Technology of Surface Coating
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Lecture-02
CVD Reaction

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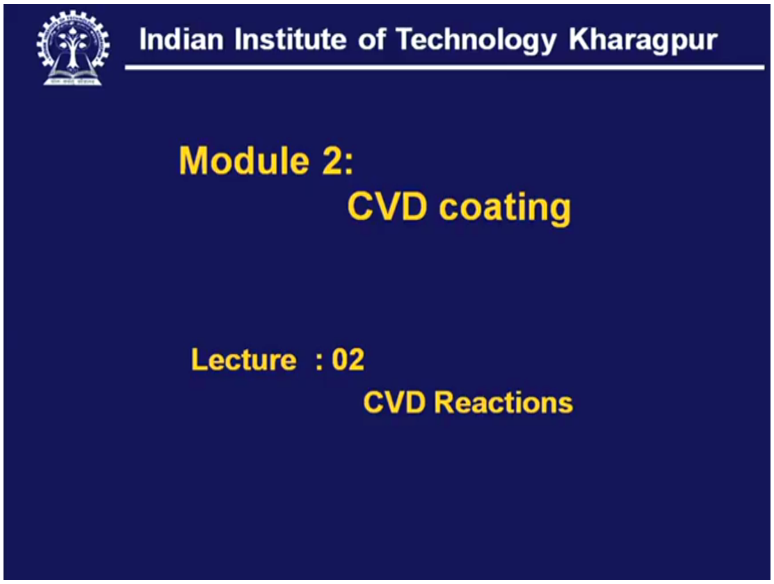

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Module 2:
CVD coating

Lecture : 02
CVD Reactions

It is not coming here. Oh, okay, in this session we discuss about CVD reactions.

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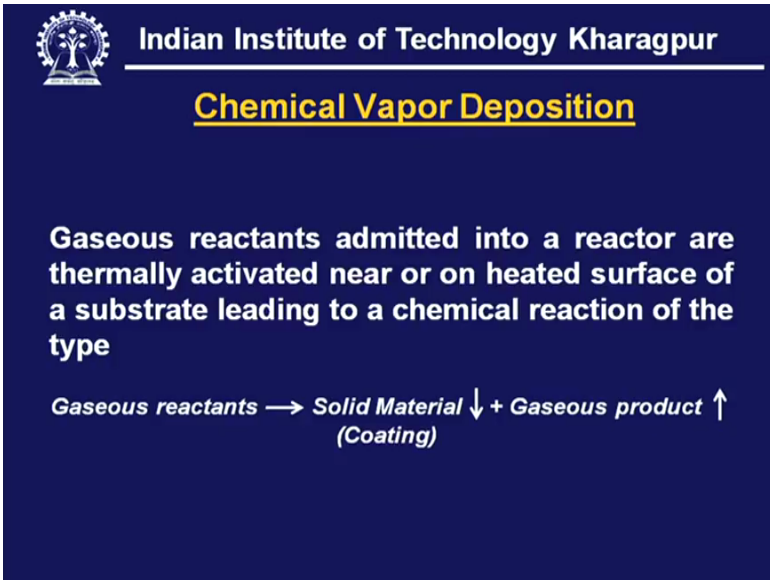

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Chemical Vapor Deposition

Gaseous reactants admitted into a reactor are thermally activated near or on heated surface of a substrate leading to a chemical reaction of the type

Gaseous reactants ⟶ Solid Material ↓ + Gaseous product ↑
(Coating)

What is meant by chemical vapor deposition? In this particular process, some of the gaseous reactants are admitted into a reactor and they are thermally activated. And near the substrate surface or on the substrate surface, a chemical reaction takes place leading to deposition of a solid material and a reaction product which is gaseous in nature.

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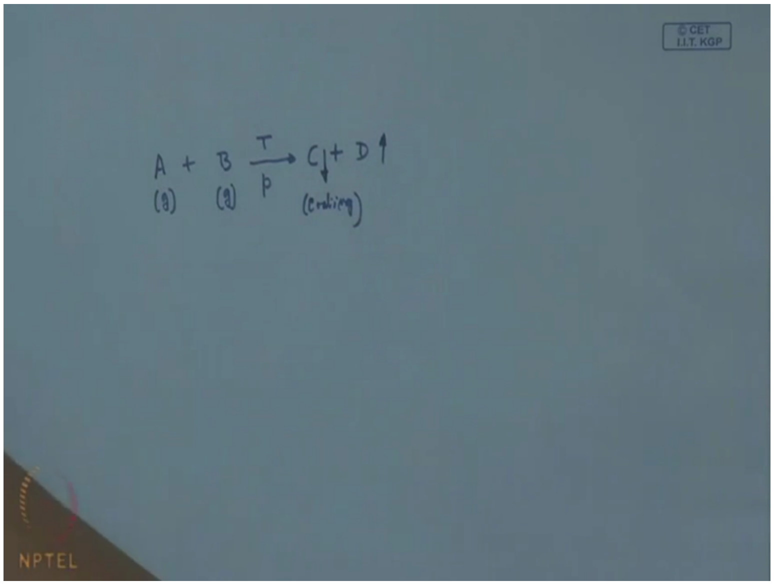

$$\underset{(g)}{A} + \underset{(g)}{B} \xrightarrow[P]{T} \underset{(\text{coating})}{C\downarrow} + D\uparrow$$

It means we have two gaseous reactants and under certain condition of temperature and pressure in the CVD reactor, we are going to have one C plus D and this C is deposited as a solid and this is actually the coating and the gaseous phase which is actually the reaction product. This is leaving the reactor, so this is basically a chemical vapor deposition process.

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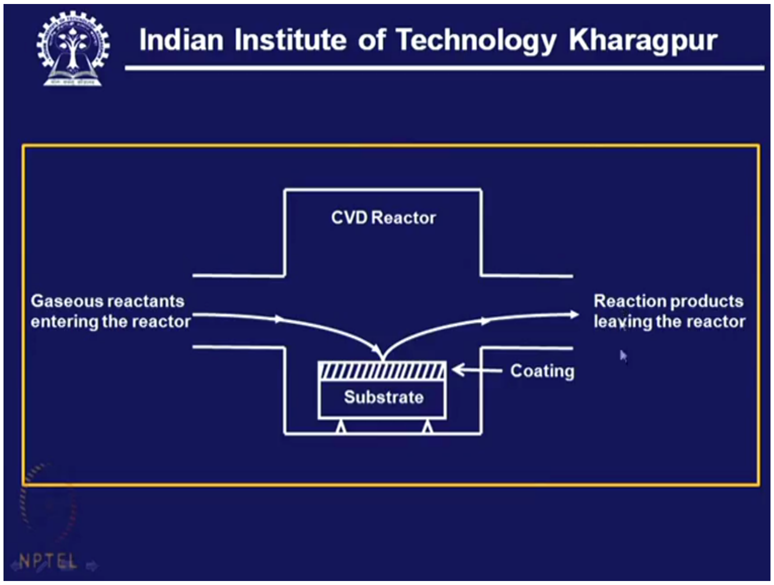

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CVD Reactor

Gaseous reactants entering the reactor

Reaction products leaving the reactor

Coating

Substrate

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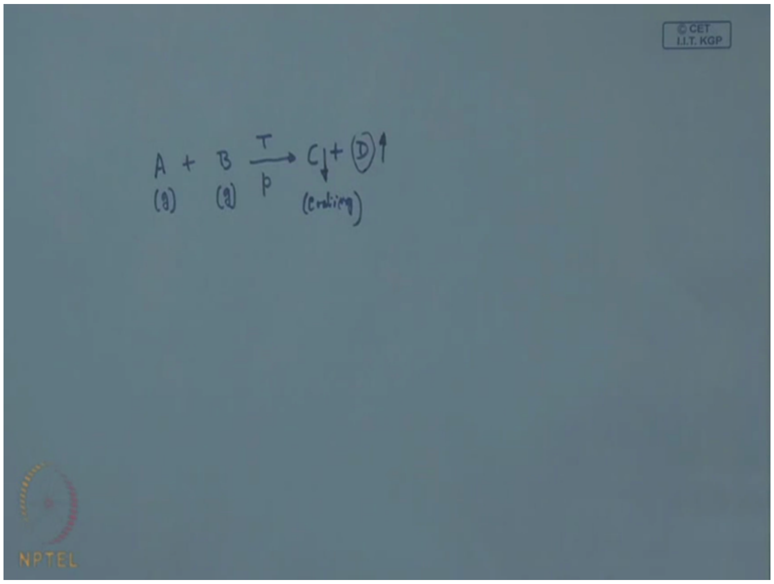

$$\underset{(g)}{A} + \underset{(g)}{B} \xrightarrow[P]{T} \underset{(\text{coating})}{C\downarrow} + \textcircled{D}\uparrow$$

Now here we see, what we see that this is a CVD reactor schematically shown. This is the location of the substrate and the gaseous reactants which are admitted into this reactor in a very controlled manner, they are coming in the vicinity of the substrate and the necessary reaction takes place over this surface. And as a result of that, a solid phase is deposited and as an outcome of this reaction, we have this byproduct which should leave this reactor. That is what we have shown here.

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Application of CVD

- Coating of functional surface of a component
- Producing coated particle
- Free standing part
- Powder
- Single crystal
- Filament
- Fibre
- Whiskers etc.

Now this application of CVD, that means this chemical vapor deposition, we have various applications. That means it can be directly used just like a coating on a substrate the way we see it.

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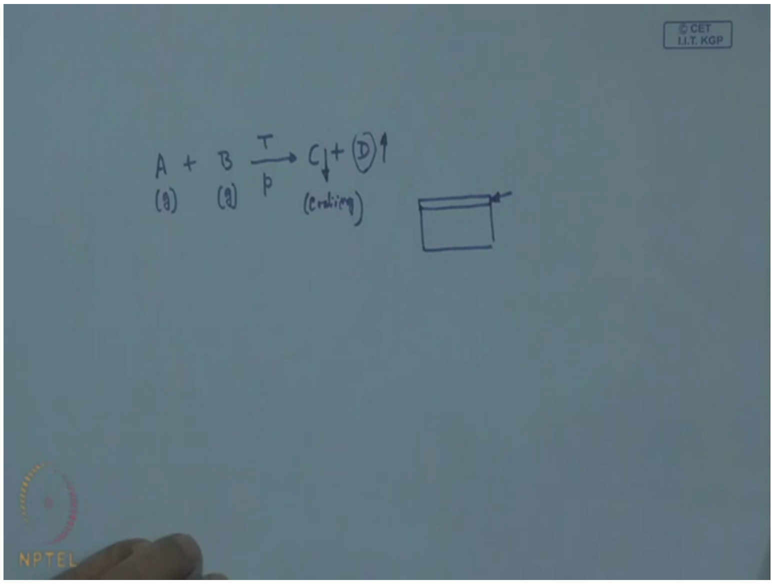

It is the substrate on which a coating can be deposited which has some functional task.

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Application of CVD

- Coating of functional surface of a component
- Producing coated particle
- Free standing part
- Powder
- Single crystal
- Filament
- Fibre
- Whiskers etc.

Then it can be also used for producing coated particle.

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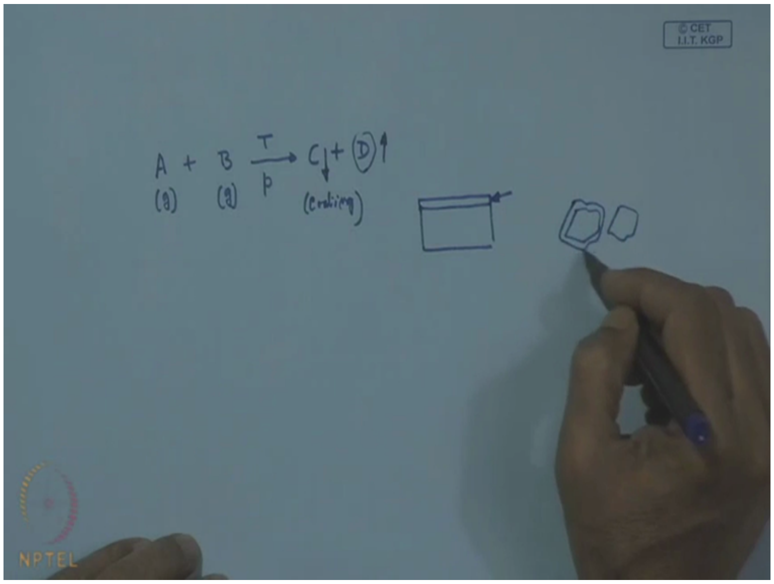

That means there are certain particle and which can be also coated by this CVD process. This coating material can be also covered or it can also cover this coated particle.

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Application of CVD

- Coating of functional surface of a component
- Producing coated particle
- Free standing part
- Powder
- Single crystal
- Filament
- Fibre
- Whiskers etc.

It can be also used for making free standing part.

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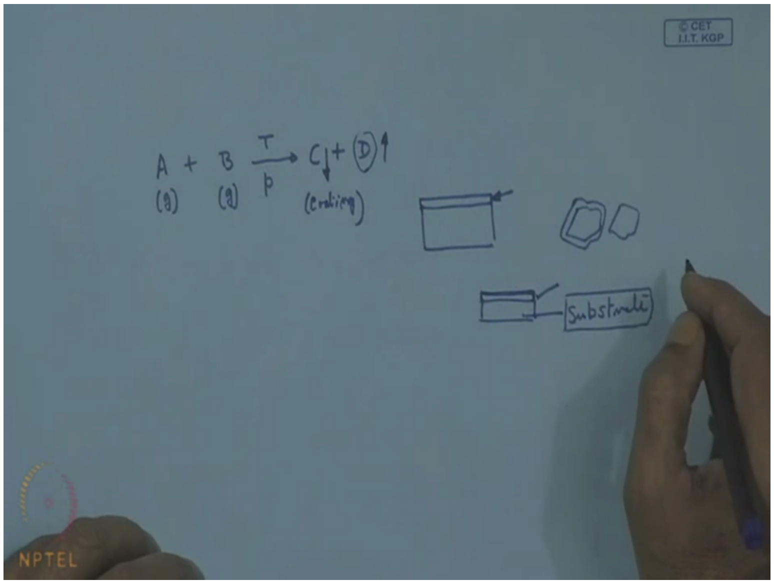

That means on a substrate, we can have a coating, a metal thick layer which can be deposited by CVD. And later, this substrate can be disposed just keeping this as the coating material and that is actually the material for engineering use.

CVD can be also used for making the powder. Here we see that this coating, it is a solid material, solid layer but this material can be also converted in the form of dust or powder and it can have various application.

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Application of CVD

- Coating of functional surface of a component
- Producing coated particle
- Free standing part
- Powder
- Single crystal
- Filament
- Fibre
- Whiskers etc.

Also, instead of a (cover) coverage or having some dust, one single crystal can be also grown and it can be also used in various application. A filament, say for example, a tungsten filament can be also made by this process. It can be as an extension of the CVD, we can also use it for making fiber or whisker.

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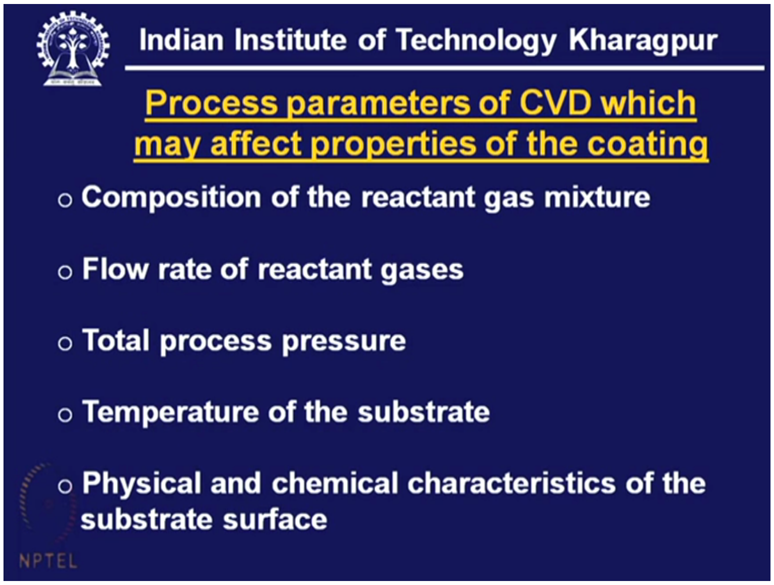

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Process parameters of CVD which may affect properties of the coating

- Composition of the reactant gas mixture
- Flow rate of reactant gases
- Total process pressure
- Temperature of the substrate
- Physical and chemical characteristics of the substrate surface

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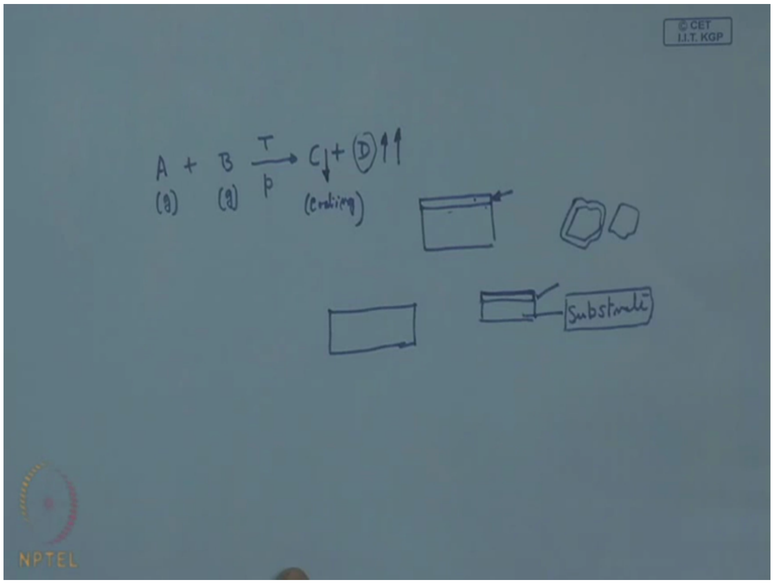

Now important things are the process parameters. To have proper control on the process, final composition of this product, this coating, its structure and all the functional properties, there must be close control or some process parameters.

And these parameters are namely composition of the reactant gas mixture, in what ratio they are admitted in the reactor. Then comes the flow rate of this reactant gas. It can be so many liters per minute or SCCM, standard cubic centimeter per minute. Then the process pressure inside the

CVD chamber, we have to also control the process, it can be atmospheric, it can be also atmospheric ranging from very low to very medium or high.

More importantly, we see here temperature of the substrate because it is the goal of this process to have this reaction on the surface. That means this A plus B which is actually converted into C plus D, D goes out, leaves the reactor as the reaction gaseous product. But D has to be deposited and this D means here the temperature of the substrate is extremely important, otherwise, this synthesis may not take place on the substrate. Then one thing also should, we should consider, that means this is the physical and chemical characteristics of the substrate surface because we have to know that this is going to be the substrate surface, this is going to be the receptor surface.

So naturally here physical compatibility and chemical compatibility too, these two are the requirement to have proper deposition. That means sticking of these reacting species over the surface so that necessary reaction can be initiated.

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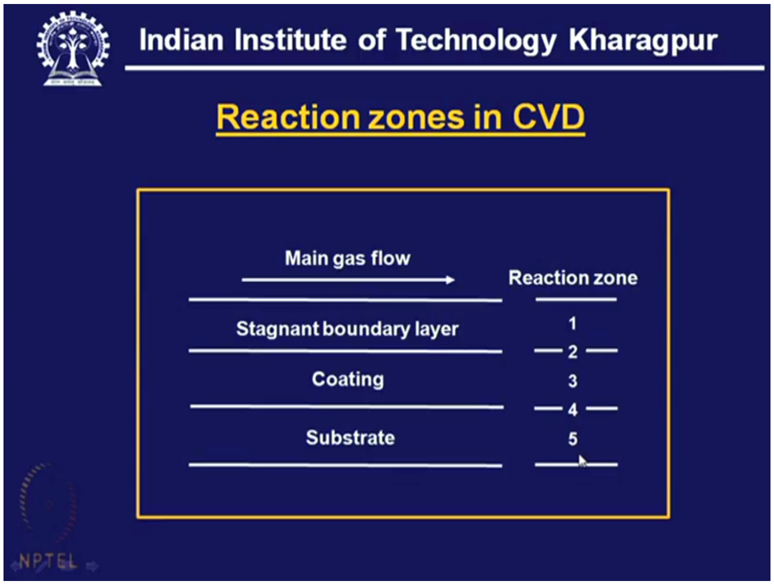

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Reaction zones in CVD

Here we try to understand the various reaction zones in a CVD process. What we see, this is actually the substrate. Over that, coating is gradually growing and this is the main gas flow which is admitted. But from this fluid mechanics point of view, there have to be a stagnant boundary layer which does not move, which does rather stick to this. Now at the very initial phase of substrate, this stagnation occurs at this substrate surface. And once this coating grows, then this boundary layer moves up and it now keeps the contact with the coating.

So what happens here, we find that reaction zone that means this is the reaction Zone 1. That means in the boundary layer, within the boundary layer there we can have some reaction. Then this is the reaction Zone 2 that is the phase boundary between the stagnation layer and the solid phase coating. Then we have the interface between the coating and the substrate. And then this is the Zone 5 that is the substrate as a whole.

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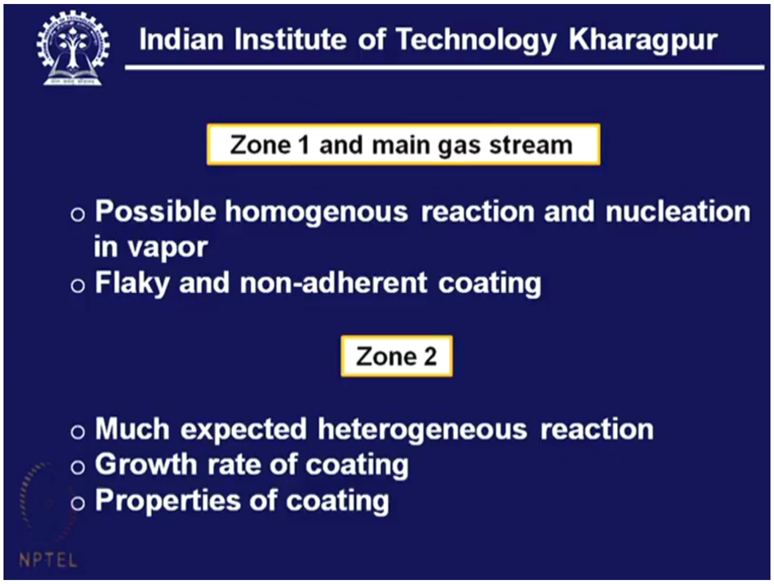

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Zone 1 and main gas stream

- Possible homogenous reaction and nucleation in vapor
- Flaky and non-adherent coating

Zone 2

- Much expected heterogeneous reaction
- Growth rate of coating
- Properties of coating

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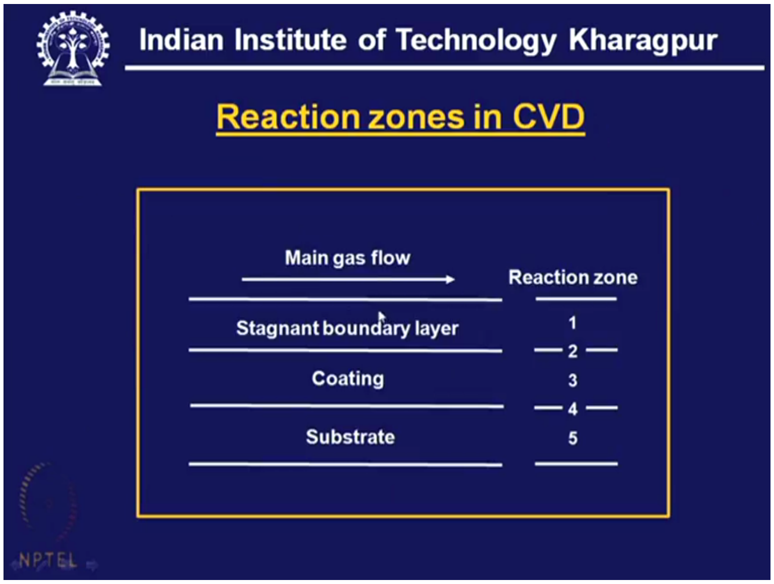

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Reaction zones in CVD

Now Zone 1 and the main gas stream, here we can see if we have certain favorable condition, that means in the zone and in the main gas flow what is going to happen? We may have homogeneous reaction and nucleation in vapor phase and that may lead to flaky and non-adherent coating which is most undesirable in any CVD process when we like to have a well adherent functional coating.

Then we arrive at this Zone 2, much expected heterogeneous reaction. That means here either it is between this vapor phase and the solid surface of the substrate or once the coating grows, it is between the coating and this stagnant boundary layer. That means the vapor phase and the coating, that contact layer. So here we want the much expected heterogeneous reaction and this actually governs the growth rate of coating and properties of the coating.

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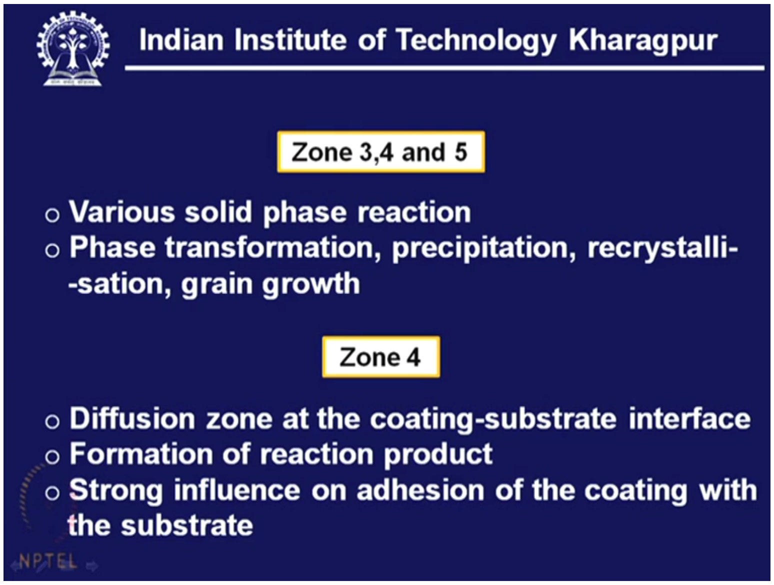

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Zone 3,4 and 5

- Various solid phase reaction
- Phase transformation, precipitation, recrystalli--sation, grain growth

Zone 4

- Diffusion zone at the coating-substrate interface
- Formation of reaction product
- Strong influence on adhesion of the coating with the substrate

We have Zone 3, 4, 5 where various solid phase reaction may take place. And this can be phase transformation, precipitation, recrystallization and grain growth.

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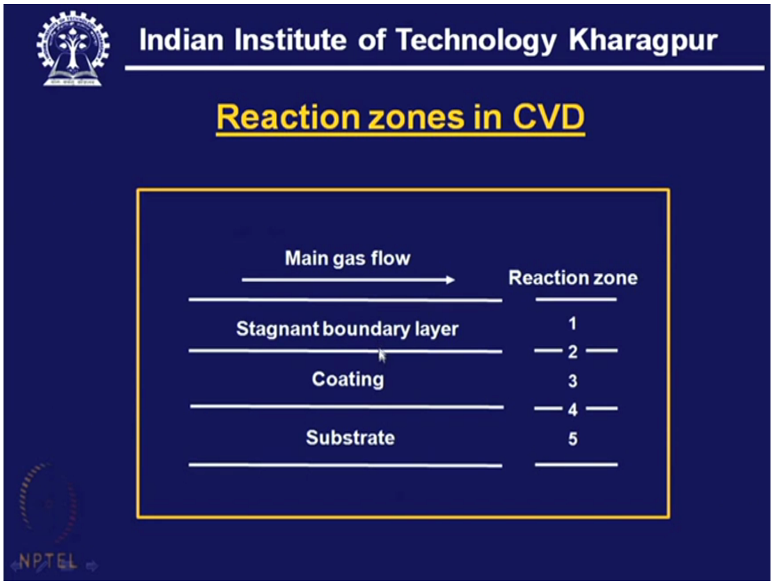

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Reaction zones in CVD

That means if we get back to this figure, we have this 3, 4, 5; this is the solid phase and here we can expect this reaction in the solid phase.

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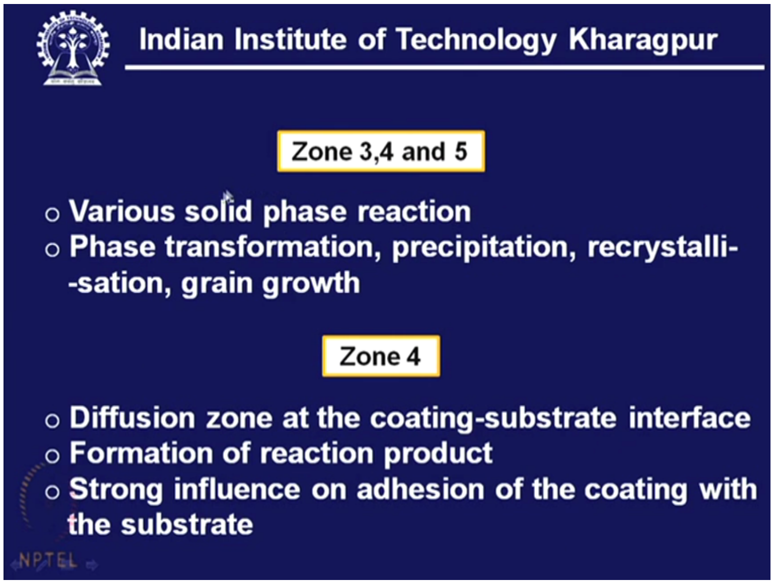

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Zone 3,4 and 5

- Various solid phase reaction
- Phase transformation, precipitation, recrystallisation, grain growth

Zone 4

- Diffusion zone at the coating-substrate interface
- Formation of reaction product
- Strong influence on adhesion of the coating with the substrate

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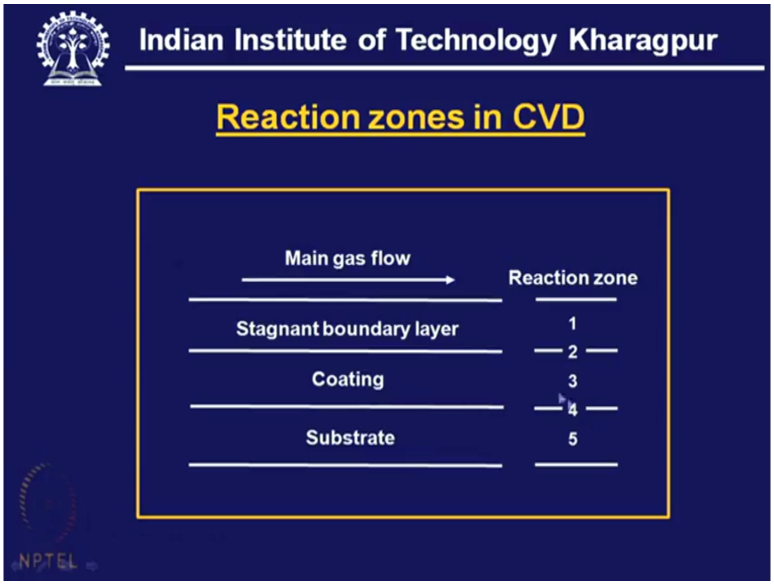

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Reaction zones in CVD

Main gas flow

Reaction zone

	1
Stagnant boundary layer	2
Coating	3
	4
Substrate	5

Now we should put our concentration in Zone 4. This is actually the diffusion zone. This is the diffusion zone between 3 and 5 and this is actually the interface between the coating and the substrate. This diffusion is extremely important and it must be, it must take place in a very controlled manner so that we can have transportation of this material across the coating and the substrate, but at the same time not to promote a very severe diffusion leading to a very, very thick diffusion layer which may have different characteristics with respect to coating as well as with respect to the substrate. So that thick layer formation, that require to be avoided.

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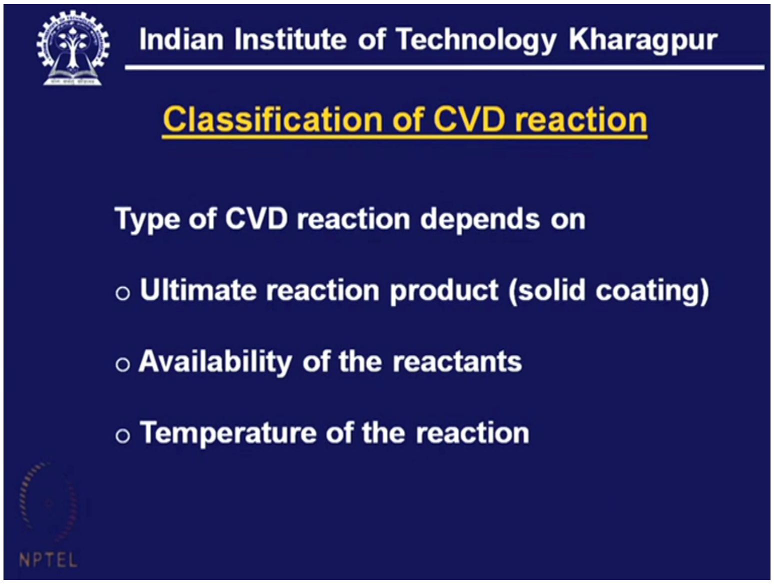

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Classification of CVD reaction

Type of CVD reaction depends on

- Ultimate reaction product (solid coating)
- Availability of the reactants
- Temperature of the reaction

Now we go to this section, classification of the CVD reaction. Now there are various types of CVD reaction but ultimately which one should be utilized? That depends upon the ultimate end-product what we like to have and also availability of the reactant, in what form it is available. Most, I mean intelligent way to, would be to find out the reactant which are available as commercial product and then, the temperature of the reaction which we can allow because it depends upon the selection of the substrate or say physics and chemistry of the substrate. So this temperature of the CVD reaction, that is also restricted considering the substrate material.

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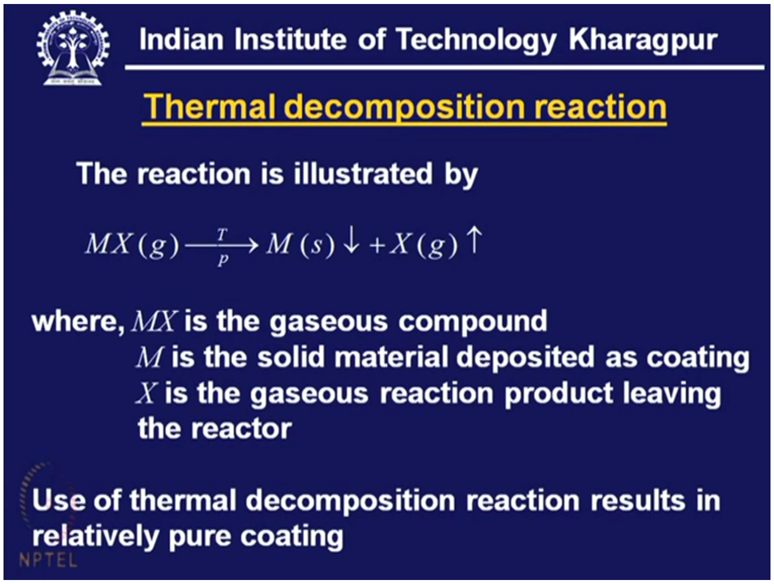

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Thermal decomposition reaction

The reaction is illustrated by

$$MX(g) \xrightarrow[P]{T} M(s)\downarrow + X(g)\uparrow$$

where, MX is the gaseous compound
M is the solid material deposited as coating
X is the gaseous reaction product leaving the reactor

Use of thermal decomposition reaction results in relatively pure coating

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We go to this first one, thermal decomposition reaction. This reaction can be illustrated by this general form where M is the metal part of this compound and X, that is non-metal, it can be one halogen or it can be hydride, that means it is hydrogen. And when we simply raise the temperature of this one in the vapor phase and under a certain condition of pressure, it is expected that there will be a separation of this metal from this non-metal part and this will be deposited on the coating as a solid phase. And this is going to leave the reactor.

So here, as we have said this is the gaseous compound which we can have as a commercial product and which can be evaporated to this, near this substrate where this necessary reaction that will take place. And this is going to leave the reactor now this use of this thermal decomposition reaction results in relatively pure coating. So this is one, I mean one point of attraction where we have to use this process for getting this metal in the form of a deposit just by splitting that compound.

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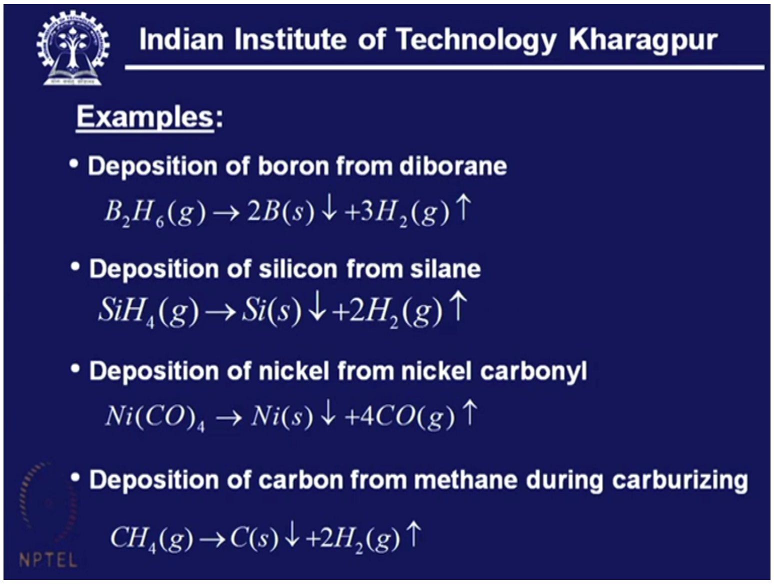

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Examples:

- Deposition of boron from diborane

$$B_2H_6(g) \rightarrow 2B(s)\downarrow + 3H_2(g)\uparrow$$

- Deposition of silicon from silane

$$SiH_4(g) \rightarrow Si(s)\downarrow + 2H_2(g)\uparrow$$

- Deposition of nickel from nickel carbonyl

$$Ni(CO)_4 \rightarrow Ni(s)\downarrow + 4CO(g)\uparrow$$

- Deposition of carbon from methane during carburizing

$$CH_4(g) \rightarrow C(s)\downarrow + 2H_2(g)\uparrow$$

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We go to these various examples. It is actually diborane which will be split into boron as solid and hydrogen, this will leave the reactor. We may consider another example, that means silicon deposition from silane. It is also a hydrogen, hydride. So we can also split silicon as deposit, I mean releasing hydrogen. There is another compound called nickel carbonyl, it is a low temperature decomposition is possible, just at 200 it will split into nickel as a film and this CO in the form of gas.

We can also see that methane can be also used for this CVD. If it is thermally excited, activated, we can have splitting of this hydrogen and carbon. This carbon can be deposited and this can be used in many of the well-established heat treatment process just like carburizing, that means enriching the surface of any material, most likely it is a steel by carburizing process.

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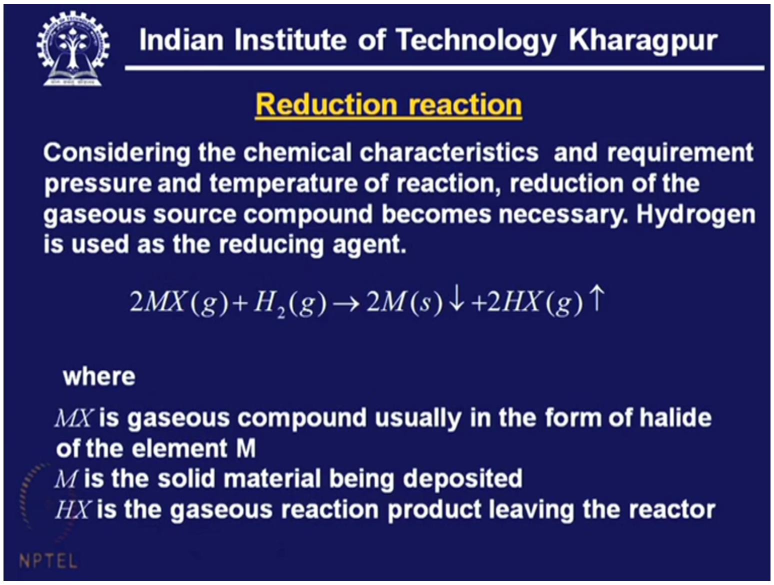

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Reduction reaction

Considering the chemical characteristics and requirement pressure and temperature of reaction, reduction of the gaseous source compound becomes necessary. Hydrogen is used as the reducing agent.

$$2MX(g)+H_2(g)\rightarrow 2M(s)\downarrow +2HX(g)\uparrow$$

where

MX is gaseous compound usually in the form of halide of the element M
M is the solid material being deposited
HX is the gaseous reaction product leaving the reactor

NPTEL

This is reduction reaction. Now considering the chemical characteristics and requirement of pressure and temperature, it may not be always possible to have this deposition of a material simply by thermal decomposition. And here we have to take help of hydrogen and hydrogen will do the necessary reduction of metal just splitting this halogen and making a hydride of that halogen. That means in case of chlorine, it could be a hydrogen chloride. In case of iodine, it can be hydrogen iodide and like this. So here we feel, see that this reduction, that means getting this metal in the form of a coating is possible by reduction of hydrogen, and this is to leave the reactor.

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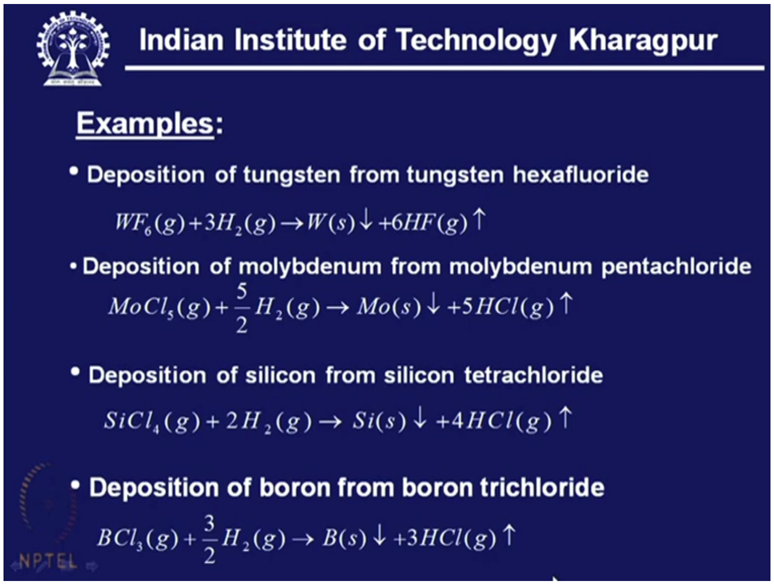

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Examples:

- Deposition of tungsten from tungsten hexafluoride

$$WF_6(g)+3H_2(g)\rightarrow W(s)\downarrow+6HF(g)\uparrow$$

- Deposition of molybdenum from molybdenum pentachloride

$$MoCl_5(g)+\frac{5}{2}H_2(g)\rightarrow Mo(s)\downarrow+5HCl(g)\uparrow$$

- Deposition of silicon from silicon tetrachloride

$$SiCl_4(g)+2H_2(g)\rightarrow Si(s)\downarrow+4HCl(g)\uparrow$$

- Deposition of boron from boron trichloride

$$BCl_3(g)+\frac{3}{2}H_2(g)\rightarrow B(s)\downarrow+3HCl(g)\uparrow$$

We can see those examples. One of the very interesting CVD is most commonly used as getting a film or coating of tungsten. And here tungsten hexafluoride is commercially available at around 500 to 550. The reaction will be product favored and by this hydrogen it is possible to move this reaction in the forward direction releasing this tungsten and also with the formation of hydrogen fluoride.

Similarly, we have molybdenum pentachloride and this molybdenum pentachloride also can undergo this reduction process by this hydrogen and here it is hydrogen chloride which comes like the reaction product. Deposition of silicon from silicon tetrachloride, that can be also utilized by this reduction of hydrogen. We can have another one boron chloride.

So we have numerous examples and all these whether it is tungsten, molybdenum, silicon or boron, each has its own use just like a metal or it can interact with the substrate making one composite having the desired property to do the necessary function. So these are the few examples of CVD reaction by hydrogen reduction.

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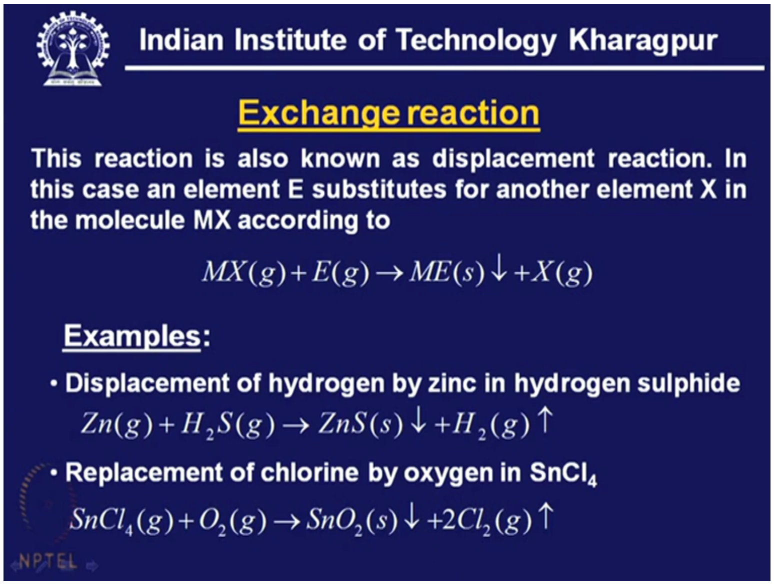

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Exchange reaction

This reaction is also known as displacement reaction. In this case an element E substitutes for another element X in the molecule MX according to

$$MX(g)+E(g)\rightarrow ME(s)\downarrow+X(g)$$

Examples:

- **Displacement of hydrogen by zinc in hydrogen sulphide**

$$Zn(g)+H_2S(g)\rightarrow ZnS(s)\downarrow+H_2(g)\uparrow$$

- **Replacement of chlorine by oxygen in $SnCl_4$**

$$SnCl_4(g)+O_2(g)\rightarrow SnO_2(s)\downarrow+2Cl_2(g)\uparrow$$

Now we go to this exchange reaction. Exchange reaction is also known as displacement reaction. In this case, say this is one metal halide, it can be metal halide. And we have one gas in the form, it is E, that is one element, it is the gas, gaseous phase. And then there will be exchange of this position of X by E, that means E is displacing X and releasing X in the form of gas. This is called exchange reaction and we can use it in actual chemical vapor deposition just if we follow these following examples.

It is hydrogen sulfide, this is in the form of E and zinc, this is in this form. So here also we can find that this metal is converted into zinc sulfide releasing hydrogen free. So this is exchange of this position and this Zn taking up the position of hydrogen and hydrogen is set free, it is in the form of gas. Similarly replacement of chlorine by oxygen, this is also possible. That means this chlorine is displaced by oxygen giving this oxide of tin and releasing chlorine.

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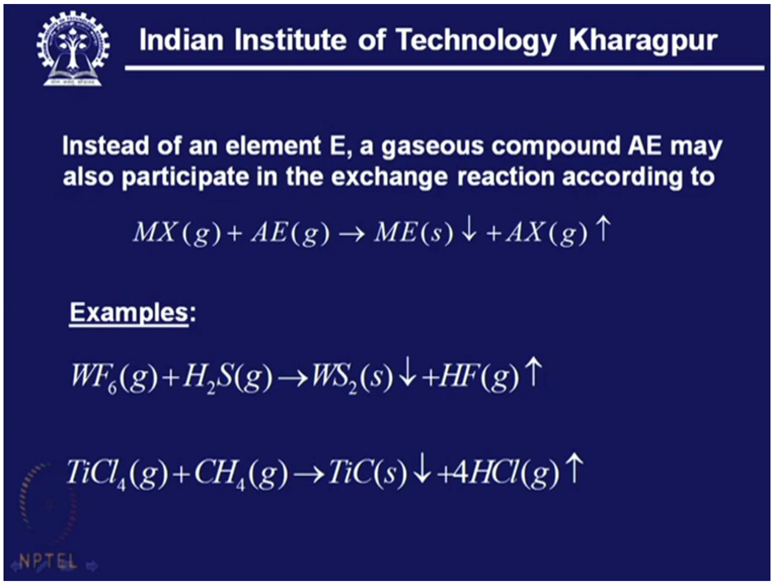

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Instead of an element E, a gaseous compound AE may also participate in the exchange reaction according to

$$MX(g) + AE(g) \rightarrow ME(s)\downarrow + AX(g)\uparrow$$

Examples:

$$WF_6(g)+H_2S(g)\rightarrow WS_2(s)\downarrow + HF(g)\uparrow$$

$$TiCl_4(g)+CH_4(g)\rightarrow TiC(s)\downarrow + 4HCl(g)\uparrow$$

Instead of element E, what we have considered so far, one element E is participating in this exchange or displacement. But instead of the element, one gaseous compound can also be very active and participate in this exchange reaction, which is shown here by this general form. AE is the gaseous reactant and MX which can donate this metal, and it is going to be a combination of ME instead of just metal. This is going to be a compound having some interest in many engineering application. And AX come in the form of a gas and which is the byproduct.

So here we can find out this example. The tungsten hexafluoride which was reduced in the previous example by hydrogen reduction, but now it is both have been brought together, this tungsten hexafluoride and hydrogen sulfide resulting in formation of tungsten disulfide and HF. And this tungsten disulfide has numerous use in mechanical application, in tribological application.

We can take another, consider another example. Titanium tetrachloride and in this case it is methane. And there also exchange of the position between chlorine and carbon, so carbon is taking up this position and chlorine is actually occupying the position of carbon. And we have here titanium carbide and the result is also the formation of hydrogen chloride.

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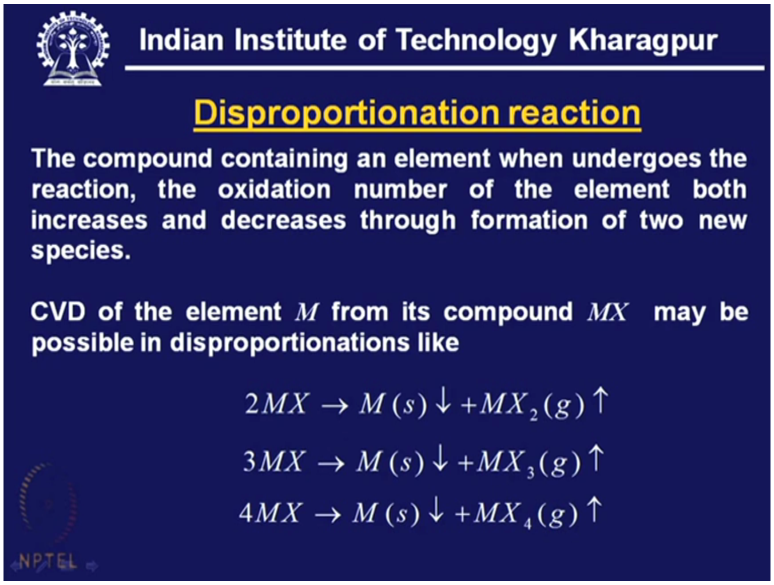

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Disproportionation reaction

The compound containing an element when undergoes the reaction, the oxidation number of the element both increases and decreases through formation of two new species.

CVD of the element M from its compound MX may be possible in disproportionations like

$$2MX \rightarrow M(s)\downarrow + MX_2(g)\uparrow$$

$$3MX \rightarrow M(s)\downarrow + MX_3(g)\uparrow$$

$$4MX \rightarrow M(s)\downarrow + MX_4(g)\uparrow$$

This is called disproportionation reaction. In this reaction, what happens? The compound which is thermally activated but in this case what we see that we can have the metallic form but at the same time this compound actually gain another state. That means its oxidation number can increase and decrease. Let us see this example. MX where we can have, this results in metallic M and now it is MX2. Formally, it was just MX, that means one atom of oxygen. Now it is two atom of X2 which can be a chloride, which can be anything.

Similarly, we can see here it is MX. So that means this original MX can lead to this reaction or it can be this one or it can be even this one. It depends upon the chemical properties of this material and also the bond strength of the reaction product. So it can be just metallic M and MX3, or it can be metallic M and MX4.

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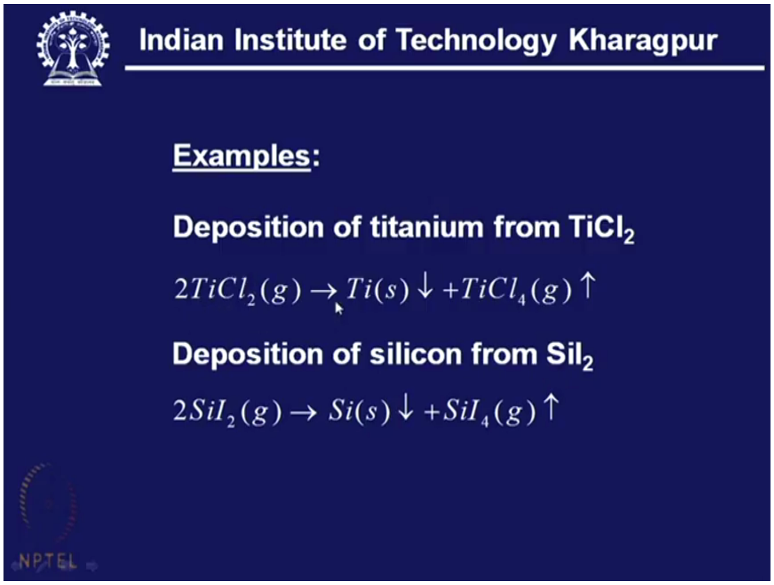

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Examples:

Deposition of titanium from $TiCl_2$

$$2TiCl_2(g) \rightarrow Ti(s)\downarrow + TiCl_4(g)\uparrow$$

Deposition of silicon from SiI_2

$$2SiI_2(g) \rightarrow Si(s)\downarrow + SiI_4(g)\uparrow$$

NPTEL

So here we see it is TiCl2 and this TiCl2 can be converted into metallic titanium plus titanium tetrachloride. So it is a chloride, higher chloride and this is a lower chloride. It is TiCl2 and this is TiCl4. Similarly, we can also have deposition of silicon from silicon iodide. So as it is excited, it results in splitting silicon but with the resulting silicon iodide which is having four atoms of iodine in combination with silicon.

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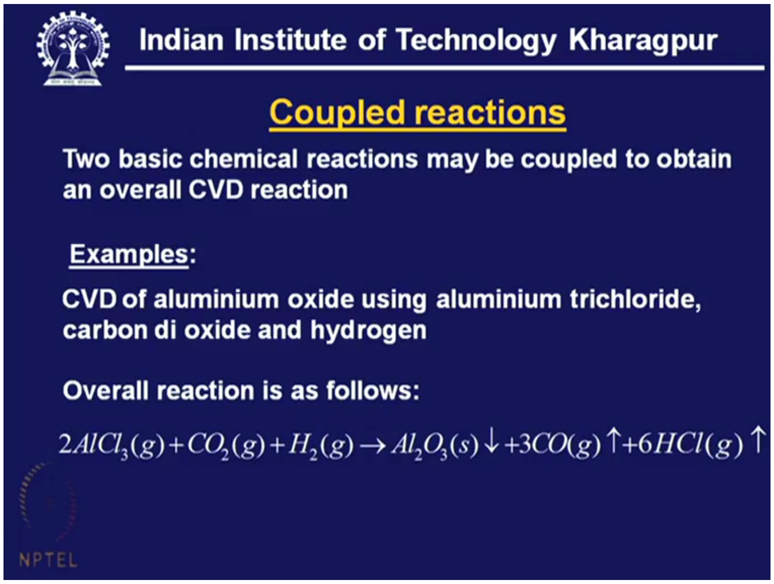

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Coupled reactions

Two basic chemical reactions may be coupled to obtain an overall CVD reaction

Examples:

CVD of aluminium oxide using aluminium trichloride, carbon di oxide and hydrogen

Overall reaction is as follows:

$$2AlCl_3(g)+CO_2(g)+H_2(g)\rightarrow Al_2O_3(s)\downarrow+3CO(g)\uparrow+6HCl(g)\uparrow$$

NPTEL

We have here coupled reaction. Coupled reaction means actually two reactions are combined. It can be one exchange reaction, it can be one reduction reaction or thermal decomposition. Two are combined to have one overall CVD reaction. Let us consider this example: deposition, chemical vapor deposition of aluminum oxide using titanium trichloride as the source material with help of carbon dioxide and hydrogen.

So here we see that overall reaction is as follows. It is AlCl3, CO2 and hydrogen, they put together, so this is the reactant side. And we can see what are the thing are going to form on the product side. We see the synthesis of aluminum oxide, as a solid it will deposit in the form of the coating and with the formation of carbon monoxide reaction product. HCL, that is also reaction product.

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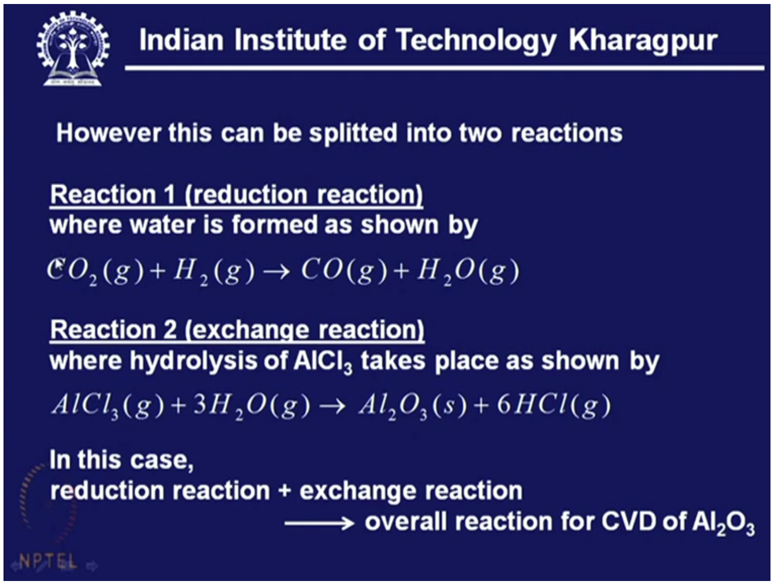

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However this can be splitted into two reactions

Reaction 1 (reduction reaction)
where water is formed as shown by

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$

Reaction 2 (exchange reaction)
where hydrolysis of $AlCl_3$ takes place as shown by

$$AlCl_3(g) + 3H_2O(g) \rightarrow Al_2O_3(s) + 6HCl(g)$$

In this case,
reduction reaction + exchange reaction
⟶ overall reaction for CVD of Al_2O_3

But if we split it, see in detail that reaction 1. Reaction 1 is actually the reduction reaction. That means CO2 plus H2 that become CO plus H2O. So that is the reaction, reduction reaction which takes place in the first step. And now comes this vapor of this H2O, that comes in contact with AlCl3 and it is going to be a hydrolysis of AlCl3 which results in formation of Al2O3 and 6 HCL.

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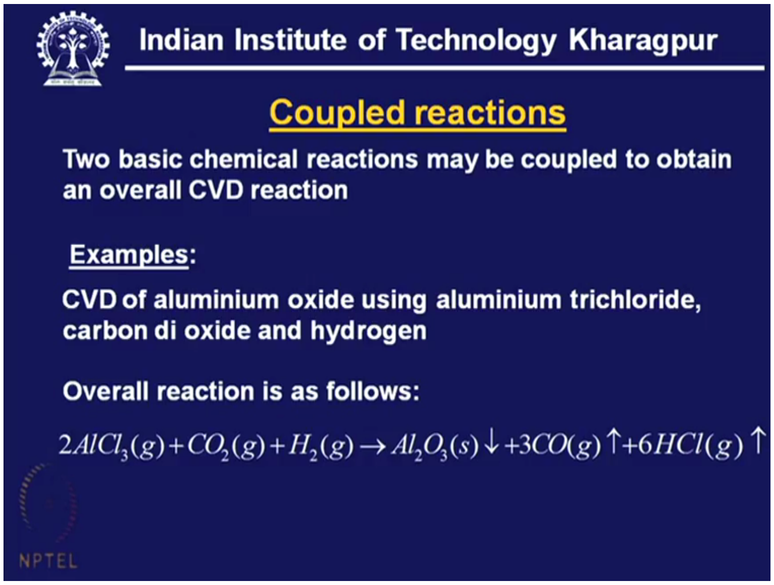

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Overall reaction is as follows:

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NPTEL

So in this case, we finally if we add them, we get back to this original overall CVD reaction.

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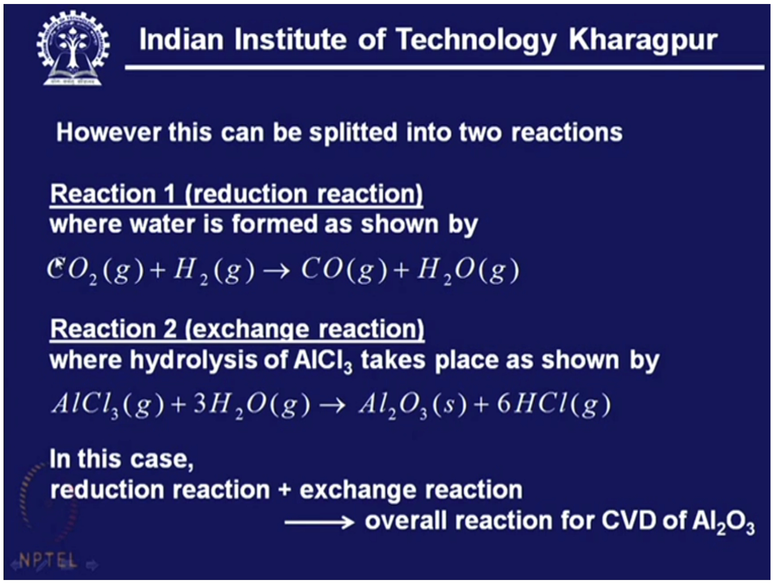

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In this case,
reduction reaction + exchange reaction
$\longrightarrow$ overall reaction for CVD of Al_2O_3

NPTEL

And here what we see, a reduction reaction plus one exchange reaction, that leads to overall reaction for CVD of aluminum oxide.

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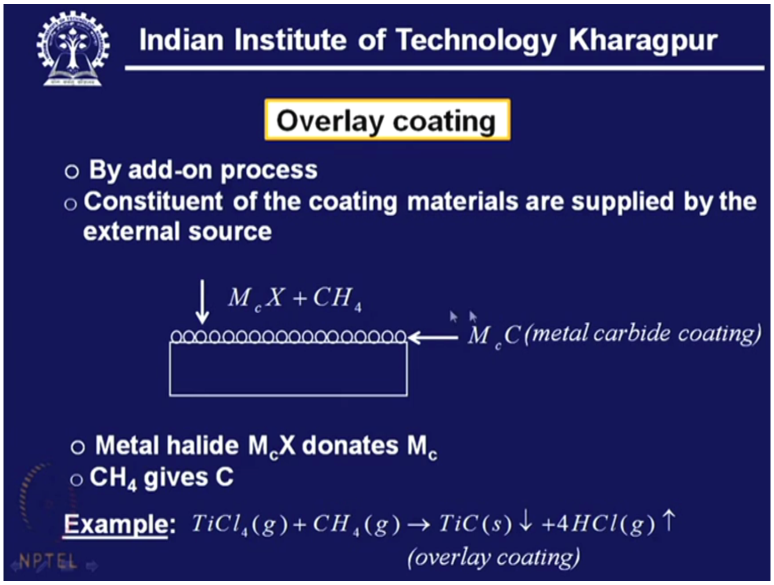

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Overlay coating

- By add-on process
- Constituent of the coating materials are supplied by the external source

$M_cX + CH_4$

M_cC (metal carbide coating)

- Metal halide M_cX donates M_c
- CH_4 gives C

Example: $TiCl_4(g) + CH_4(g) \rightarrow TiC(s)\downarrow + 4HCl(g)\uparrow$

(overlay coating)

Here we see that coating, CVD reactions are used to deposit a coating of choice, a coating with desired property, a coating which is expected to function either mechanically or otherwise. And here we find at least two types of coating which can be deposited by this CVD process. One we call as overlay coating. Exactly what does it mean? In the overlay coating, we find that all the resources material they actually supplied from the external agent.

That means in this case of deposition of a metal carbide coating, we have the metal halide and methane, they are supplied. So metal donor and carbon donor, both are coming from some outside agent. And then you have the necessary reaction with the formation of this McC. So best example would be that titanium tetrachloride gas and that means this vapor plus methane gas which will lead to titanium carbide solid and HCL and this we call overlay coating. That means both of them are coming from some external source.

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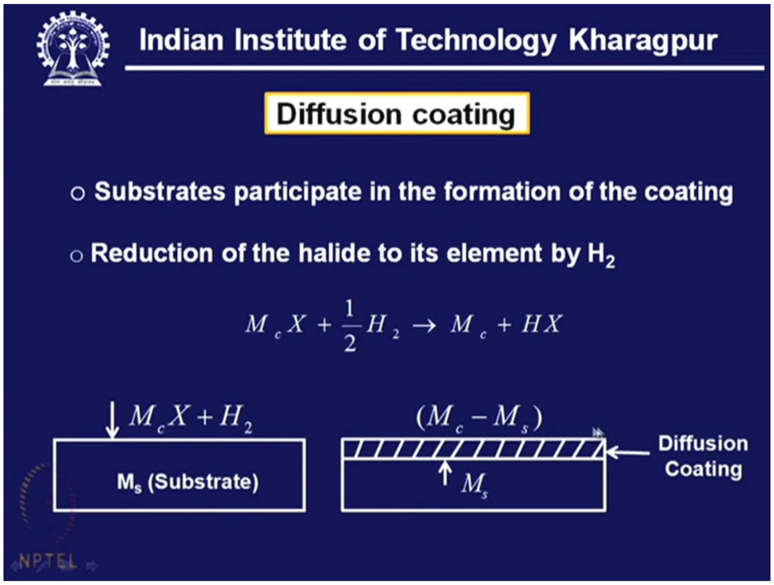

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Diffusion coating

- Substrates participate in the formation of the coating
- Reduction of the halide to its element by H_2

$$M_cX + \frac{1}{2}H_2 \rightarrow M_c + HX$$

Now we come to this diffusion coating. In diffusion coating, the one of the component of the coating is supplied by the external agent. However, the substrate participate actively. Without its participation, no fruitful coating can develop or grow. So, here we can give this example. So this is McX, that means this is the metal halide. Mc stands for the metal and it can be reduced by hydrogen leaving this Mc and this will be released and this should escape that reaction zone.

Now, this Mc, which will be reduced to Mc, so this is the thing which is actually arriving here and then we have Mc from this source, outside source. And Ms participates from this side and we have Mc-Ms combination and this is called a diffusion coating. So then diffusion coating, substrate participates, the externally applied metal donor that participates and we have this formation of Mc-Ms combination.

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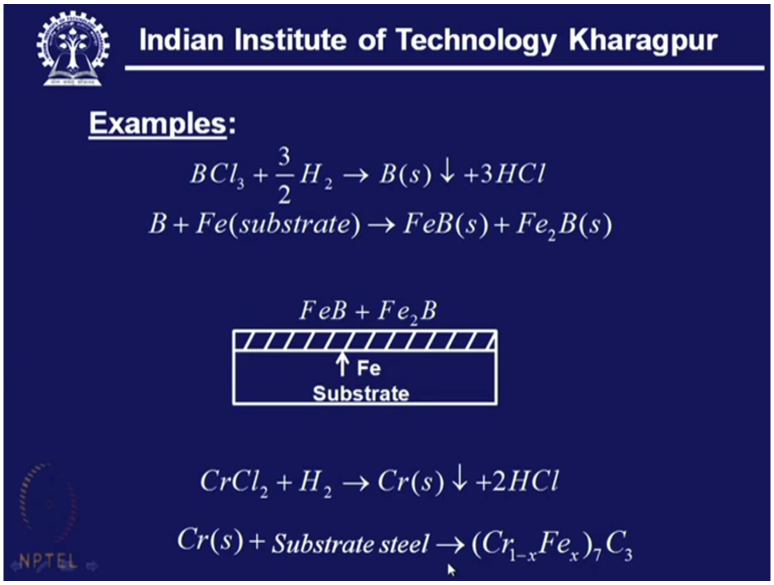

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Examples:

$$BCl_3 + \frac{3}{2}H_2 \rightarrow B(s)\downarrow + 3HCl$$

$$B + Fe(substrate) \rightarrow FeB(s) + Fe_2B(s)$$

$FeB + Fe_2B$

↑ Fe

Substrate

$$CrCl_2 + H_2 \rightarrow Cr(s)\downarrow + 2HCl$$

$$Cr(s) + Substrate\ steel \rightarrow (Cr_{1-x}Fe_x)_7C_3$$

Example we can have. Say boron chloride reduction releasing free boron and now this boron can go inside and then you have cross-diffusion of iron making FeB plus Fe2B. And this boride of iron has many mechanical properties which can be judiciously used. And this surface have some augmentation or improvement of property. We can consider another example where chlorine is, chromium is reduced by hydrogen releasing chromium which will be deposited on the substrate and this is a steel substrate. And this is, steel substrate have iron and carbon.

So in this case, carbon and iron they are sharing some of their lattice position and then we have a combined carbide of chromium iron in the form of Cr 1 minus- x and Fex 7 C3. So here chromium from the outside and iron from the substrate, they combine together to form a complex carbide in this form.

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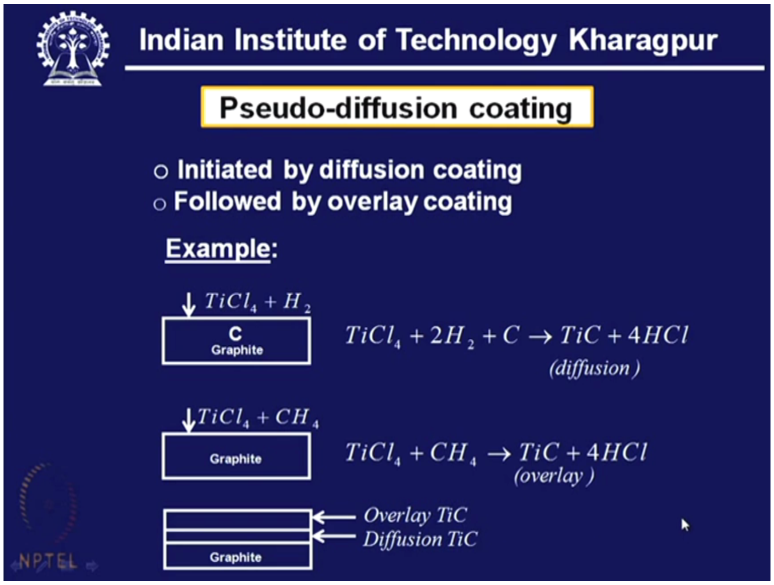

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Pseudo-diffusion coating

- Initiated by diffusion coating
- Followed by overlay coating

Example:

$TiCl_4 + H_2$

$$TiCl_4 + 2H_2 + C \rightarrow TiC + 4HCl$$

(diffusion)

$TiCl_4 + CH_4$

$$TiCl_4 + CH_4 \rightarrow TiC + 4HCl$$

(overlay)

Now it comes to pseudo-diffusion coating. So in this case, what we do? First, we start the process just like this one, so the titanium can form titanium carbide by picking up carbon from graphite. And later on, this diffusion process can be switched over to overlay coating process. So at the beginning CH4 is not supplied but in the latter half CH4 is supplied and this becomes overlay process while the initiation is done by diffusion process. So we have diffusion coating and overlay coating.

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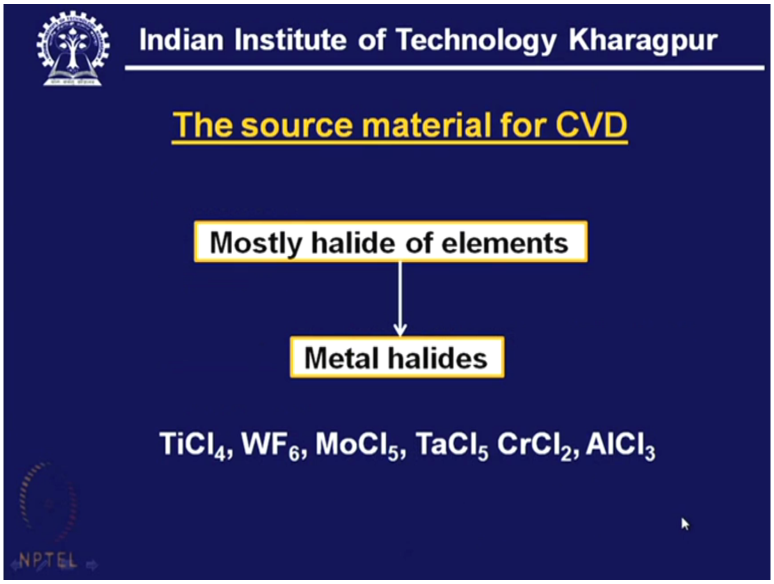

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The source material for CVD

Mostly halide of elements

↓

Metal halides

$TiCl_4$, WF_6, $MoCl_5$, $TaCl_5$ $CrCl_2$, $AlCl_3$

Now these are the source material. Mostly, they are formed in the, they are available in the form of halide. And these halide, their thermodynamic property will dictate what should be the temperature, what should be the pressure, at what condition we can have the metal removal, metal coating or some compound of the metal which can be also used as a coating.

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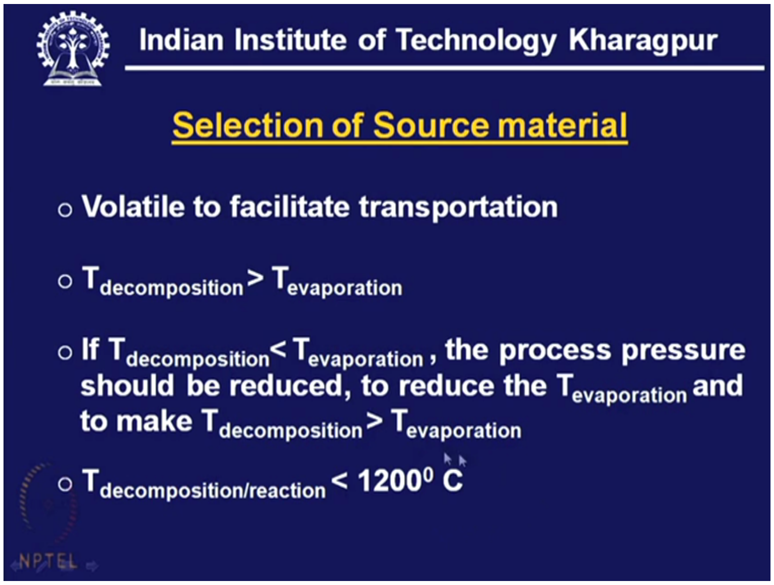

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Selection of Source material

- Volatile to facilitate transportation
- $T_{decomposition} > T_{evaporation}$
- If $T_{decomposition} < T_{evaporation}$, the process pressure should be reduced, to reduce the $T_{evaporation}$ and to make $T_{decomposition} > T_{evaporation}$
- $T_{decomposition/reaction} < 1200^0$ C

So selection of source material selection of source material means the decomposition should not take place before this is evaporated. That means in simple language decomposition temperature should be higher than the evaporation temperature because in most of the cases these are available in the form of liquid which needs evaporation. So this evaporation point and decomposition point, we should pay attention here.

If this is so that decomposition is, can occur at a lower temperature, then naturally process pressure should be reduced to reduce the evaporation point and to make decomposition temperature greater than evaporation. Normally this decomposition or reaction that it takes place well within 1,200 and this is one of the temperature of technical interest while conducting the CVD.

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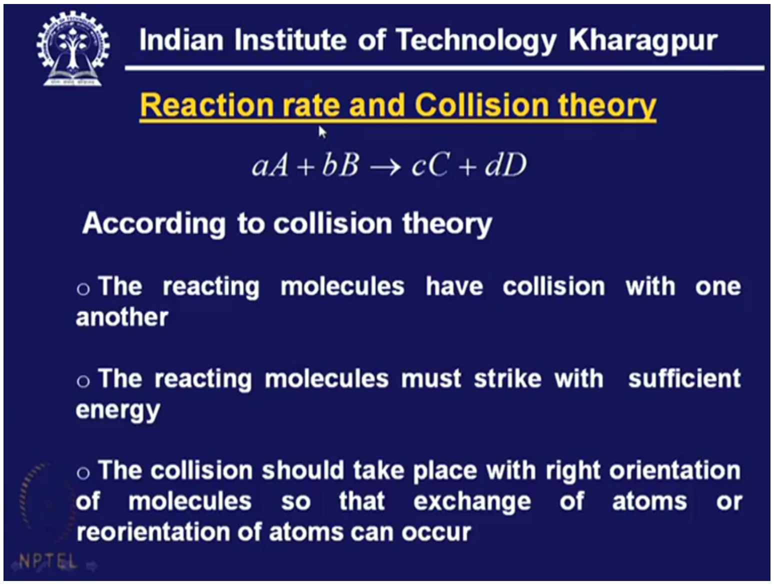

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Reaction rate and Collision theory

$$aA + bB \rightarrow cC + dD$$

According to collision theory

- ○ The reacting molecules have collision with one another
- ○ The reacting molecules must strike with sufficient energy
- ○ The collision should take place with right orientation of molecules so that exchange of atoms or reorientation of atoms can occur

Now this comes the reaction rate. In any CVD process or operation, one would be interested in that, what would be the reaction rate?

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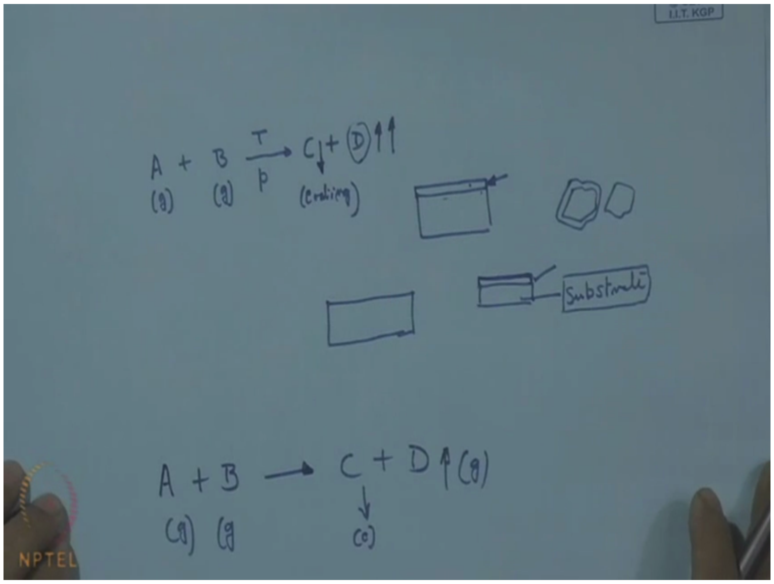

That means at what rate this, if we have A plus B is equal to C plus D which comes in the form of coating and this is the gas escaping and this is also in the form of gas, that means one would have immediate interest, at what rate this conversion is taking place, that rate. And at the same time to what extent we can convert this A and B to C and D, what proportion of A and B will be converted into C and D. At the same time what is the spontaneity of the reaction? That means whether this reaction is product favored or not? Whether we can carry forward the reaction with some driving force?

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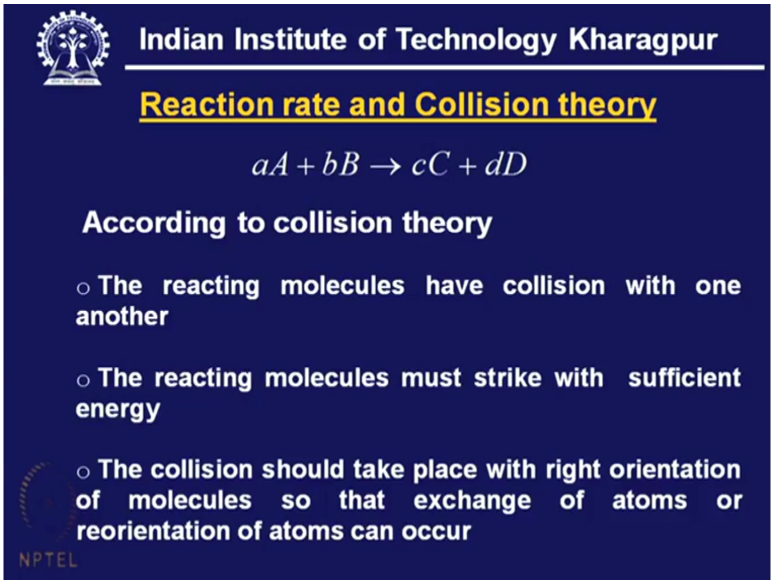

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According to collision theory

○ The reacting molecules have collision with one another

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○ The collision should take place with right orientation of molecules so that exchange of atoms or reorientation of atoms can occur

So here to have this reaction in the forward direction, what is immediately needful? That means this is stated by the collision theory. That, the reacting molecules must have collision and they must have collision with sufficient energy, and also this collision should not only take place with sufficient energy but with correct orientation. So we find there are some necessary condition and when we put all the necessary condition, we get the sufficient condition for this reaction to occur and reaction to move in the product direction.

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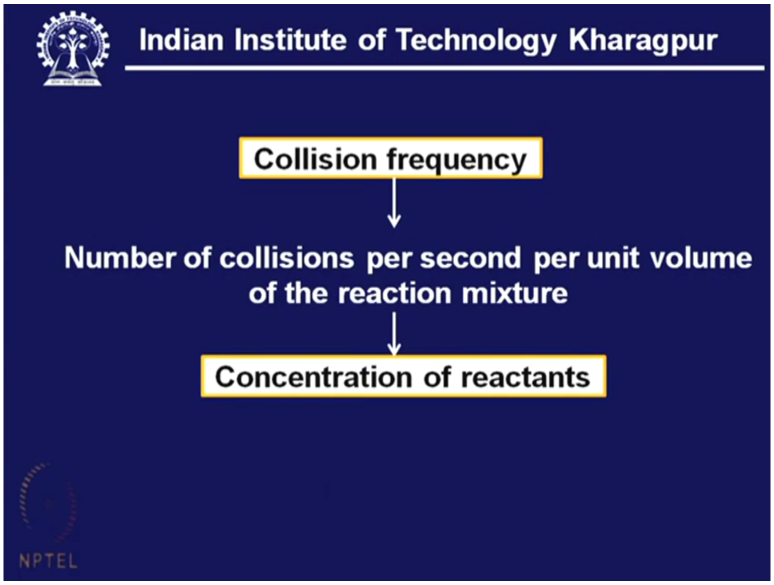

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Collision frequency

↓

Number of collisions per second per unit volume of the reaction mixture

↓

Concentration of reactants

NPTEL

So here we find this is collision frequency, which is very important parameter and this collision frequency depends on the concentration of the reactants.

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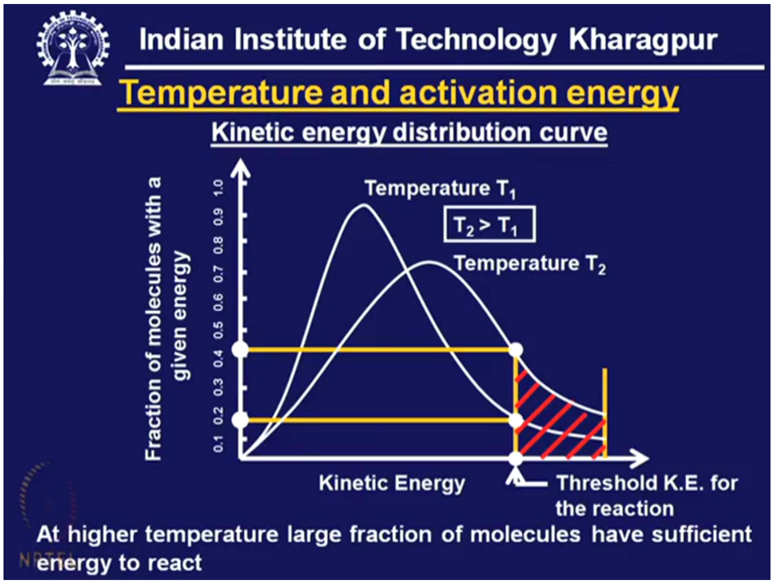

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Temperature and activation energy

Kinetic energy distribution curve

At higher temperature large fraction of molecules have sufficient energy to react

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Here we find that the temperature of where it is activated or the activation energy, that has a big role to play. If we see that this is a distribution of the energy of different molecules in the different energy level and this is more or less the fraction of the molecules having different level of energy. Now this, we have one shape of this distribution at a particular temperature T1 and when we move to a higher temperature T2, we can see that with the threshold point, that means threshold energy necessary for this reaction to occur, we can see that at this point we get a more large fraction of the molecules which are having that threshold energy. That means we can say by activation through this rise of temperature, we can also have more number of collisions.

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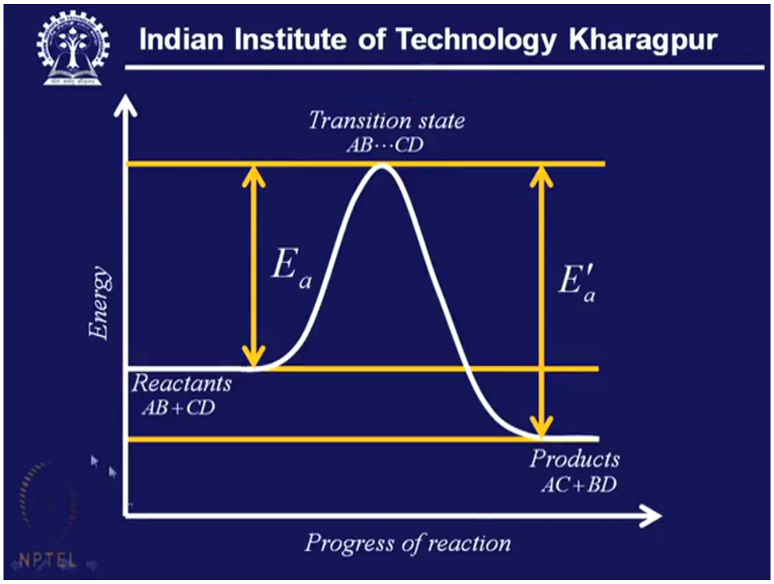

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Now this is actually the energy barrier. That means for this reaction to happen, A plus B plus C plus D, which becomes AC plus BD. So AB plus CD should become AC plus BD and to make it happen the whole thing has to be, the whole thing it must attend this transition state and where this exchange will take place and finally it becomes the product. So this is actually the activation energy when the reaction moves in the product direction.

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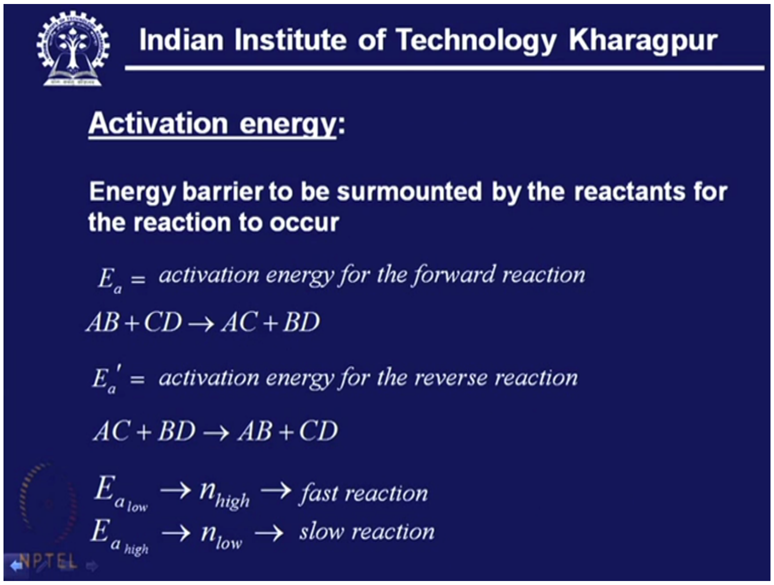

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Activation energy:

Energy barrier to be surmounted by the reactants for the reaction to occur

E_a = activation energy for the forward reaction

$AB + CD \rightarrow AC + BD$

E_a' = activation energy for the reverse reaction

$AC + BD \rightarrow AB + CD$

$E_{a_{low}} \rightarrow n_{high} \rightarrow$ fast reaction

$E_{a_{high}} \rightarrow n_{low} \rightarrow$ slow reaction

So here find that if we have low activation energy, we have large number of molecules participating in that collision and we have a first reaction. And if it is high, requirement is high, we have low which leads to slow reaction.

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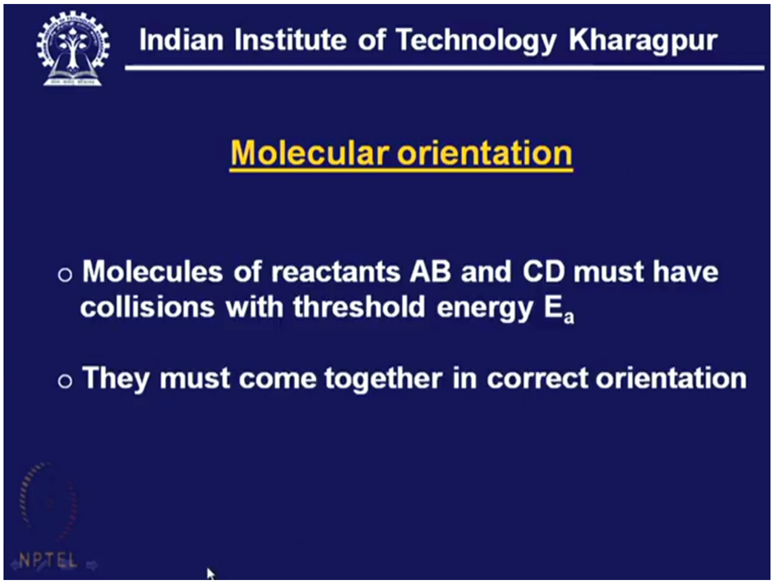

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Molecular orientation

- Molecules of reactants AB and CD must have collisions with threshold energy E_a
- They must come together in correct orientation

This is molecular orientation. Unless we have this thing in the correct orientation, then the requirement is not totally fulfilled. So it is totally the question of threshold energy and collision but at the same time correct orientation has to be also attained.

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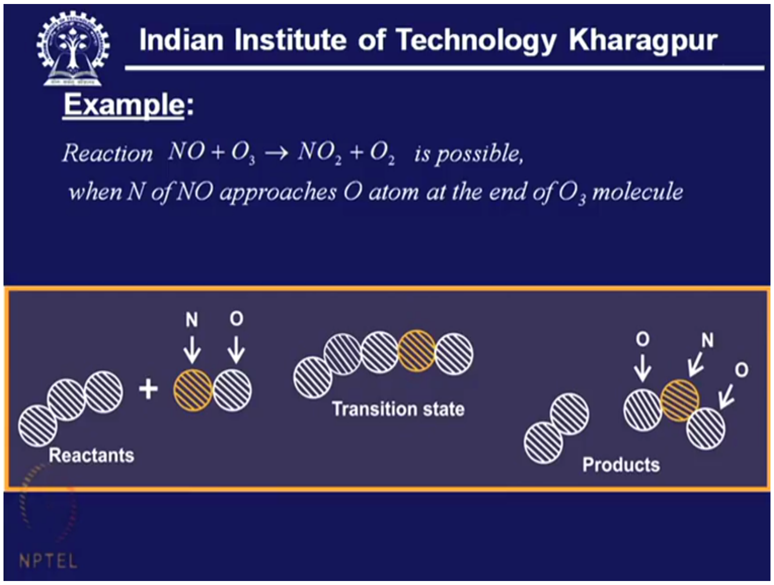

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Example:

Reaction $NO + O_3 \rightarrow NO_2 + O_2$ *is possible,*

when N of NO approaches O atom at the end of O_3 *molecule*

So this is one example. What we see here, say NO plus O3, Ozone and nitric oxide and that will become NO2 plus O2. This is possible when N of NO approaches one oxygen atom at end of this O3 molecule. That means this has to approach one of those which is situated at the end and then we have this activated complex and then we have this O2. That means this O will be now attached to this NO making it NO2 and this is O2 which will be a stable state.

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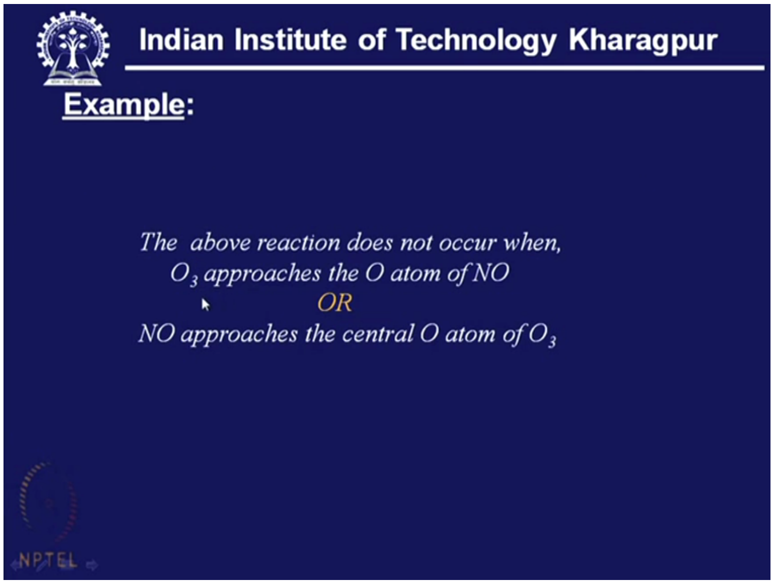

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Example:

The above reaction does not occur when,
O_3 *approaches the O atom of NO*
OR
NO approaches the central O atom of O_3

If it does not happen, that means if it is the case that O3 approaches the O from atom, O3 approaches, that means if O3 approaches O atom, then this reaction is not possible.

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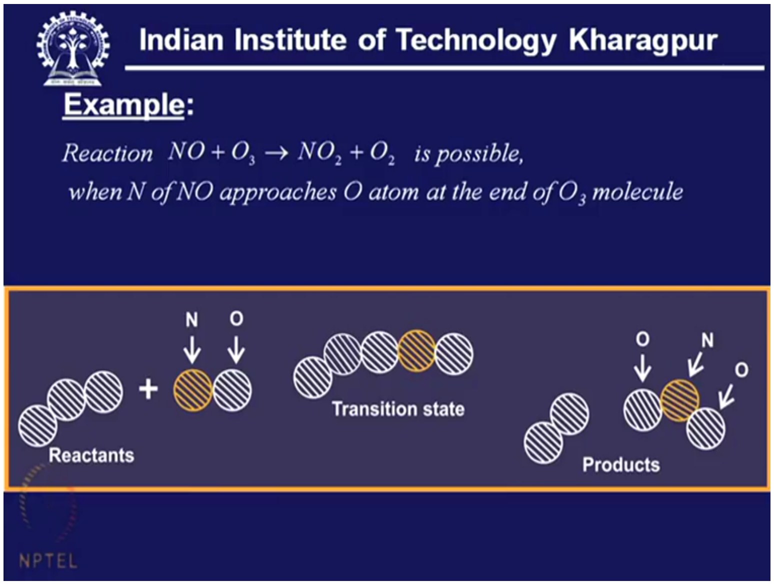

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Example:

Reaction $NO + O_3 \rightarrow NO_2 + O_2$ *is possible,*
when N of NO approaches O atom at the end of O_3 *molecule*

Also, if NO approaches the central O atom of O3, getting back if this N approaches the central atom, then also the reaction will not take place. That means it has to approach one end atom. So this is the illustration how this orientation comes into picture and it plays a very decisive role.

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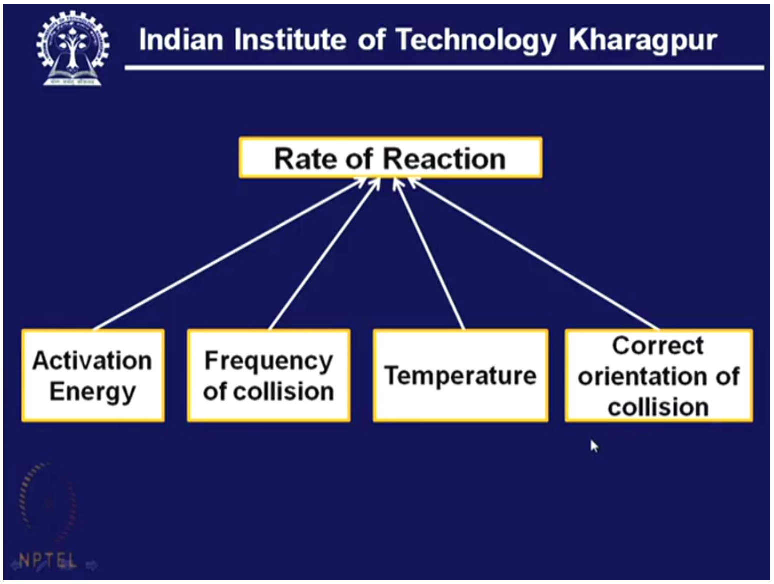

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Rate of Reaction

Activation Energy

Frequency of collision

Temperature

Correct orientation of collision

So finally we find the rate of reaction is governed by activation energy, frequency of collision, temperature, and correct orientation of collision.

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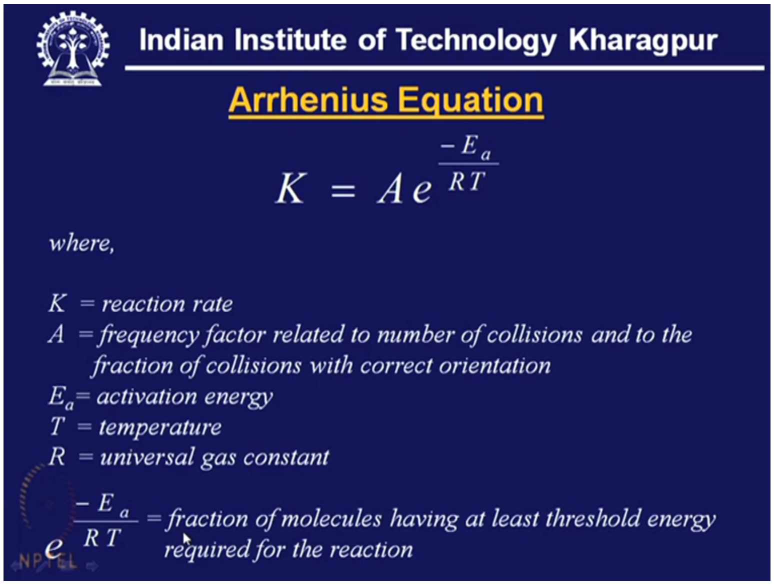

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Arrhenius Equation

$$K = A e^{\frac{-E_a}{RT}}$$

where,

K = reaction rate
A = frequency factor related to number of collisions and to the fraction of collisions with correct orientation
E_a = activation energy
T = temperature
R = universal gas constant
$e^{\frac{-E_a}{RT}}$ = fraction of molecules having at least threshold energy required for the reaction

So this is called Arrhenius equation where K is the reaction rate, A is the frequency factor and Ea is the activation energy, universal gas constant and this temperature at that point of activation. So here A is significant in that. This frequency factor related to the number of collisions and fraction of collisions with correct orientation. So this actually tells us, gives us the impression what is the level of collision and how many collision can take place with this correct orientation.

And this part, second part of this equation, e into, minus-e to the power Ea by RT, that is actually the significant number, fraction showing the fraction of molecules having at least that threshold energy required for the reaction to occur.

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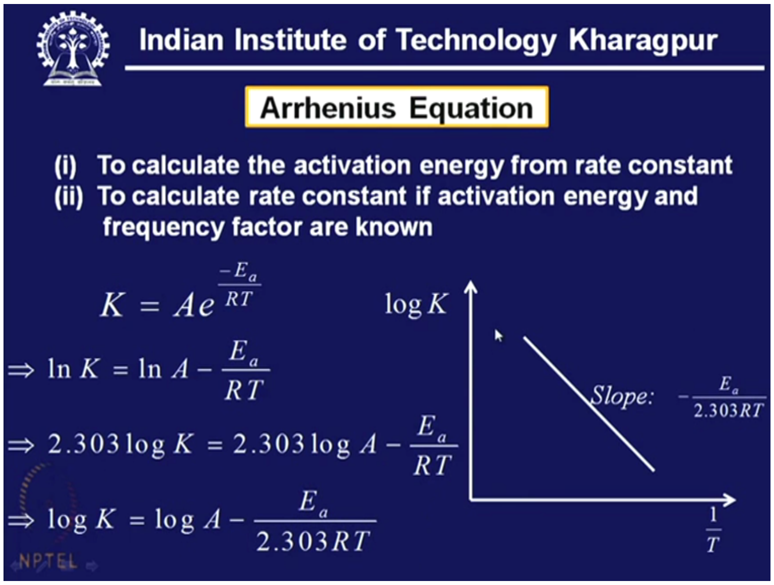

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Arrhenius Equation

(i) To calculate the activation energy from rate constant

(ii) To calculate rate constant if activation energy and frequency factor are known

$$K = Ae^{\frac{-E_a}{RT}}$$

$$\Rightarrow \ln K = \ln A - \frac{E_a}{RT}$$

$$\Rightarrow 2.303 \log K = 2.303 \log A - \frac{E_a}{RT}$$

$$\Rightarrow \log K = \log A - \frac{E_a}{2.303RT}$$

So from this we can get a plot. So from this plot, either it is possible to calculate the activation energy from the rate constant or we can also calculate the rate constant if the activation energy are known. So both are important information to make the thing happen and to take the reaction in the forward direction.

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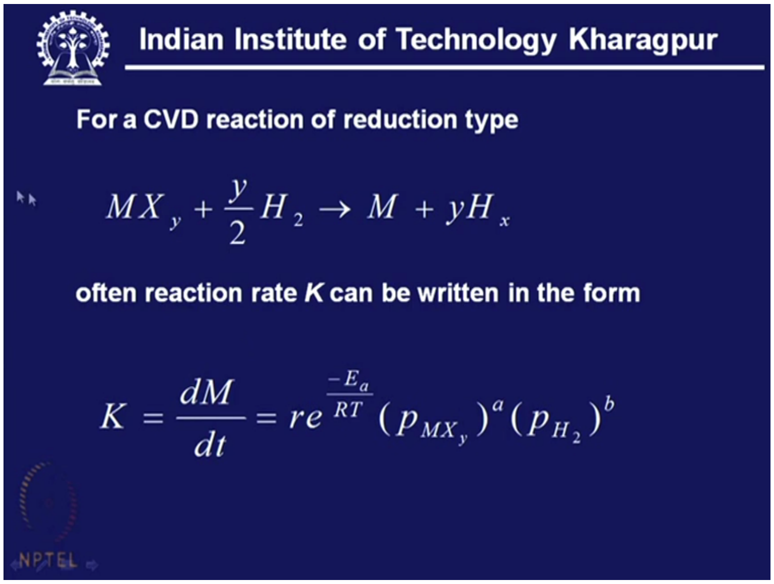

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For a CVD reaction of reduction type

$$MX_y + \frac{y}{2}H_2 \rightarrow M + yH_x$$

often reaction rate *K* can be written in the form

$$K = \frac{dM}{dt} = re^{\frac{-E_a}{RT}}(p_{MX_y})^a(p_{H_2})^b$$

Now what we can find here that if you consider those principal and apply in a CVD reaction, just like a reduction reaction, we can often write this K as the reaction rate as dM dt. That means how much conversion, either change in mass of product or change in mass of the reactant. And this is given by r into e to the power minus-Ea by RT, into, since these are gaseous phase, we put this partial pressure in this case, pMXy, that means partial pressure of this halide say for example to the power a and partial pressure of hydrogen to the power b. So this concentration of these reactants, that will give us some indication, that means at what rate this reaction will proceed.

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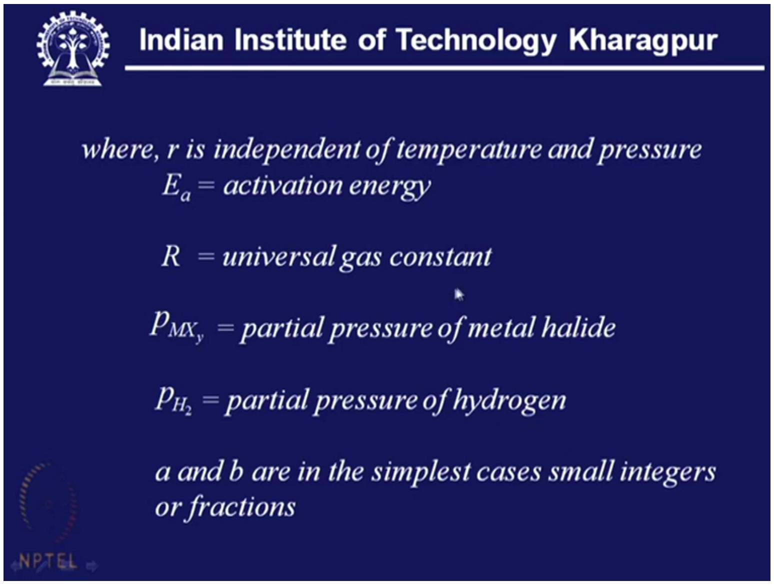

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where, r is independent of temperature and pressure

E_a = *activation energy*

R = *universal gas constant*

p_{MX_y} = *partial pressure of metal halide*

p_{H_2} = *partial pressure of hydrogen*

a and b are in the simplest cases small integers or fractions

So these are already explained, these notations.

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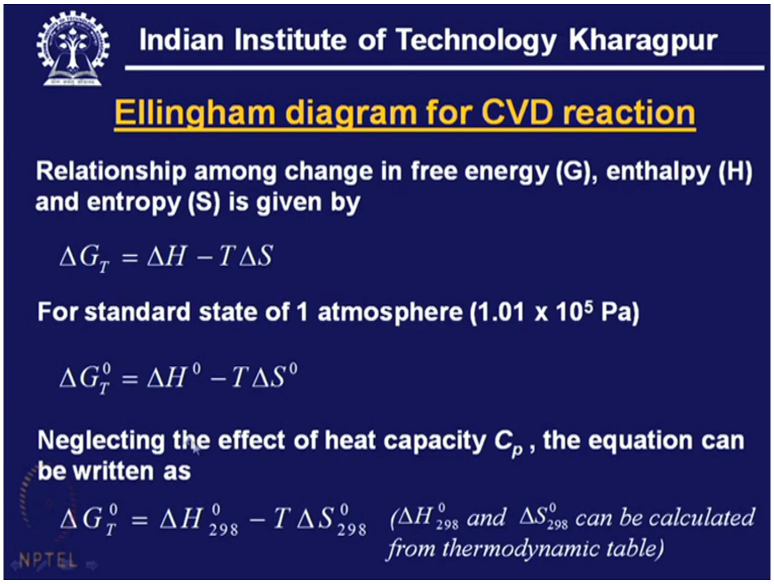

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Ellingham diagram for CVD reaction

Relationship among change in free energy (G), enthalpy (H) and entropy (S) is given by

$$\Delta G_T = \Delta H - T\Delta S$$

For standard state of 1 atmosphere (1.01 x 10^5 Pa)

$$\Delta G_T^0 = \Delta H^0 - T\Delta S^0$$

Neglecting the effect of heat capacity C_p, the equation can be written as

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0$$

(ΔH_{298}^0 and ΔS_{298}^0 can be calculated from thermodynamic table)

Now come one important diagram, Ellingham diagram of CVD reaction and that give us a guidance how to choose the particular temperature for this CVD reaction. So here we see that change in free energy is related to change in enthalpy and change in entropy by this equation. And for a standard state of 1 atmosphere, we can put this superfix o here. So this is a equation. Now neglecting the effect of heat capacity, this equation can be rewritten as a first step of approximation.

Now from this, looking at from this thermodynamic table, it will be possible to find out this G0T, G0T is equal to in terms of this enthalpy of reaction and this change in entropy of, that means the entropy of reaction. So this is one way of finding the, assessing the value which is a function of temperature where this reaction is favored.

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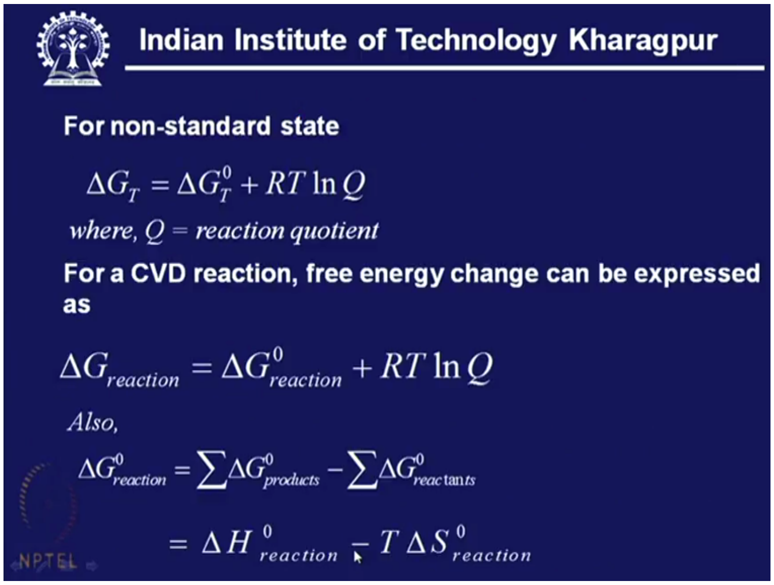

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For non-standard state

$$\Delta G_T = \Delta G_T^0 + RT \ln Q$$

where, Q = reaction quotient

For a CVD reaction, free energy change can be expressed as

$$\Delta G_{reaction} = \Delta G^0_{reaction} + RT \ln Q$$

Also,

$$\Delta G^0_{reaction} = \sum \Delta G^0_{products} - \sum \Delta G^0_{reactants}$$

$$= \Delta H^0_{reaction} - T \Delta S^0_{reaction}$$

Now here what we find that for a non-standard state, we can write the delta GT is equal to delta G0T plus RT into lnQ.

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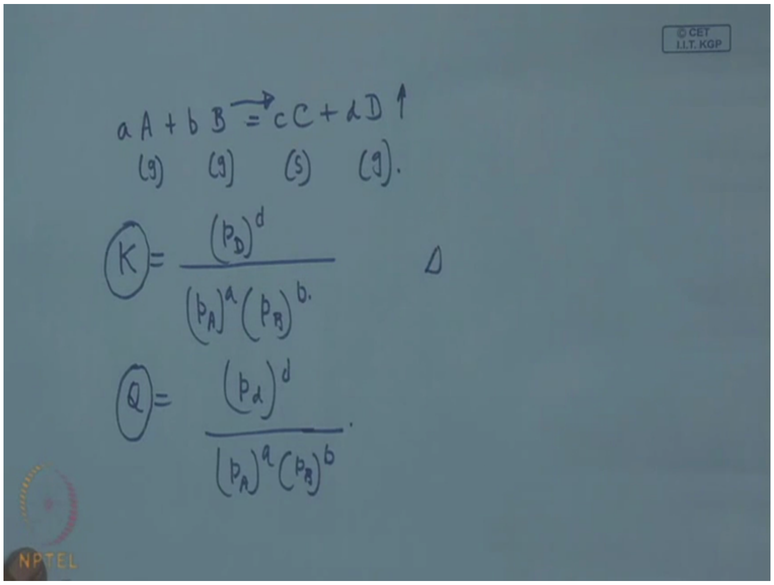

$$\underset{(g)}{aA} + \underset{(g)}{bB} \overset{\rightarrow}{=} \underset{(s)}{cC} + \underset{(g)}{dD}\uparrow$$

$$K = \frac{(p_D)^d}{(p_A)^a (p_B)^b}$$

$$Q = \frac{(p_d)^d}{(p_A)^a (p_B)^b}$$

In fact, what we can write here, if we consider such kind of CVD reaction, this is the stoichiometric coefficient of this gaseous reactant. This is also gaseous reactant. This is the coating, that means that is the solid phase and this is the byproduct of this reaction, this is also gaseous phase. Then in terms of partial pressure, we can write that this is going to PD to the power d divided by PA to the power a into PB to the power b.

Now from this, we get a clear indication that this is called equilibrium constant. So equilibrium constant give us a clear idea that what is the, whether the reaction is product favored or reaction is reactant favored. So from this, we can find out a particular condition where the value of K can be adjusted in favor of product. That means we can also write this K substituting in the form of this relation PB to the power b. That means here we call it equilibrium constant and here we call this is as the reaction quotient, this as the reaction quotient.

This we call as the equilibrium constant and this we call the reaction quotient. Now when this, so this is actually moving in this direction. So, unless it attains the equilibrium, we express this conversion of this reactant to product by this term what we call reaction quotient. And when equilibrium is reached, then this Q becomes equal to K.

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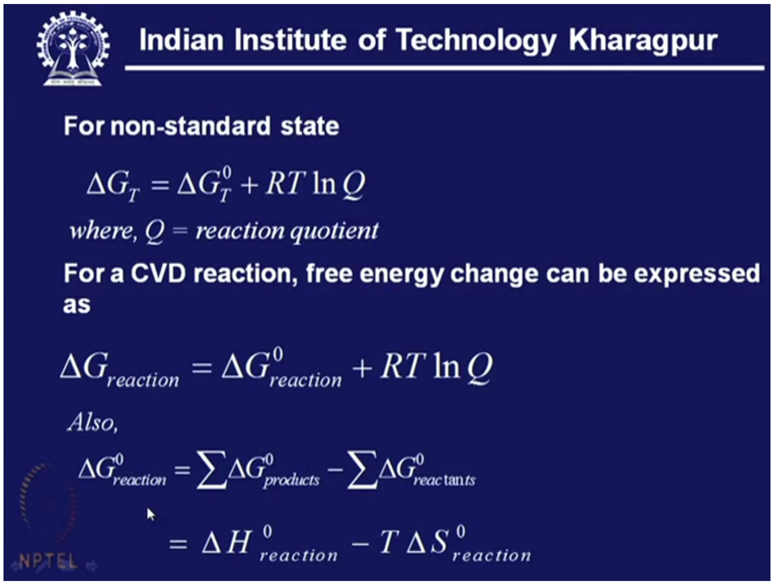

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Now this relation, we also write here what we have seen that delta G0 reaction, that is equal to actually delta H0 reaction minus T delta S0 reaction. That means in CVD reaction, this is the change in free energy, this is the change in enthalpy of the reaction and this is the change in entropy of the reaction. Now to have the reaction in the product direction, that means product favored, it should be always negative.

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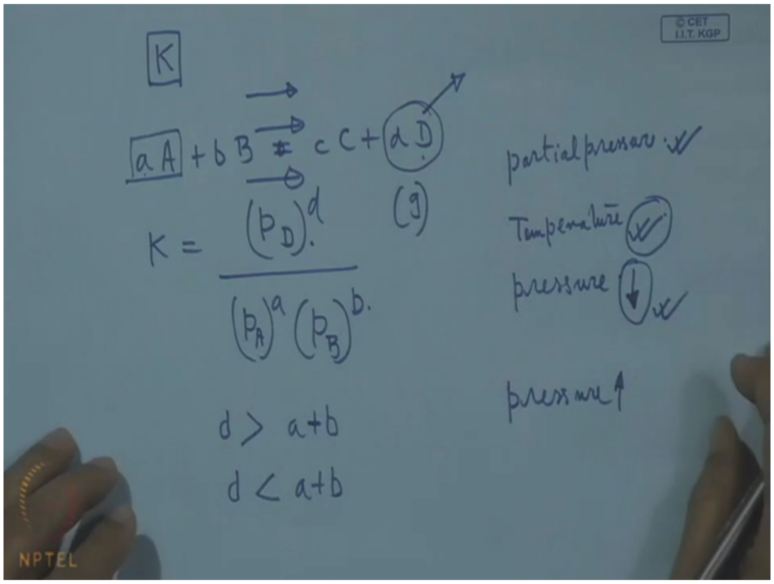

$\boxed{K}$

$\boxed{aA} + bB \rightleftharpoons cC + dD$

(g)

$$K = \frac{(p_D)^d}{(p_A)^a (p_B)^b}$$

$d > a+b$

$d < a+b$

partial pressure ✓

Temperature ✓

pressure ↓ ✓

pressure ↑

So this equilibrium constant, this value of this equilibrium constant which we write as, this is the reactant side and this is the product side, we call it like this, PD to the power d, that is the index divided by PA to the power a into PB to the power b. Now here we find that the role of this partial pressure of the reactants and product, this is number one. Number two, that means the partial pressure, then comes the temperature and the pressure, that means the system pressure.

All these three can affect this value of K and it is obvious higher the value of K, means more is the favorable reaction for the product formation. That means reaction will be more and more product favored higher the value of K. So this value of K can be little bit disturbed and disturbance can be done just by adjusting the value of this PD, PA or PB. Say for example, if we put more A, that means increasing the partial pressure of A, then the reaction will, this reaction will move in the forward direction.

Similarly if we have some arrangement for quick escapement of this gaseous product from this reactor, similarly there will be shortfall of this D, that means this partial pressure will fall. Similarly it will adjust itself and reaction will also move in this direction. Similarly this temperature, temperature means when we have an endothermic reaction, endothermic reaction means if we have, so heat will be absorbed.

So if we increase the CVD temperature, then also reaction will move in the forward direction. Now, pressure, pressure means here say a and b, these are the a moles of A and b moles of B and this is d. So if we find out the number of molecules of A and B which is actually transformed into D, so if d is greater than a plus b, that means here you have certain increase in volume and in that case if we reduce the pressure, increase in volume will be favored by reduce of pressure and then the reaction will move in this direction.

However if it is contrary to that, if d is less than a plus b, that means number of molecules is less, in that case this reaction will be favored, that means it will move in the forward direction if we increase the pressure. So this is the way this value of K can be also adjusted. It is to the advantage of CVD reaction, that means to make the reaction more and more product favored. That means favorability towards product can be achieved by just adjusting this partial pressure, by regulating the temperature and by regulating the total pressure inside the reactor.

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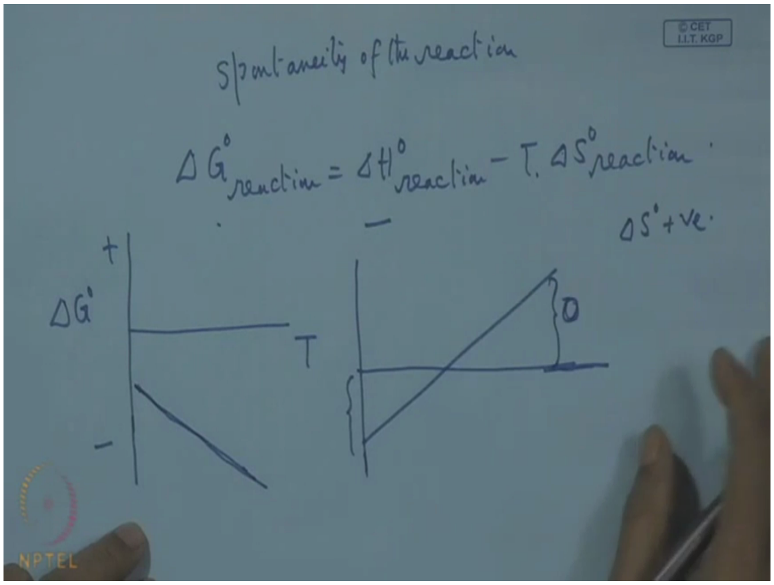

Spontaneity of the reaction

$$\Delta G^0_{reaction} = \Delta H^0_{reaction} - T.\Delta S^0_{reaction}$$

ΔS^0 +ve

Now comes spontaneity, spontaneity of the reaction and this is decided by value of delta G0 reaction. And here what we find, this is represented by this reaction - T delta S reaction. Now we can have illustration like this. This side, we have temperature and this is delta G0. This is plus and minus. Now we can have 4 situations. Suppose this is one exothermic reaction and in exothermic reaction always delta H reaction, it is negative. Now if this change of entropy is positive, that means this is negative and this is also negative, so curve takes this form, so all along throughout we have a negative delta G, so the reaction is spontaneous.

But it can be also like this. We have this delta H, that means enthalpy of reaction is negative but however for some reason delta S0 that is positive, so in that case reaction can be product favored provided this whole, I mean this enthalpy and this entropy, their total effect should be negative. And to have that, it is obvious that temperature should be on this side. That means at a lower temperature, we can have this reaction to move in the forward direction.

If it is higher temperature, then this side will be very positive and which can neutralize and the total delta G0 will be positive and the reaction cannot be product favored, it will be reactant favored. So this is for exothermic reaction.

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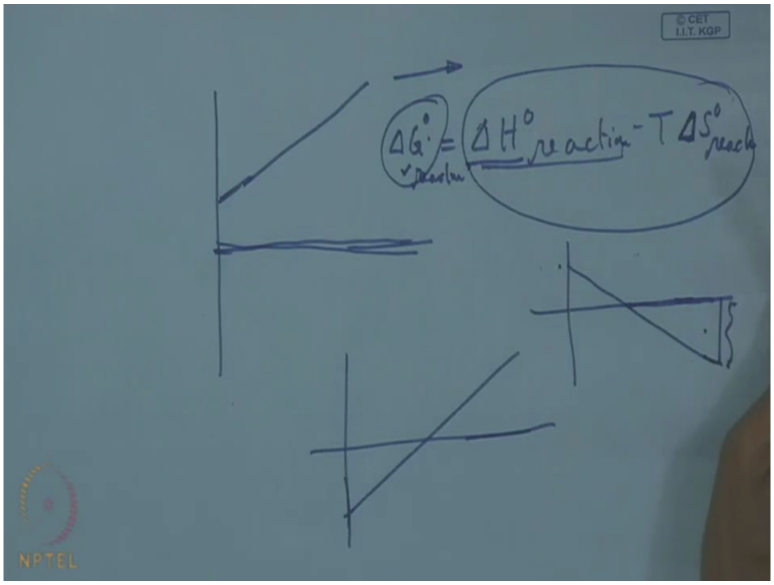

When we have endothermic reaction, it can be like this. So here it is always absorbing the heat. So here this delta H0 reaction minus delta S0 reaction which is equal to delta G0 reaction, this is the equation. Now in this case, this is already positive. Now if we have this value which is positive, in that case at a very high temperature we can have, so when we have such situation, in this case what we have that this is the actually the formation. Here delta H reaction is positive but if we go to high temperature with entropy, in that case we find that the combined effect of this enthalpy and entropy that is found out to be negative and the reaction goes in the forward direction.

That means for a endothermic reaction, we can also have the reaction as product favored provided the reaction is, the whole operation is conducted at a high temperature so that this part is negative and that neutralizes the positivity of delta H0 and the whole effect will be negative and in that case, the free energy of the reaction happens to be negative. So we find in summary that this effect of low temperature on exothermic reaction to carry forward in the product direction and the influence of high temperature on this effect of delta G0, that means free energy of formation also to carry forward this reaction in the product direction.

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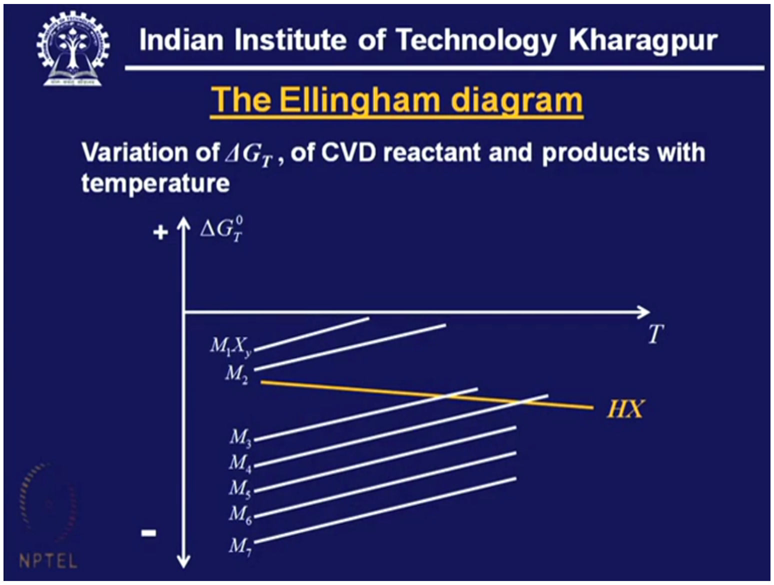

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The Ellingham diagram

Variation of ΔG_T, of CVD reactant and products with temperature

So this is the Ellingham diagram which shows that the stability of metal halides with respect to the byproduct of this CVD reaction and here we find how to find out the temperature where actually this reaction is possible or feasible.

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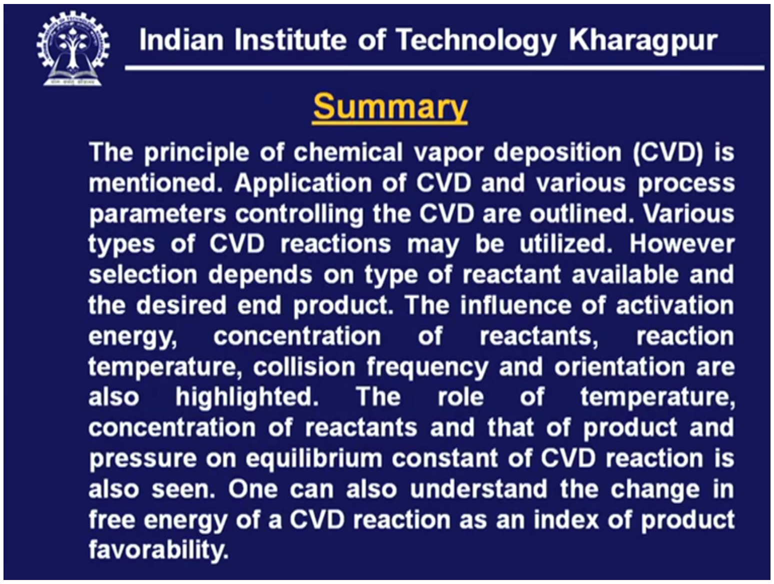

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Summary

The principle of chemical vapor deposition (CVD) is mentioned. Application of CVD and various process parameters controlling the CVD are outlined. Various types of CVD reactions may be utilized. However selection depends on type of reactant available and the desired end product. The influence of activation energy, concentration of reactants, reaction temperature, collision frequency and orientation are also highlighted. The role of temperature, concentration of reactants and that of product and pressure on equilibrium constant of CVD reaction is also seen. One can also understand the change in free energy of a CVD reaction as an index of product favorability.

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The role of temperature, concentration of reactants and that of product and pressure on equilibrium constant of CVD reaction is also seen. One can also understand the change in free energy of a CVD reaction as an index of product favorability.