Collinear

$P(b) \downarrow$

$$P(b) = p \quad b \leq b_{max}$$
$$= 0 \quad b > b_{max}$$

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

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

$$= 2\pi \cdot \frac{b_{max}^2}{2} = \pi b_{max}^2$$

Means with the specific configuration, specific reaction may take place; so that is the underlying significance of steric requirement. Consider a simple reaction, that is, atom exchange reaction, that is, deuterium plus H 2 giving rise to H D plus H.

And if the energy of the system is such that these, I mean, two entities; one is D, another is H 2; if they come close in almost collinear fashion like this, almost collinear, then the reaction can take place; but if it is not a collinear situation, then maybe possibly reaction probability is less.

That means reaction will fail if they do not approach each other in a collinear geometry in almost collinear geometry. Now, at each value of b, at each value of the closeness factor, all possible reactant orientations will contribute, I mean, you have a specific b value and you have to consider all possible orientations of the reactant and then you have to average out.

So, due to collision with unfavorable orientation, unfavorable orientation means the orientation which does not contribute to any effective reaction to take place; therefore, your P b, the opacity function will go down further because of this unfavorable geometry, I mean, unfavorable orientation factor.

So, therefore, what is happening? that So, that means, it will reduce and maybe sometime it will not be able to reach its value, that is, it is value maybe P b to some unit value. So, therefore, in that case your step function that we started with in calculating sigma will have to be modified. So, we started with this calculation, it is your P b opacity function; we started with some value 1 and maybe it is b max it is b. And we have calculated sigma, and sigma to be equal to you have, that was found to be equal to pi b square sigma; hence for this, sigma is equal to 2 pi integration 0 to b max into b d b, so b max square by 2, so twice pi into b max square by 2 is pi b max square.

But now as I told you because of the unfavorable orientations, unfavorable orientations means your this P b value, P b that is the value to 1 that should reduce to some number, because it will not reach unity because of this steric requirement.

So, that means, in that case what you have to do? You have to modify this one to another step function that P b is equal to p when b is less than equal to b max and is equal to 0; when b is greater than b max therefore, the corresponding figure will be corresponding figure will be although it is unity, now it will be reduced like this; I mean maybe value somewhere over here it is p. So, that is your P b, that is, this is p and this is b max therefore, your sigma will now be equal to twice pi p has to be I mean it is an awaiting factor I mean how much it is reduced to what extent it is reduced? Integral b d b assuming a step function, but it is a reduced step function 0 to b max and which becomes pi into p into b max square.

So, therefore, this the factor, I mean, the steric factor specific geometrical requirement like I told you in case of D plus H 2, if it is almost collinear like this, then reaction may take place; but if it is not collinear, then reaction, I mean, it is difficult; I mean reaction will not take place, so collisions will not be will not be reactive. So, that is why your sigma will be multiplied with a factor p which takes into account of the of the steric factor.

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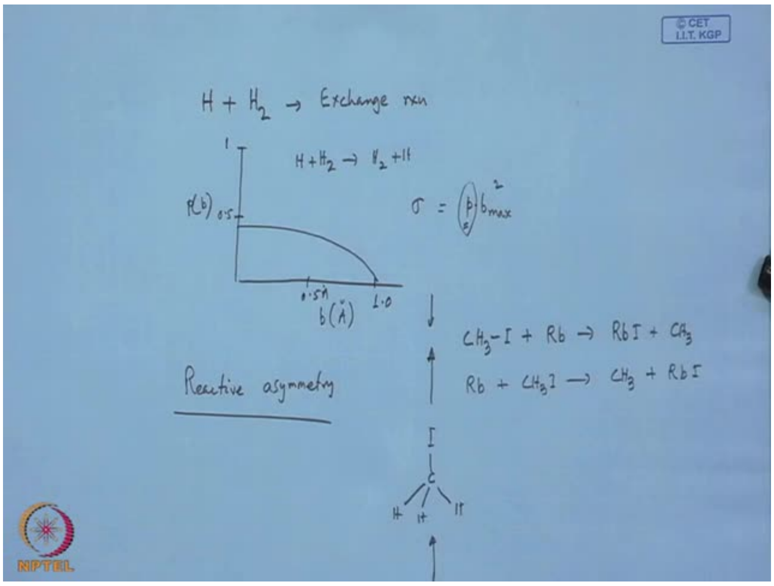

Another example, that hydrogen exchange reaction H plus H 2, there is exchange reaction. So, there a functional form of this kind say this is b in angstrom it has been, I mean, adopted from a general resource that value is 1; this is about half; this is P b for H plus H 2 reaction H 2 plus H and say it is value is 1 angstrom, so this is 0 . 5 angstrom; so this type of curve has been used.

So, the thing is the measurement of sigma cannot alone determine the value of the of this one, I mean, p into b max whole square. I mean if you measure this value of sigma several other requirements are, I mean other informations are required to determine the value of this; I mean simple measurement of this will not help us means, additional things are to be carried out to find out this p factor; this is an important factor.

So, that is about and… also another thing another important point is reactive asymmetry. Think of a reaction like C H 3 I plus rubidium giving rise to rubidium iodide plus C H 3 in dot form and another situation R b plus C H 3 I giving rise to C H 3 plus R b I.

Now, in that case, reactive asymmetry means, it may be called as a favorable orientation than this one; so reaction is expected to be occurring more favorably over here than this pathway. Now, so as I told you that additional information additional means a force had to be given to find out p that can be done using the oriented reactant molecule. Because it is a polar molecule, I mean, it is a polar molecule; if you use an electric field in the appropriate direction, then these molecules can be properly oriented, maybe it is oriented like this along this axis, and then, if you allow rubidium to come from this side or maybe from this side, you should be able to find out the asymmetry reactive asymmetry, and then, this will help in finding out this this steric factor.

So, using oriented molecules oriented reactants, you should be able to, I mean, using this concept you should be able to find out this steric factor, which is a very important factor. So, you see that, not only collision, but in addition to collision, the geometrical requirement, then configurational requirement is very important means, I mean, whether it is in case of hydrogen deuterium exchange whether they are approaching in a linear fashion or maybe something else, that point I mean that has to be invoked into your calculation in calculating your sigma the reaction cross section. So, this point is important this point is very important.

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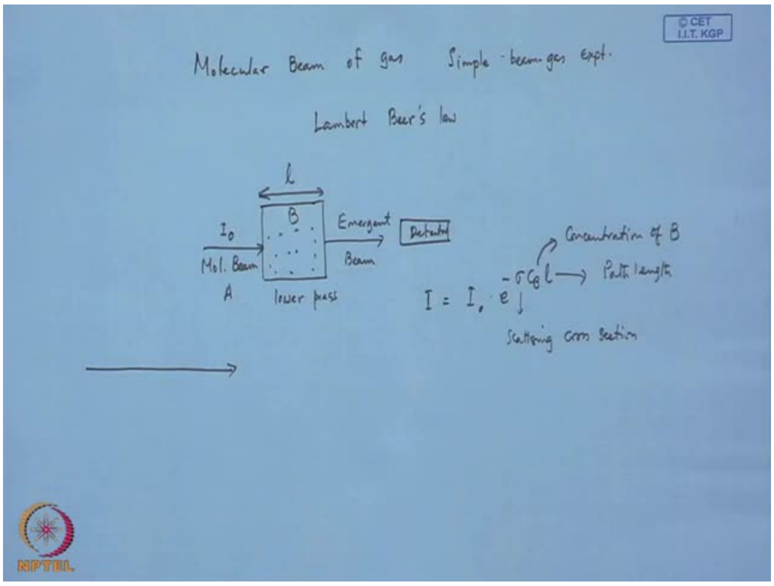

Next is inelastic and elastic scattering. Now, simple measurement of cross section, how to measure the cross section in a simplistic manner? Now, think of a molecular beam of gas, it is a beam gas simple beam gas experiment; you have to make use of this like something like, Lambert beer's law. The law states that, like a chemical reaction, I mean, you have to have make use of the similarity of your chemical reaction and physical process that, when you shine, say colored substance with light, suppose you have got a colored substance in a container maybe say like this say a green colored substance; think of this, say it is a cubit containing this green colored substance, that means, green color is because of the fact that in white light since there are seven colors, mostly, I mean, into in I mean grossly so this is green because all the other colors are absorbed excepting this green color that is why it is looking like green. So, if you shine the sample with white light and you measure the intensity of the emergent light in this side, so you should be able to find out how much of the substance, I mean, how much substance is there means, if you increase the concentration or if you decrease the concentration, I mean, how much extent to how much extent you have increased or to how much extent you have decreased that you can calculate using the lambert beer's law that there is one to one correspondence that photons are absorbed; so if photons are absorbed, emergent intensity will be less.

So, that idea will be used over here to find out the reaction cross section. So, say this is your reactant, say b reactant b maybe say at lower pressure and you allow you allow the molecules, I mean, molecules of a to enter here; this is I 0. So, molecular and it is a molecular beam and here you have B inside, so what is happening? that if there If there is a reaction, then this A molecule will no longer remain A; it will combine with B. So, the emergent beam, this is the emergent beam; emergent beam will consist of A, unreacted A, unreacted B and A B.

So, if you know the initial concentration or any similar quantity and if the final concentration by means of a detector, you should be able to find out the reaction cross section. You The thing is that, when molecules of A collide with molecules of B, then these A molecules will be deflected or if collision, that collision maybe reactive collision, that collision maybe nonreactive collision.

So, this beam of A molecules which was initially linear, I mean, like this; if there is a collision, then this beam will be deflected little bit or maybe it will be deflected a little bit or maybe it will be attenuated attenuated, means, that as if some portion of the beam I mean molecules will be is chopped. So, that will make use of means, we want to find out how much attenuation of the beam when it is passed through B, that is, when it passes through B, it collides with B therefore, it gets deflected. So, that is why lower pressure, if it is under high pressure, then the situation will be further complicated, because much of collision will be there and maybe it will happen that you would not be getting; you may be getting full attenuation of this A beam that is why low pressure has been used over here.

And using this similar to Lambert beer's law we can form a equation like I 0 into e to the power minus sigma C B concentration of B into l and sigma is the scattering cross section, concentration of B and this is the path length, that is, the path length of B through which A passes, that means, this is your l; it is very similar to Lambert beer's say in connection with absorbance spectroscopy.

So, this way maybe we can find out using beam gas experiment, we can find out the simple reaction, I mean, very simply this is the reaction cross section.

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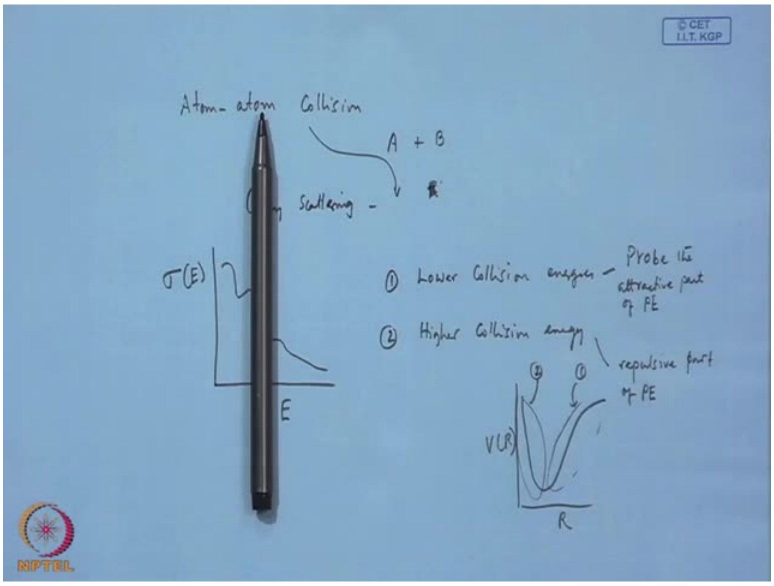

Next is, next is suppose if it is an atom atom collision, say atom A plus atom B, so what is happening that, if there is an there is a quantum mechanical interference that happens between two paths, I mean, paths of two paths like two d brogley webs leading to scattering in forward direction, which an oscillation in signal is observed is called your glory scattering.

Glory scattering, it is mostly seen in case of your in case of atom atom scattering say, so what is happening that, if you plot sigma versus E energy sigma E, then you will be seeing that, like something like this. So, it is basically the glory oscillations that arise from the quantum mechanical interference between two pathways means, there are there could be two alternative pathways for energetically favorable pathways, then there is there is interference between these two and that may lead to glory oscillation.

The frequency of oscillations varies with collision energy, that is, this E, because of the phase difference between two pathways that will vary with velocity. So, when velocity is different, then corresponding phase is different, I mean, phase is different therefore, it is very much dependent on the velocity, that is, it is very much dependent on the collision energy. So, velocity different means, collision energy will be different.

So, situation one- lower collision energies and situation two - higher collision energy. So, in this case, attractive part of the potential we can prove; the attractive part of potential energy in this case, we can probe repulsive part potential energy potential energy. So, that means, say this is your attractive part and this is repulsive part, that is, energy is increasing V R as a function of R; so this is means, lower collision energy we can probe into this part.

So, using the using glory scattering glory oscillations, which is which means we can find we can probe into attractive part and repulsive part of the potential energy surface so and this frequency of oscillation is very much dependent on the collision energy; low collision energy whatever oscillations we will be getting will be will be correspondingly probing into the this part, that is, the attractive part; in the same way, higher collision energy we will be probing into this part. So, it is nothing but the quantum mechanical interference between the two parts. So, this glory oscillation is nothing but the quantum mechanical oscillation due to the interference of the two parts, two energetically favorable, I mean, I mean two favorable parts.

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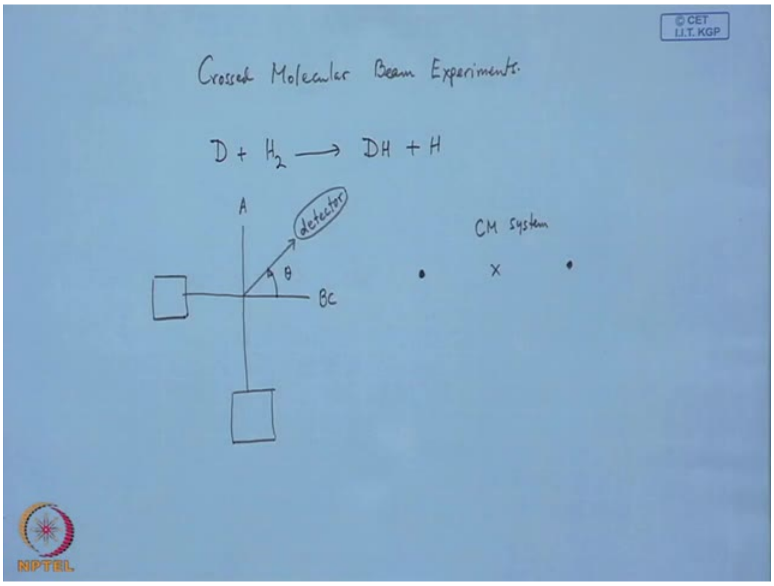

Crossed Molecular Beam Experiments.

$D + H_2 \longrightarrow DH + H$

Next is, we have to in order to find out the angular distribution of the products, we have to go with this crossed beam crossed molecular beam experiment. So, crossed molecular beam experiments, so what is crossed molecular beam experiment? So, the thing is that, as I told you that when it is the case of hydrogen exchange reaction, that say deuterium plus H 2 giving rise to D H plus H and it is told that that when these two interacting entities are close, I mean, close to linear, I mean, this internuclear axis and this approach of D, this is in one line or almost linear, then the reaction will take place; otherwise, the reaction probability is less. So, on that ground we talked about this steric factor.

So, now, here what we are going to do? that We use two molecular beams: one is for one reactant, another is for another reactant. So, with crossed molecular beams what we are trying to find out is, the additional information that we are getting that like one beam is like this; another beam is like this; so these two beams are crossed like this, crossed molecular beam. So, this is the region, where interaction is taking place; here, interaction is taking place that is the common intersection point and you put your detector somewhere over here, like the detector is rotated from this to that in theta angle; this is your angle with respect to maybe one beam; so then you gradually change this angle and try to find out you find out the angular distribution of product by the help of the detector.

So, this is one beam; this is another beam. So, this is A; and this is B C and this is angle theta, the detector. theta angle theta So, you move your detector this way and try to find out, detect your products, maybe there are other several means maybe by light induced fluorescence, laser induced fluorescence means if you want to detect your product, maybe suppose your product is such that it is fluorescing or maybe if the product is firm then suppose with the help of another laser source, if your product or product is formed over there, then it will absorb light and it will fluoresce. So, laser induced fluorescence or other techniques you can detect your desired product, and then, you find out angular distribution means in which direction how much in which direction is it has been distributed that gives you additional information.

So, whatever data you obtained, the scattered spaces, whatever data you are obtaining is in the laboratory frame, then you have to convert this to center of mass system. So, center of mass is basically your, say you have got A over here, B over here; so center of mass could be somewhere over here; so you have to convert this data to center of mass system. I mean the distribution has to be translated in terms of center of mass system, C M system; so you have to transform there transformation, I mean axis transformation is needed.

Now, next, we will we would like to talk on we would like to talk on this differential cross section, what is this differential cross section? So, before that, again using crossed molecular beam, it is a very popular technique, that if you try to look into study the reaction dynamics, then and in molecular beam crossed molecular beam experiments are very useful, but they are very tricky. The point is that, you to make sure that two beams overlap, that is one point, and then, again you have to select velocities as I told you, if it is a supersonic, using a supersonic nozzle or if you use a just effusing source, anyway you have to select velocities.

So, in that case, you have to select velocities in some cases, I mean, in one case, and then, as a function of velocity selected velocity, I mean, you detect the product distribution in different angles. So, product distribution in different angle from the product distribution of different angle, you should be able to get many information so and this experiment is very tricky experiment so and detection is another point. As I told you, that not only this laser induced fluorescence method, but other techniques you may need to adopt to detect your products means, how they are distributed in three dimensions products or maybe scattered products scattering product anyway.

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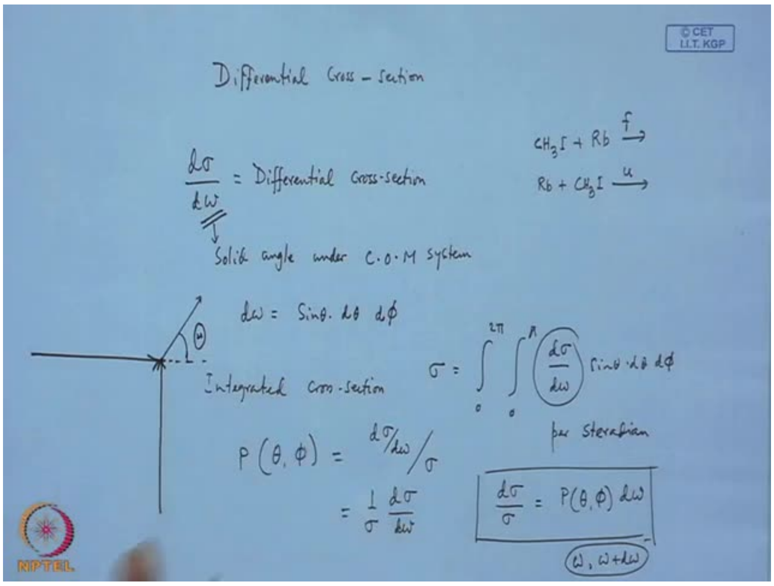

Differential Cross - Section

$\frac{d\sigma}{d\omega}$ = Differential Cross-Section

Solid angle under C.O.M system

$d\omega = \sin\theta . d\theta \, d\phi$

$CH_3I + Rb \xrightarrow{f}$

$Rb + CH_3I \xrightarrow{u}$

Integrated Cross-Section

$$\sigma = \int_0^{2\pi}\int_0^{\pi} \frac{d\sigma}{d\omega} \sin\theta . d\theta \, d\phi$$

per Steradian

$$P(\theta, \phi) = \frac{d\sigma/d\omega}{\sigma} = \frac{1}{\sigma}\frac{d\sigma}{d\omega}$$

$$\boxed{\frac{d\sigma}{\sigma} = P(\theta, \phi) \, d\omega}$$

$\omega, \omega + d\omega$

Then differential cross section, differential cross section then comes the question concept of differential cross section, so what is that? So, you have to as I told you, that you want to find out the product distribution in various angles. So, you have got your crossed beam over here and you try to find out the product distribution this way; your experiment is to find out the product distribution in certain angle. So, here and then you find out the cross section reaction cross section as a function of scattering angle and this quantity is quantified. I mean differential cross section is quantified by the term d sigma d omega is the differential cross section and this represents this d omega represents the solid angle, I mean, it is the solid angle under center of mass C center of mass system and this d omega is equal to sin theta d theta d phi.

So, this is the differential cross section. So, if we integrate over the over different, I mean, integrate over the space, that is, then you will be getting the integrated cross section, that is, the integral cross section or integrated cross section. So, integrated cross section sigma is equal to integration 0 to twice pi integration 0 to pi d sigma d omega sin theta d theta d phi and dimension of this one will be per steradian per solid angle solid angle in steradian.

So, therefore, angular distribution in products, that is, distribution function will be, basically will be given by will be expressed as P theta phi, because it is in three dimensions. So, possibility is that, you have got since you are detecting your reaction product in dimension, so angle will be like, one way you can change this angle; so basically with respect to your z axis, you have got one angle theta; another angle phi in three dimensional case. So, that is why it is p provided function as a function of theta and phi.

And which is probability function is your d sigma d omega per unit per integrated cross section therefore, by sigma. So, it is 1 by sigma d sigma d omega. So, that means, what does it mean what does it mean, I mean, what does this p mean? It means that, I mean we can write in this fashion that d sigma by sigma can be written as p theta phi d omega p theta phi d omega. So, it is nothing but the probability it is nothing but the probability of finding the product scattered into solid angles between omega and omega plus d omega.

So, in a given solid angle, the probability of finding your product is given by this p theta phi d omega; so it is in between omega and omega plus d omega, so probability of finding the product. So it is a so it is a scattered, I mean, when there is a molecular beam experiment when there is a molecular beam experiment the products are scattered in all possibly three dimension, so you have to integrate over the space to find out sigma cross section.

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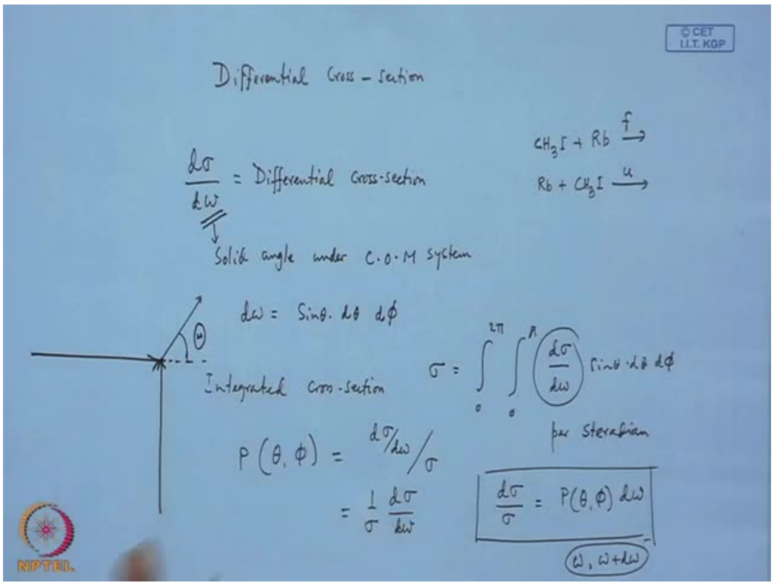

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$= \frac{1}{\sigma} \frac{d\sigma}{d\omega}$

$\boxed{\frac{d\sigma}{\sigma} = P(\theta, \phi) \, d\omega}$

$\omega, \omega + d\omega$

And this differential cross section, I mean, from the differential cross section, you find out this p theta phi, and p theta phi d omega is nothing but it represents the probability of finding your product in the solid angle omega and omega plus d omega; provided in this case reactants are not oriented. So, when this beam is going this way, another beam is going this way, so no additional constraints are there; that that your reactants are oriented in a specific manner; so that that is not there. So, this differential cross section and the angular distribution are independent of angle phi and which is because of the dartboard averaging over the impact parameter.

So, thus whenever you we do any cross beam experiment now and also importantly when cross beam experiments are done for this particular thing for this differential cross section for this differential cross section, we need to make sure that the reactants are not oriented. But remember in one case, I gave you one example that C H 3 I plus R b and R v plus C H 3 I in one case this is a favorable orientation, so f and this is an unfavorable orientation; so we do not do anything like this. In this particular case, you can have your favorable orientation or unfavorable orientation by applying an external field that, this dipoles will be this C H 3 I dipoles will be oriented in a definitive fashion with respect to with respect to that external dipole, I mean, external electric field.

Here in cross beam experiment, we are just allowing these two cross beams to interact at an angle 90 degree, and then, you find out the differential cross section. Because differential cross section means, you are in means how these products are distributed in three dimension and then means that is a better way of looking into sigma. So, because it is averaging over all possibilities, it is not that a collinear just collinear, two beams are interacting or maybe they are interacting. So, it is the more general way it is a more general way of looking into experiment, rather than doing in this specific fashion.

So, that is why this is done and when you do the experiment, you get your data in laboratory frame, then you have to convert to center of mass. Center of mass means, you have got one mass, another mass so then and your center of mass is somewhere over here, so you have to do this axis transformation; everything should be interpreted in terms of center of mass. So, then you transform center of mass and then you find out the differential cross section. So, differential cross section to integral cross section, I mean, in an integrated cross section, so that takes care of the all possible options; therefore, sigma is expressed like this is your reaction cross section and it is a differential cross section; so you are averaging I mean integrating over all possibilities.

And this one is per unit steradian therefore and then you express your probability. So, angular distribution function is expressed in this way and this is nothing but your probability of finding the particle, that is, your desired product; finding the particle in this solid angle omega and omega plus d omega. So, only thing that you have to think, that no oriented reactant should be there; so we are allowing all possible orientations so that a homogeneous, I mean, a nice distribution is obtained.

And of course, differential cross section and angular distribution, are means if there is I mean if reactants are not oriented, if you do not orient them in a definitive fashion, then it should not depend on the angle phi. So, angle theta is this; you have got your crossed beam like this; this is your angle theta. So, if you do not use any oriented molecule, so it will not depend on the other angle phi, but it will depend only on this angle. Because of because you will think that, your that your impact is basically similar to hitting something, hitting by a hitting with a magnet onto the dartboard.

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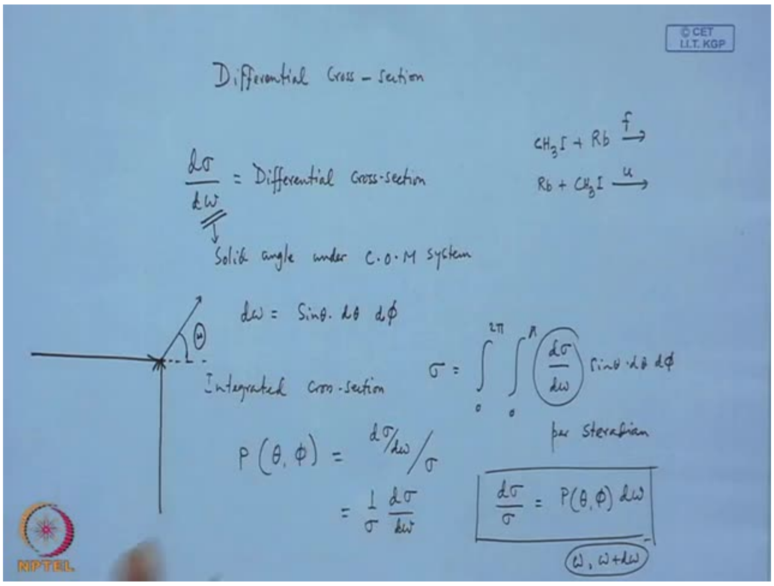

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$\omega, \omega + d\omega$

So, what we have learnt in this piece of piece of lecture? That we started to talk with like let us see started to talk with your the steric factor steric; factor is a factor that takes care of specific geometrical requirement and in that case, your opacity function does not reach unity; so it is something less than unity. So, that takes care of the fact that, if a specific geometry has not been maintained, then the reaction probability will be less opacity function will be less.

So that we talked about that is called your steric factor, then we talked a little about your molecular beam gas experiment, then we tried to give an idea about the glory scattering that is oscillation and from that oscillation glory oscillation and from that it is basically interference between the two d brogley webs corresponding to two paths for the reaction and from that, you can find out the repulsive; you can probe into the repulsive and attractive part of your potential energy surface, then we talked about the crossed molecular beam experiment and it is benefits, that you can find out the reaction cross section that is integrated reaction cross section probability of finding out.

I mean the angular distribution all this and using the concept of differential cross sections, we find out the integrated cross section of the reaction and if oriented molecules are not used, then the angle phi is not that important; only it depends on the angle theta that is the detector angle with respect to line that corresponding to maybe one of the line corresponding to one beam.

So that we tried to cover over here in the next piece of lecture; we will concentrate onto inelastic scattering the transfer of energy and how this energy is transferred from a translational to different other modes like rotational, vibrational and electronic mode. Because if you think of a molecule, then it will have various degrees of freedom, so how energy can be transferred into various degrees of freedom and what is the cause of, I mean, what is the effect of that? So, that that is inelastic scattering and corresponding energy transfers. So, we will take up that issue in the next piece of lecture, so till then have a nice time. Thank you.