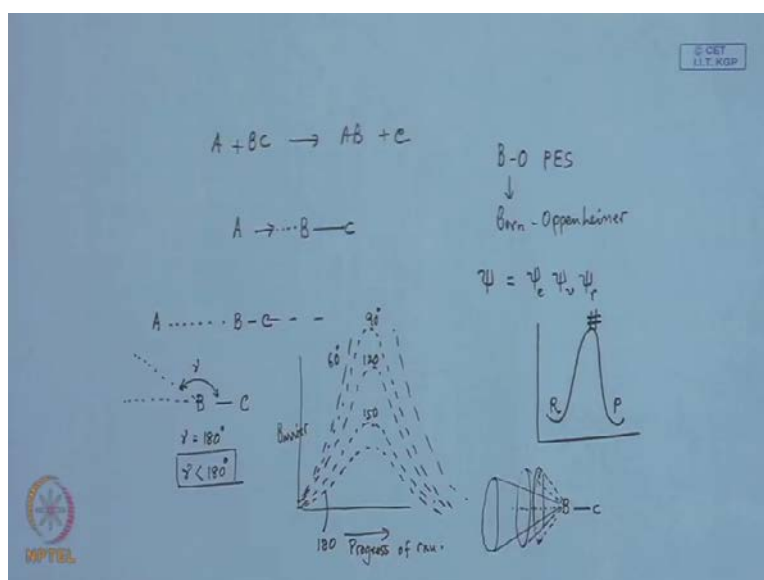


Rate Processes
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Lecture No. # 39
Reaction Dynamics: Concluded

Hi, good morning friends. Today, we are back with this Reaction Dynamics. The concluding part of Reaction Dynamics, that **some of the, as I**, you know, mentioned in the last lecture, that, maybe little portions which are yet to be, you know, talked about. So, today, that I will cover, of course; I will give some introduction to that and then I will switch onto a topic which we did not, you know, talked about. It is, you know, basic, very basic idea of corrosion; I mean, rate processes related to corrosion, how to measure rate of corrosion, a preliminary idea of that. Now, so far as reactive scattering is concerned, now quantum scattering theory is very useful, you know, in dealing with the potential energy surfaces.

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Now simple reactions like, you know, A plus BC giving rise to AB plus C. So here, you know, this, now this dynamics of this chemical reaction is very much dependant on the

topology of the Born-Oppenheimer potential energy surface **Born-Oppenheimer potential energy surface**; this is Born-Oppenheimer, Born-Oppenheimer potential energy surface. Now this, you know, in quantum mechanics, total wave function is, you know, it has got, you know, this electronic part, vibrational part, rotational part and nuclear part. So, you know, if you think of electronic motion, then electronic motion, motion is very fast compared to vibration and vibration is even faster compared to, you know, rotation.

So, the point is that, **if you**, if you think that, **if you think that** like as they are separated in time scale, **as they are separated in time scale**, now you know, **so**, Born-Oppenheimer potential energy. So, basically, you know, electronic, vibrational, rotational and these motions. So, as you, they are widely separated in time scale, therefore, you know, total wave function ψ can be written as the product of individual contribution; that is, you know, ψ electronic, ψ vibration, ψ rotation. So, you can write it in this way.

So, based on this, you can, I mean, this is **this is** the total wave function, you know, electronic, vibrational, rotation and maybe you can include the nuclear part as well. So, the thing is that, based on that, you can **you can** generate the potential energy surface; that is which is dependent on the, I mean, Born-Oppenheimer approximation. And, the dynamics of this chemical process is very much dependant on the **on the**, I mean, topology of the Born-Oppenheimer potential energy surface. Now, even without the exact calculation, you know, quantitative idea on the chemical dynamics can be gained from inspecting the properties of the potential energy surface. Now, here, if you see that, **this is**, this is $A + BC$ giving rise to $A + C$.

So, this is, as I told in the last lecture, that this is RPC; that is distance between B and C. And RPC, it is the distance between A and B, and this is your, this is the, you know, cross-section; I mean potential energy, I mean equal energy line, I mean contour for the corresponding equal energy line. So, this is the minimum energy path. So, **giving rise to**, giving rise to the product $AB + C$, this arrow; and this is the highest energy point which is called the transition state and reaction profile for a linear approach of the three reactants.

So, in this case, **it is an**, it is a linear approach approaching, this way it is approaching; it is a linear approach. And the path of minimum energy from the reactant to the product of the potential energy is termed as the reaction path or the reaction coordinate. So, this is

your reaction coordinate, this is your reaction coordinate and this corresponds to DEI mean electronic dissociation energy for BC. This corresponds to the electronic dissociation energy for ABCD. Anyway, so, at the energy barrier, that is the saddle point; this energy barrier separating the reactant and product values is termed as the transition state.

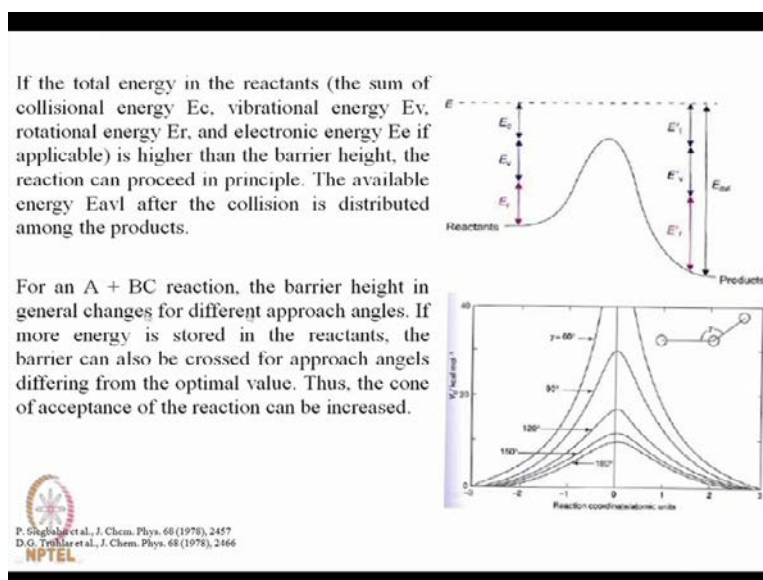
So, this is basically, you know, when we draw, in normal case, that we draw like this. So, this is your transition state, this is your reactant side, this is your product side. So, this is separating these two, you know, values. So, **you can**, you can do this thing on the basis of this; I mean on the basis of the applicability of Born-Oppenheimer approximation, that motion, I mean, motion of electron motion of electrons are much faster compared to vibration, and that is much faster compared to rotation. So, therefore, they can be separated as the product and therefore, accordingly, your solution to Schrodinger's equation becomes easier than when they are mixed together; these, you know, electronic vibrational rotational motions, I mean, these are, these coordinates are, I mean, mixed together anyway.

So, and if the total energy of the reactant, that is sum of the collisional energy, then I mean, sum of the collisional energy; that is EC, termed as EC, then vibrational energy EV and the rotational energy ER and of course, the electronic energy, if there is an electronic energy available, that is higher than the barrier height. So, if you add them, all of them, rotation, vibration, then, collisional energy; of course, if there is any electronic, you can add that. So, if it is higher than the barrier height, the reaction can proceed in principle; so, that means, it is above. So, energy is above than the barrier head. So, your reaction, **can be**, can proceed.

So, the available energy EAVL after collision is distributed among the, **among the**, products; so, this amount of energy is distributed among the products. So, this is your initial, this is your final; so, this is your reactant side, this is your product side. So, this means, if this sum is more than your this side, then the reaction can proceed in principle; but if it is less, then, you know, in principle, the reaction may not be possible. Now, again think of this line of approach; I mean, say this is A, this is BC, you join them with line and then what you do? That, you know, draw another diagram where BC is there, but A is approaching at some angle, so, maybe that angle is gamma.

So, **in that respect**, in that respect, what happens is that, your reaction maybe a less **facile** or maybe in some cases, if that is the optimal angle, then reaction may proceed in a better extent. So, in the thing, the point is that this barrier height maybe dependant on this angle of approach.

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So, in that case, for an $A + BC$ reaction, the barrier height is in general, changes in barrier height; general changes for different approach angles, and if more energy is stored in the reactant, their barrier can also be crossed for approach angles differing from the optimal value; and there is a cone of acceptance of the reaction, I mean, that can be increased, means if the energy stored in the reactant is more, then maybe other angles are possibly accepted.

So, suppose if this is your optimal, say this is your optimal angle γ , say γ is equal to 0.8 degree, **then the** then in another case if γ is less than 180 degree, in that case what is happening? That maybe, you need more energy to overcome this barrier; that is, this barrier is more. So, if you plot, you know, if you plot basically, this probability, I mean, barrier height **in terms of**, in terms of various angle, then you will be seeing that for this particular reaction.

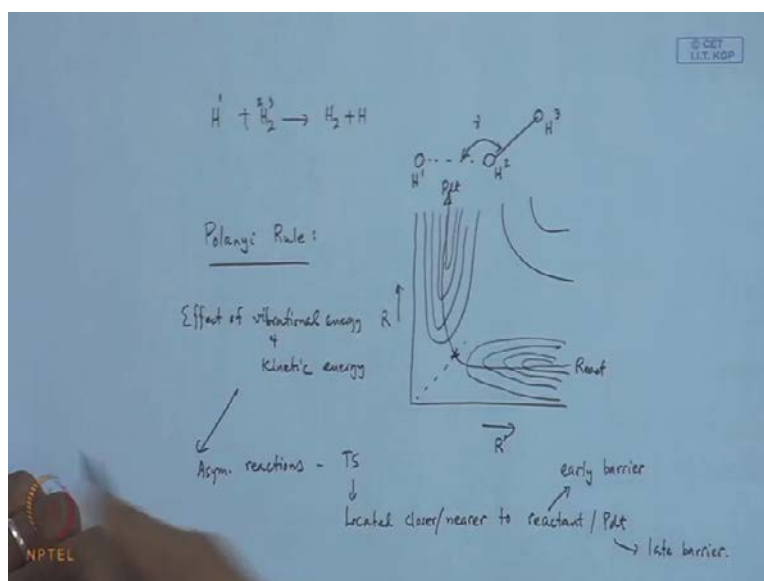
So, barrier height may be increasing; barrier height is still higher for other angle, very high barrier. So, maybe this is the lower one, is 180, then maybe 150, then 120, then maybe another maybe 90 degree which maybe even more 90, and the other one is maybe

60 degree. So, this is barrier height and this is your **progress of reaction** progress of reaction. So, therefore, angular approach, I mean, angle of approach is an important factor. So, if you change the angle from the optimal value, then barrier height accordingly gets altered.

So, therefore, this and of course, if your energy, I mean, energy stored in the **in the in the** reactant is more, then cone of acceptance for the reaction maybe increased. I mean, you have got your like BC, and say optimal angle is 180 degree, maybe your reactant can approach this way, so, this is your cone of acceptance. So, if this, you know, cone of acceptance may change, cone of acceptance may change; so, that means, here, more energy is required to overcome the barrier and barrier height is also more in this way, you know; this is another cone of acceptance, its **its** cone of acceptance is more.

So, thus, cone of acceptance of the reaction can be increased, and if the energy is stored in the reactants is more, then the barrier can also be crossed for approach angles differing from optimal value; so, optimal value is 180 degrees. So, that can be **that can be** overcome. **So**, and this is your, this is the potential energy profile; I mean, whatever I have shown over here, energy shown over here, is the potential energy profile along the reactant coordinate for this reaction.

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I mean, this is, this example is given for the reaction H plus H2 is the potential energy curve, H plus H2 giving rise to H2 plus H. So, this is the potential energy profile along

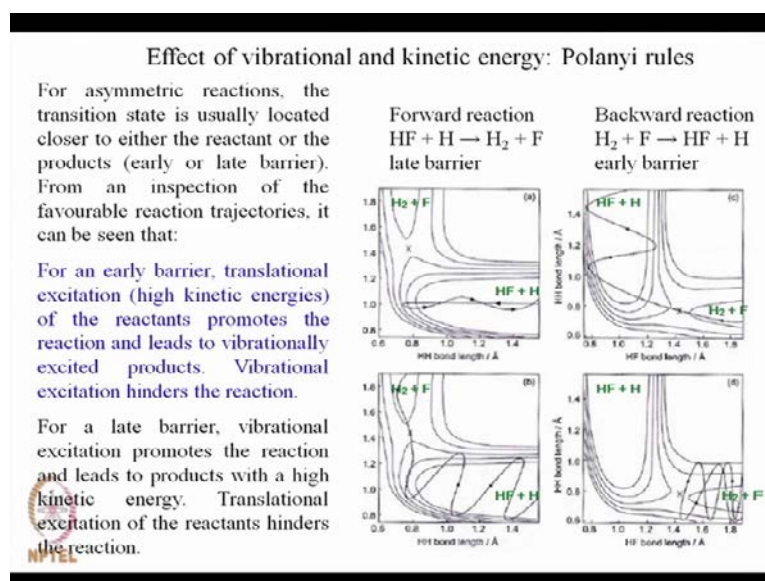
the reaction, coordinate along the reaction, coordinate for different values of this approach angle. Say this is your hydrogen, and say this is your dihydrogen. So, this is the, well this is the, this is gamma. So, H, this is H, another H, say H1, H2, H3, 1; this is 2, 3, next effect of vibrational and energy and kinetic energy. So, I have already given you a little idea in the last lecture and which is known as the **Polanyi's rule**, Polanyi's rule.

So, we will just give you a little idea now for symmetric reaction; when the reaction is symmetric, then your potential energy, I mean the transition state, transition state is symmetrically, I mean, located this contour. And, say this is your minimum energy path, this is your transition state for the symmetric reaction. So, this is $1r$, this is r primed. Now, what happens? That is, if your transition state is resembling your more, you know, you know, product like or more reactant, like then, what is going to happen? So, for that is why the effect of, you know, vibrational kinetic energy is more important.

So, effect of vibrational energy and kinetic energy is very important now for asymmetric reaction or the reaction which is not symmetric, the transition state usually located. So, the case is, if it is not, you know, symmetric reaction, say, your transition state is symmetrically distributed in the, you know, reactant side and product side, but if it is not symmetrically distributed, then what will happen? Either this will come close to this side or maybe it will go to this side.

So, for asymmetric reaction, the transition state is usually located closer either to **either to** reactant or product side; if it is close to reactant side, so, asymmetric reactions **asymmetric reactions**, the transition state located, which is located closer to or nearer to reactant or product. If it is near to reactant, it is called the early barrier or early transition state; early barrier, that is, barrier is closer to your reactant side or maybe if it is product side, it is called the late barrier.

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Now, if we, if we, now if we, then inspect, that is, if we inspect carefully, the favorable reaction trajectories, it can be said that for an early barrier, if it is an early barrier like this, see this barrier is early, this is the early barrier case and this is the case. That is, the reaction will proceed and this is the case that no reaction will, hindrance of reaction does not take place; that is, if the arrow is not, you know, the path is not like this as it is, you know, it is shown that the path is basically coming back to its reactants, you see.

So, what is the situation for an early barrier translational excitation? That is, having higher kinetic energy, translational excitation of reactant promotes the reaction; that is, if it is high, higher translational energy, you see that it promotes, that is, it allows crossing this barrier and leads to leads to vibrationally excited, vibrationally excited; this represents vibrationally excited, you see. Vibrationally excited means it is following, you know, this maybe, it is not following, you know, lowest energy, but the path which it is following, it has got higher energy and that that must be vibrationally excited product. And, what happens? That vibrational excitation, if it is vibrationally excited, then what happens? It is going, this, like this.

So, it cannot cross this, going like this; and after sometime, it cannot cross the barrier, but it remains in this, in this you know, valley; it cannot cross this, cross line or this saddle point. So, reaction does not occur. So, vibrational excitation hinders the chemical

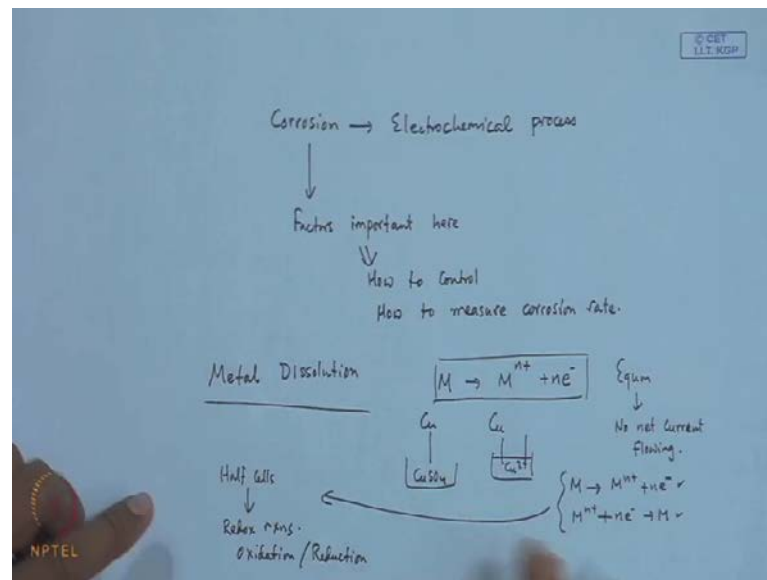
reaction for an early barrier, **for an early barrier**. So, you see, that is, Z plus F giving rise to HF plus H. So, early barrier corresponds to, **corresponds to**, you know, vibrational excitation corresponds to hindrance of reaction, but translational excitation corresponds to **corresponds to** a product with vibrationally excited situation. Next, when the case is, **it is** the case of late barrier, when it is the case of late barrier, I mean, **I mean**, barrier is here, it is nearer to product side, **it is nearer to product side**. So, what is happening? That is, you see this is your initial side; this is your final side. So, for a late barrier vibrational excitation promotes the reaction and leads to products with high kinetic energy.

So, vibrational excitation, it will lead to, you know, vibrationally excited state. So, this will ultimately help, you know, in crossing this barrier, and then it will move to the product side. But, since it is vibrationally excited, **so, excess energy**, excess energy will be **will be** transferred to the product in the form of the **in the form of the** kinetic energy. But what happens when **it is the**, it is the translational excitation? When it is translational excitation, you know, it is reflected back. So, it is reflected back to, you know, here.

So, therefore, for later barrier, that is, for later barrier or later transition state, what is happening? That is, that vibrational excitation promotes the reaction and leads to product with high kinetic energy, and translational excitation of reactant hinders the reaction. So, these are the two opposing situation, when it is late barrier and when it is early barrier; I mean, the same reaction has been represented in **opposite way** opposed ways. In this case, we are considering the backward reaction to be like this, and in this case we are considering the forward reaction to be like this. So, for the backward reaction, it is early barrier, and for the forward reaction, it is the late barrier, but the situation is different. So, that is, the effect of vibrational and vibrational excitation and also the kinetic, I mean translational excitation.

So, that is, you know, about this Polanyi's rule. Now, **next, so**, that will conclude more or less the chapter of, you know, this reaction dynamics, there are other aspects also in less things are there, but because of, you know, the scope, we should stop over here; and the topic that which topic which I am now going to cover is different from your, this dynamics, I mean reaction dynamics; that is your corrosion.

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So, corrosion is a thing that we have not dealt with earlier, but this part, I guess, I should talk, at least, you know, I should give you a little idea of these things, that this is basically an electrochemical process, corrosion is an electro-chemical process, **corrosion is an electrochemical process, electrochemical process**, and how this corrosion can be controlled, and what are the factors that are responsible for corrosion to occur. So, factors are important here; and, how to control and how to measure rate, corrosion rate. Now, let us start from metal dissolution. Metal dissolution - what is metal dissolution? I mean, when a metal is dipped into, **is dipped into**, a solution, then what is happening? That metal loses electron. So, M goes to M^{n+} plus N electron.

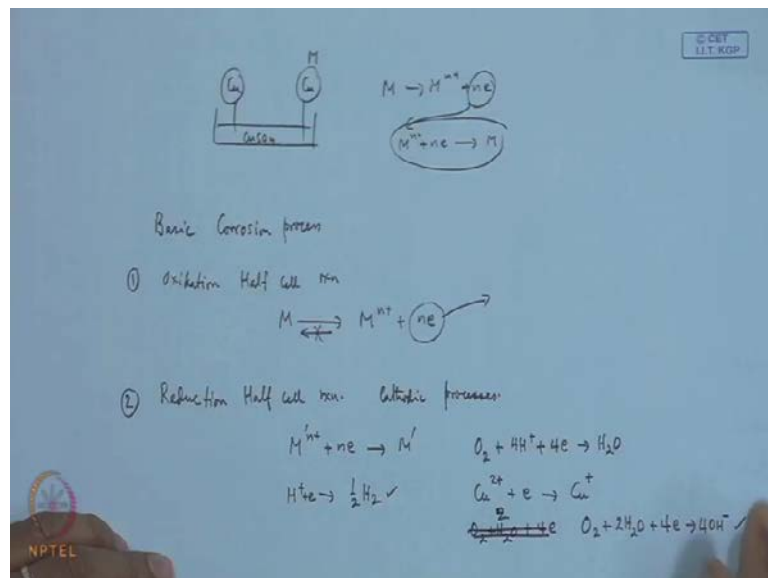
So, now, in most of the corrosion processes, **excepting** cathodically controlled processes, metal will dissolve, because corrosion is mostly related to metals. So, metals will dissolve, and we should have an understanding of the principle behind the metal dissolution process, and that will be an important part for understanding corrosion. So, in this case, consider a piece of pure metal M in a solution which contains its own ion. Say, like copper, which is dipped into copper sulfate. So, copper sulfate means Cu, Cu plus Cu, and here it is **it is** dipped Cu 2 plus. So, in this case, the metal has solubility in the solution in which it is placed, and like, you know, copper in copper sulfate.

So, general equilibrium reaction is like this, is the general equilibrium reaction; and at equilibrium, there is no net current. So, in equilibrium, no net current is flowing. So, in

one case, no net current is flowing. So, in one case, the reaction is like $M \rightarrow MN$ plus NE minus and the reverse process. So, reverse process is that, because, and the reverse process is like MN plus NE giving rise to M ; so, there is no net current. So, electrons produced in the reaction above, I mean here, it is combined with the metal N plus to give you M ; and, that is, **that is, that is** deposited onto the metal surface. So, this way, situation occurs; I mean, this may be the **may be the** two processes that could happen. So, I mean, in one case, it is dissolution; in other case, it is, **it is**, you know, deposition.

So, basically, if you have another copper over here, **so**, this reaction will take place; I mean the second reaction will take place. So, these are the half-cell reaction, half reactions. So, these are half-cells or half-cell reactions. So, these individual reactions are called half-cell reactions, as they, **as they** produce electron; one of them would produce electron and the other will consume it. So, oxidation actually produces electrons. So, this is oxidation, it produces electron and the reduction is the consumption of the electron, and both this oxidation and reduction reactions, so, half cells means redox reactions. So, both these reactions, that is, oxidation, reduction, **oxidation reduction** these are very important, you know, in corrosion.

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Now, what is happening? That is, that suppose, like as I mentioned that, you know, when metal dissolves, say copper sulfate; this is Cu , this is Cu , so, copper dissolves; and if there is nothing happening, then I mean that electron is again collected by copper 2 plus

2 deposit over here; but one thing is, what is happening? That half-cell reaction, if this half-cell reaction, you know, if they do not involve the same element. So, then what is happening? The electrons produced in, **electrons that is produced in**, say in this reaction, suppose this is copper and this is another element, say M, and what is happening? That is, if this electron produced in the forward reaction, that is, say dissolution process is not available for the back reaction, then that will, **that will**, you know, the electron which is generated over here will replace other ions back to the metal state. I mean, like $M \rightarrow M^{n+} + n e^-$. So, this electron is used up for reducing another $M^{n+} + n e^- \rightarrow M$. So, if that does not happen, that is, instead electrons from oxidation reaction are consumed by a different reaction, resulting a new reaction product. This leads to secondary reaction between products of oxidation reaction half-cells to form stable material.

So, if that does not happen, but secondary reactions are taking place, giving rise to stable products, then what is happening? This can further react with environment to form stable compounds such as rust, and these are then very difficult, you know, to get back to its original case; that is, original metal; so, that means, because of this secondary reactions, you know, this whatever products are generated, react further to produce something like rust, and rust is, you know, it is very difficult to get back to, you know, iron, and that is basically, **that is basically** the corrosion process.

So, basic corrosion process, **basic corrosion process**, it is, you know, first one is oxidation half-cell reaction, **oxidation half-cell reaction**. So, this is basically your metal to $M^{n+} + n e^-$. So, this $n e^-$, you know, if it is, you know, if this, if there is no, you know, current flowing, what is happening at equilibrium? Again, you know, it will go back over here to get back your metal; but, if that, you know, suppose this is stopped, **so**, say this is not there or maybe this is, I mean, this is further used up in other modes, then this equilibrium is shifted towards the right. So, when there is no net current flowing, then equilibrium is expected to be established; but if there is a net current, that is, if this is taken up by **some** something, then, you know, **you know**, cathodic process like this, in the, you know, anodic process.

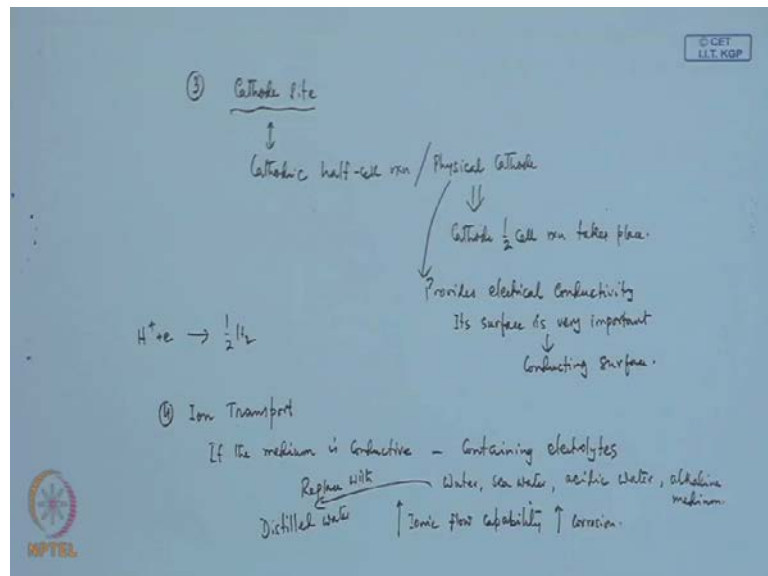
So, you know, if it is cathodic process, think of a cathodic process, where this electron is used up; so, reduction half-cell. Other second step is your reduction half-cell, **reduction half-cell** reaction. So, cathodic, you know, maybe second process, secondary process cathodic processes, **cathodic processes** like, say $M^{n+} + n e^-$, giving rise

to M primed metal, this could be one process. Another process could be like, if **this**, these electrons are used up, **used up** in other reaction, like, say, converting H plus proton to half H₂. So, this plus electron giving rise to half H₂.

So, this could be one reaction; another is, maybe another possibility is O₂ in presence of H plus 4H plus 4 electron giving rise to 2H₂; if you see that, these are used up. So, equilibrium is now shifting this way, maybe say Cu₂ plus electron giving rise to Cu plus; that is one step, maybe O₂ plus H₂O plus H₂O plus 4 electron 4 H₂O plus 2H₂O plus 4 electron.

Let me write it again. O₂ plus 2H₂O plus 4 electron giving rise to 4 OH minus. So, these are the reactions that may, **that may** happen as the **as a second step as a** second step. So, for many practical situations, this reaction these reactions, I mean, this particular reaction is very important in this case, you know, oxygen present in the, **present in the, in** water will dissolve and giving rise to alkali. So, that is the giving rise to OH minus, that is, alkali and this is a slow dissolution process. So, this is your second step. Now third step or rather a part of this may be regarded as the part of the redox, so, both half-cell reactions.

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So, next will be, third one is your cathode site. So, important feature is that, we have to distinguish between the cathodic half-cell reactions. So, we have to distinguish between cathodic half-cell reaction; and what is meant physically by cathode and the, **and the**,

physical cathode? Now, this physical cathode is a localized region, is a, **is a**, location where the cathode half-cell reaction occurs. So, here, in this physical cathode here, cathode half-cell reaction takes place, here cathode half-cell reaction takes place. And, cathode only provides, **now**, this cathode, this physical cathode, this provides; what does it provide? It provides the electrical conductivity necessary for electron transfer for cathode half-cell reaction.

So, it provides electrical conductivity, provides conductivity, electrical conductivity, which is necessary for electron transfer to occur at the cathode; and, this reaction will occur on a surface which has the capability to conduct electron; so, surface is very important. So, it provides electrical conductivity, **and the surface**, and its surface is very important, so, it should have the capability to conduct.

So, conducting surface, conducting surface, and in some cases, what is happening? That is, some other non-metallic materials maybe, which is conducting, can act as the, **as the as** cathode as well. Electrically conductive materials can be cathode and it should also be apparent that the cathode does not, in that case, dissolve and can be termed as being as cathodically protected, I mean, it is **it is** a protected one, which does not dissolve another cathode reaction; it is the reduction of hydrogen ions, as I told you. And, in this case, hydrogen gas will be, **will be**, nucleated, over there at the cathode. So, for this half H₂, which is generated from H plus electron; so, reduction of H plus.

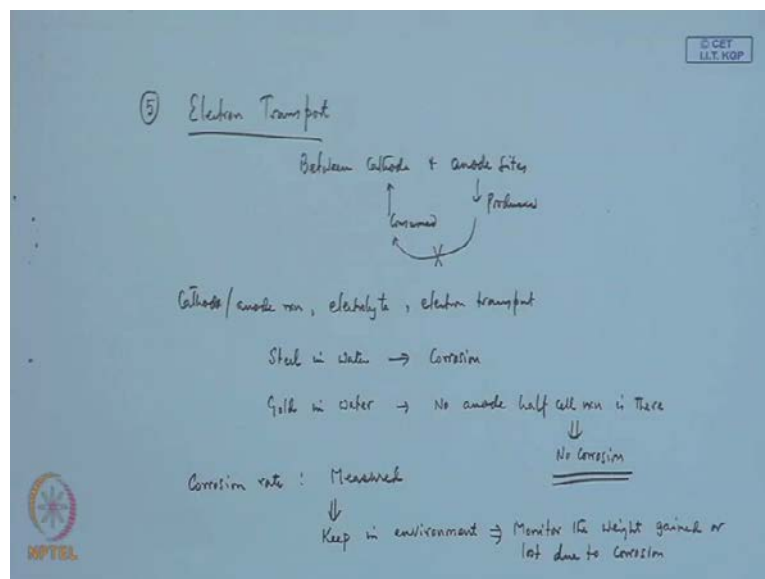
So, this, as a result of this, hydrogen will be, **will be**, you know, will be covering the cathodes, cathode surface, **so**, nucleated, and this hydrogen will be nucleated, and this distinction between cathode reaction and cathode material is important. When we look into the localized corrosion, localized corrosion means, the corrosion when the corrosion is very much localized in nature; basically, it may be, **it may be** thought that there were regions which are not corroded, or maybe cathodically protected. Next is the fourth one, is your ion transfer.

Ion transfer: now, this process where, you know, ionic transfer is very important. So, if the medium, **if the medium**, like if electrolyte is present, **so**, if the medium is conductive, that is containing maybe containing electrolytes, **containing electrolytes**, it is very important. So, the presence of electrolytes is of immense importance in many cases, environmental exposures like for environmental exposure, I mean, when exposure of

your material in environment like water, through water maybe sea water, maybe acidic water or maybe alkaline water or alkaline medium, is very important. The greater the ionic flow capability of the solution the greater is the corrosion rate.

So, that means, that means, conducting property of your solution when it is high, then rate of corrosion is also high. So, that means, the greater the ionic flow capability, the more is, **more is**, ionic flow capability, more is corrosion. **Thus, you know...** And another important point is, if you use distilled water with high resistance, high resistance and low conductivity, usually in this case, if you replace this, you know, if you replace all this wherever needed with distilled water, **distilled water**, replaced with distilled water, then the corrosion rate is low. So, in this case, corrosion rate, because compared to your sea water or acidic water, alkaline medium, this has got low conductivity. So, low conductivity means it does not support, you know, high corrosion. So, ion transport is very important. So, that means, ion transport, **so**, ion transport rate is important in determining the corrosion rate. Next is electron transport.

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Electron transport: so, there must be a mechanism by which the electron will be transported between the cathode side and anode side. So, electron transport between cathode and anode sides: now, since electrons are produced by oxidation in anodic half-cell reactions, electrons are produced half-cell reactions and consumed by the cathodic reaction. So, it is produced, and here it is consumed. So, that means electrons will flow

from here to here. So, without flow of electrons between anode and cathode, these half-cell reactions, you know, will not be completed. So, that means, **that means** there must be some means like electrical, I mean wire connection or like wire connection, I mean the electrons flow along wire from anode to cathode could be away.

So, if by some means we can hinder this electron, you know, flow from one side to the other, then possibly, **we can**, we can reduce the extent of corrosion. So, if we can **impair**, I mean, if we can stop it, then maybe corrosion can be, **can be**, you know, can be reduced. So, therefore, **so, therefore**, these points are to be, **are to be**, looked into, giving importance. So, now, the thing is that, this, in summary, what we can say? That these five points, I mentioned those five; 1, 2, 3, 4, 5 points I mentioned, that these are the, **these are the**, necessary processes that are necessary for corrosion to occur. I mean, wherever this happens, corrosion is there; so, that means these are necessary. So, that means, your **like** half-cell reactions, then cathode side ion transport, electron transport; these are important points.

So, like cathode and anode reaction, cathode anode reaction, electrolyte, then electrolyte then, you know, electron transfer, these are the very important points. As for example, many materials like steel, if we put steel in water, steel in water, and what is happening? That is, all these processes, as I mentioned in half-cell reaction transport, ion transport electron transport, all these happen. Therefore, steel in water will undergo corrosion; this will undergo corrosion; and, for other materials in some environment, maybe if we **if we** choose the environment such that, out of these steps, if one is stopped, then probably corrosion can be controlled.

So, in other environments, no corrosion may occur. For example, if we put gold in water, **gold in water**, what is happening? Because gold is used, you know, in jewelry and it is a noble metal. So, if we put gold in water now, possibly, you know, what happens? That is, no anode half-cell reaction is there, so, for gold in water, no anode half-cell reaction is there.

So, anode half-cell reaction means the, you know, like $M \rightarrow M^n + ne^-$ is there; therefore, no corrosion. That is for gold; that is why it is **it is** a noble metal. So, you do not see corrosion with gold, but maybe with, like silver, it is not that much, you know, that has good like, as good as gold in same way; steel will have corrosion. Now, how to measure

this corrosion rate? Because, it is **it is** an important thing that corrosion rate may be measured, rate can be measured, maybe in a very simple way that you put your substance; I mean, the material which is, **which is** expected material; that is, material which is going to be corroded, you put in the **in the** environmental condition.

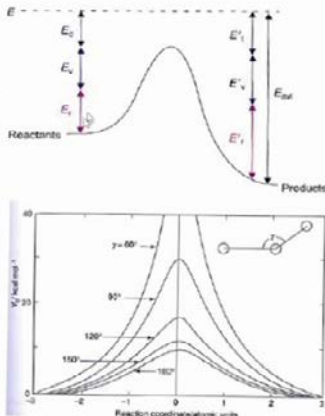
So, keep it in the environment, and what you do? That is, that you put in the environment, and then you monitor the weight gained or lost or lost due to weight gained or lost due to corrosion. So, you monitor that; that is the simplest way. Like, you take a piece of iron and maybe you keep that iron in the atmosphere; that is, a clean piece of iron, **and a clean piece of iron**, and then you want, since you want to measure the corrosion rate, you keep in the atmosphere. And, for that, you measure the weight that will give you the idea, I mean, give you the rate of corrosion, that is change of weight with time; and, it since, it is a slow process, maybe you have to wait for, you know, you have to observe for long time. Next is, it can be measured, you know, electrochemically by constructing cells, and you measure polarization, cathodic and anodic polarization and application of Tefl and Butler-Volmer equations. You should be able to find out the rate of corrosion and rate of electron transfer in these processes. So, that I already have, you know, talked about in electrodic chapter.

So, this way, you can, you can, you know, find out the rate of corrosion; that is also a rate process. So, today, what we have we have learnt? That, in this, we are about to conclude our session, I mean final conclusion will be drawn in the, **in the**, next lecture. But here, we have learnt this, you know, again we talked about this potential energy surface and how this potential energy for the reaction, I mean the potential barrier can depend on the angle of approach, and we have taken the example of H_2 plus H reaction; the more the angle, I mean, if it is 180 degree, it is the, **it is the** optimal angle, but if it is less than or greater than, then, you know, barrier increases, and that barrier can be overcome with, if your reactants have higher energy. So, that barrier can simply be overcome, that is the, if the total energy of the reactant is more, then your barrier can be can simply be overcome.

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If the total energy in the reactants (the sum of collisional energy E_c , vibrational energy E_v , rotational energy E_r , and electronic energy E_e if applicable) is higher than the barrier height, the reaction can proceed in principle. The available energy E_{avl} after the collision is distributed among the products.

For an $A + BC$ reaction, the barrier height in general changes for different approach angles. If more energy is stored in the reactants, the barrier can also be crossed for approach angles differing from the optimal value. Thus, the cone of acceptance of the reaction can be increased.



The figure consists of two diagrams. The top diagram is an energy profile showing potential energy versus reaction coordinate. It starts at a reactant energy level, rises to a peak (transition state), and then falls to a product energy level. Energy levels are labeled: E_c (collisional), E_v (vibrational), E_r (rotational), and E_e (electronic) for reactants. Corresponding levels for products are E'_c , E'_v , E'_r , and E'_e . The barrier height is E_{bar} . The bottom diagram is a reaction coordinate diagram showing the rate constant k versus reaction coordinate for different approach angles γ : 60°, 90°, 120°, 150°, and 180°. The rate constant is highest at 90° and lowest at 180°. A small inset shows a molecular model of the reaction $A + BC$ with the approach angle γ indicated.

P. Singh et al., J. Chem. Phys. 68 (1978), 2457
D.G. Truhlar et al., J. Chem. Phys. 68 (1978), 2166
NPTEL

Like this, barrier can simply be overcome. And, if you know, cone of acceptance can vary depending on your energy, total energy in the reactants. And, we also have talked about this Polanyi's rule regarding the late barrier and early barrier, and how this vibrational and kinetic vibrational energy and kinetic energy can affect the process. And lastly, we talked about this corrosion process, a very simplistic idea of corrosion over what are the, you know, factors; I mean, what are the steps that are important in corrosion, that we have talked about, and how to, you know, **you know**, control that. And also, we have given, just given you the idea of measuring corrosion rate.

So, that is all for today. So, in the next lecture, that is probably our final lecture, where we are going to conclude what we have learnt in these pieces of, you know, lectures. So, till then, thank you.