Nanostructures and Nano Materials: Characterization and Properties

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Lecture - 35

Surface Adsorption Isotherms (Langmuir/Bet)

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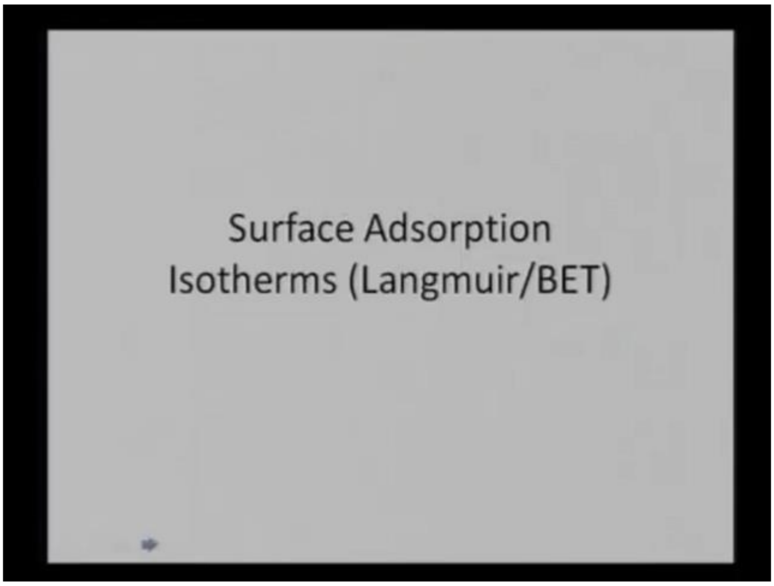

Surface Adsorption
Isotherms (Langmuir/BET)

In this lecture, we learn about surface adsorption and isotherms as we all know that surface adsorption one of the very critical phenomena in any particular processing or any particular catalyses activities.

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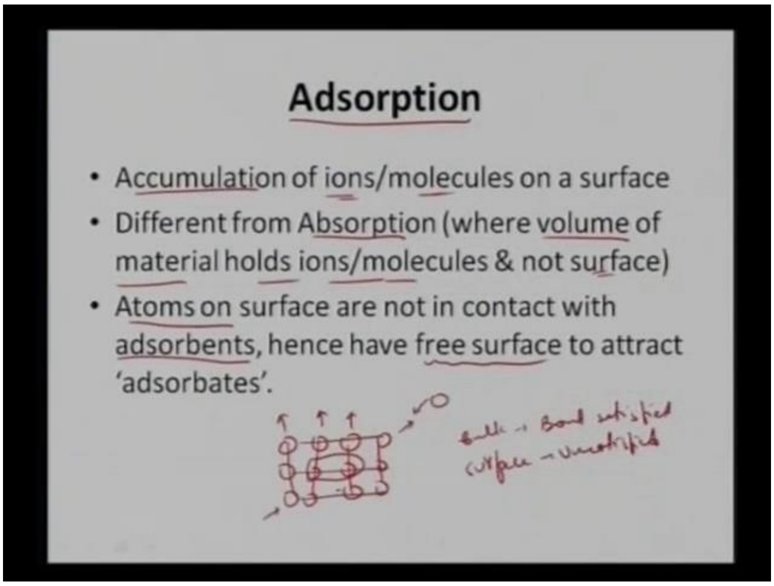

Adsorption

- Accumulation of ions/molecules on a surface
- Different from Absorption (where volume of material holds ions/molecules & not surface)
- Atoms on surface are not in contact with adsorbents, hence have free surface to attract 'adsorbates'.

bulk → Bond satisfied
surface – unsatisfied

So, in this particular place we will define adsorption; adsorption is different the accumulation of irons of molecules on a surface. As we know that, it is one of the very critical parameters of deciding the kinetic some particular process. Because, depending on how many irons or molecules on a surface that can they tend to react or they tend to form surface. So result variety of property, but again it is different from absorption, because they will absorption volume of material it holds the irons and molecules and not the surface.

So, in this particular process we have absorption in which the bulk of a material text part and terms of specious; whereas, an absorption the particular specious that can be iron, that can be molecules, the surface of a particular or a absorbent. So then, this particular manner because once we have any surface being expose to any environment, it is the surface which concern contact first.

And once surface occurred then, only it can go on further to the bulk or in term basically, volume of that particular material kind takes part in terms of dictating the subsequent phenomena. Again in this case absorption, atoms on the surface or not in contact with absorbents, so this is what that we have a free surface. So, free surface we have once we have once we see the arrangement of particular atoms, and then we can see that the atoms which are not on the bulk.

It means, the atoms which are on the surface these atoms they know have free bonds.

Hence they can attract the absorb it to their sites; this is why it happens this is, because the bulk material. The bulk material which has all the bonds satisfied, so bulk we have all the bond which are satisfied whereas, in case of surface what we have? We have unsatisfied bounds.

So, this becomes a high energy area so since definitely once we have any secondary specious have return to come or attract on the surface of this particular entity to reduce the overall surface area or the surface energy of this particular entity.

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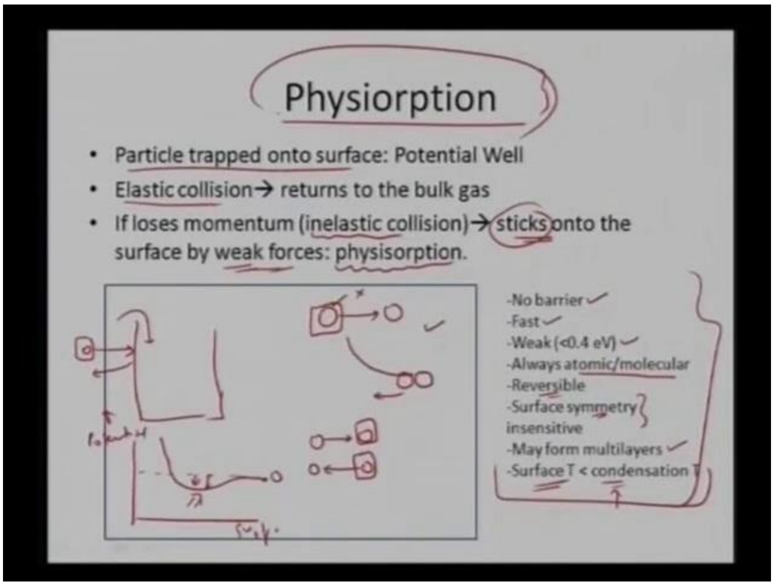

Physiorption

- Particle trapped onto surface: Potential Well
- Elastic collision→ returns to the bulk gas
- If loses momentum (inelastic collision)→ sticks onto the surface by weak forces: physisorption.

-No barrier
-Fast
-Weak (<0.4 eV)
-Always atomic/molecular
-Reversible
-Surface symmetry insensitive
-May form multilayers
-Surface T < condensation T

Again the absorption can be defined as the Physiorption option or a in case of Physiorption we have particle which is to the surface it is more like a potential well. So, I have particular entity which is entering the well and because of elastic collusion s the specious can go back to the gas.

So, we have particular entity, particular iron and atom or molecule it tried to go, but it could not because of elastic collusion it might tried to come back. But it might also happen collusion it can lose all its energy. So, it is lost so much energy that its energy basically comes down to a very lower value, and then it can just stay here without bouncing back.

So, in first case once we elastic collusion it goes try some molecules and then it comes back or goes to some other location without sitting along this particular sight. But in this case, but in case once it is losing all its momentum because of inelastic collusion it will remain stuck to the surface via some week forces. Those can be wonder wall forces all and an attraction so this being called as a Physiorption.

So, in this particular case we have Physiorption and Physiorption we have particle which is not trap on to the surface. So, in this particular specious we can see that that we have a 0 potential we have a 0 potential and then it basically stays in the potential well for some time. So, this is our so keeping at the potential an initially we have a 0 potential, and then this the surface of the absorbent. And then, we see the particular atom or molecular iron it comes and sits and it basically gas to the potential well.

So, not require certain energy to guide from the surface and this may not happen in very quick success such session. So, the iron or molecule can stay there for a little longer time and this happen, because we have elastic collision happening with the particular molecules. So in case, at the molecule starts loosing the energy were inelastic collusion is it might guide to the potential well, which is now the surface of a particular material and that second iron or molecule which is coming and surface.

Now, it is reduce energy of the surface and that why it is harder for it to go back, because it is lost all its energy and satisfying the inelastic collusions. So, it sticks to the to surface the forces which is in the Physiorption. So, ideally this particular process has no barrier, because this is more like compacting yourself on a particular wall; so that, you can lower energy.

So it does not have any barrier it is more like a physical attraction or a physical moment of particular atom or a molecule to surface side that is very fast. Because, in this case it wants to reduce the surface wants to reduce at energy so whatever molecular atom is coming on there, it is basically trying to get bonded with the particular specious so in terms of making at stuck on it surface.

Again, this interaction of very they have low energy it is less than 0.4 electron volt that is what is happening out here and there always atomic a molecular nature. And since there is no chemical bond which is coming out here, they are always reversible. At the same time they are, because it is go like a physical moment of particular atom to a particular location.

So, there to a surface cemetery in case surface has some cemetery they do not basically pick up a particular cemetery under particular sense; it may not want to go to particular site. Because, they are not sensitive on the sensitive to the particular molecule which is setting on the particular surface and they can also lead to go on forming multi layers. Because, they specious a secondary specious come and sits on the surface you know that particular absorbs it is specious now, again they has some free surface available to it.

So, it can again keep forming some multi layers and the surface temperature has to be lesser than the temperature. So that, the particular specious ca lose its energy and it can stay on the surface for a pretty long time. So, this is the overall deal with the Physiorption that they do not have a barrier they process very fast, because surface wants to somehow reduce its energy; surface energy. And these are week interaction of less than 0.4 electron volt and they are always a coming atomic or molecular in nature.

Because a this has happen by atom to atom, molecule to molecule and since this only physical entity which are basically moving and a going to rest on particular surface been help by a some week or forces. So, this is again reversible process and there to the surface symmetry and again the newly specious on the surface. Again, it will have some surface available to it.

So, it can again keep forming multi layers and again, for these 2 all to occur the surface temperature has to be low enough. So, that the particular iron specious it can lose its energy or it can lose it movement. So, all the vibration movements can be reduced by lowering the temperature. So, surface temperature has to lower than that of a temperature in order for the Physiorption to be much for a little longer time.

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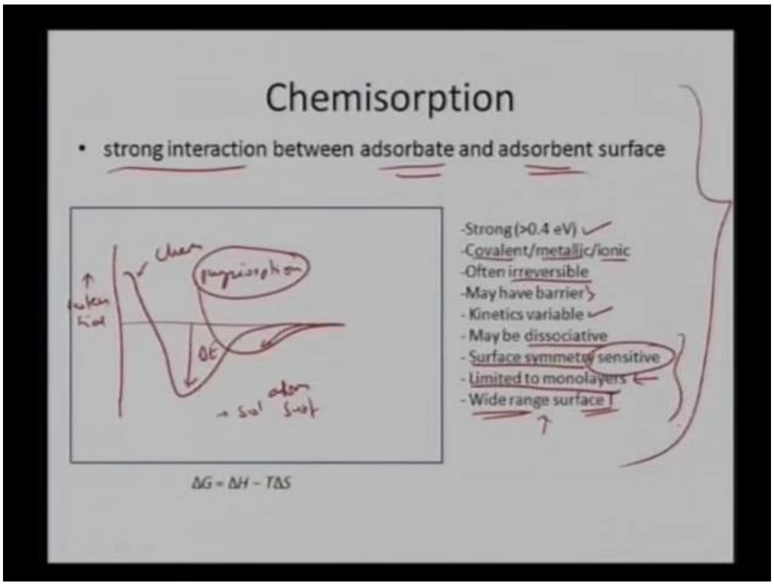

Chemisorption

- strong interaction between adsorbate and adsorbent surface

-Strong (>0.4 eV)
-Covalent/metallic/ionic
-Often irreversible
-May have barrier
- Kinetics variable
- May be dissociative
- Surface symmetry sensitive
- Limited to monolayers
- Wide range surface T

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

And going to the Chemisorptions**;** Chemisorptions is define as the strong interaction. In the earlier case in the Physiorption we at week interaction, but in this case we have a strong interaction between the adsorbate in the adsorbent surface. Adsorbent is where the overall adsorbent is the new spacious which is forming in the setting on the adsorbent. So, in this particular case we can define it like this is 0 potential and then we has some sort of a Physiorption, which can occur at the same time.

So, we can also see the chemise option is much this for the Physiorption and this for the Chemisorption depending on the potential. And this is depending on the distance on the solid solvent; solid surface, atom surface. So what is happening out here is, that the closer it is going a initially a with time Physiorption will occur.

Because, it has no much more probable that because of its lower energy particular entity can go and sit and sit on the surface, but eventually for Chemisorption it is lowering down its energy by much larger extent.

So, eventually chemisorptions is much more referred once it can lower its energy by certain value. So, in this particular case we have very strong bond which can form out here so it has strength greater of than 0.4 electron volt, it can again with covalent bond, metallic bond and ionic bond and once a particular entity is formed. Because, it is a chemical reaction it tends to be a reversible in nature.

So, again depending on that might have a barrier as well so in that, in case of a barrier it has to jump from Physiorption to Chemisorption. So, we will see that how this particular barrier can effect again, it can also have variable terms of kinetic depending on what is the overall barrier. It can reacted the overall kinetics of the particular process again, it can be again dissociative. What is that? We can come back to it, but it is very highly sensitive to the surface symmetry**.**

Because, it highly depends on if a particular item or specious surface and lets a particular tendency to attract a particular iron or a specious than that particular iron or tend to go exact at the sight were it is finding much more comfortable. So, in case of Chemisorption it is forms a very strong bond so it, because much more sensitive to the surface. So, the speed which is getting chemisette on the surface it has a it becomes very sensitive to the surface symmetry and same time, because limited to mono layers.

Because, that is so sensitive to the symmetry part or the specious part which is attracting at becomes limited; only when that particular specious available on the surface once it gets chemisorptions on the surface, there is no other iron which is available for it to deposit for that. So, once it forms a mono layer there no free subset specious available to again trap those absorbing specious.

So, that the reason at it is basically limited to the mono layers, but more than it can occur for a wider range of a surface temperature. So, in when the surface temperature pretty high or pretty low it can still occur. And the Physiorption can be a first means of leading to the chemisorptions as well; so in chemisorptions we can find that we can have much more lowering of the energy of the of the surface which can occur chemise option.

Because, it tense to form a very stronger chemical bond; the strength of the bond is pretty high it can either covalent ironic or metallic and once it is allowing the particular specious to form on its surface it is because of chemical interaction. The chemical reaction between the 2 specious it is limited surface only, but a same time it tends to form only mono layer.

Because, now once mono layers form there is no freely available surface to react with the absorb it further. So, in that particular manner it tense to form of mono layer only, but it can no occur you know variety of temperature. Because, even Physiorption can lead to chemisorptions an even at higher temperature the factor comes into play, and then again that can again need to some formation of chemical bond. And that it can release its energy to make the system much more stable.

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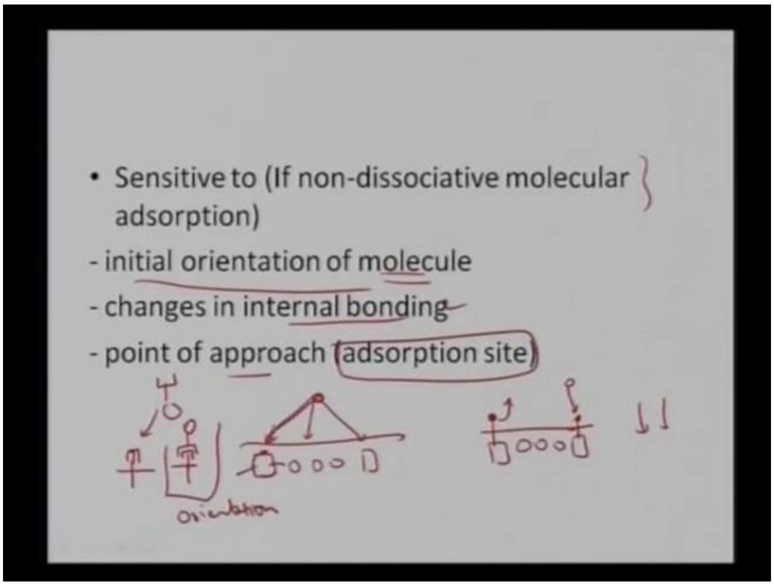

- Sensitive to (If non-dissociative molecular adsorption)

- initial orientation of molecule
- changes in internal bonding
- point of approach (adsorption site)

So, we can see that it is sensitive to the initial orientation of the molecule. Because, once we have some specious out there; some chemical specious attract the absorbing. So, it will depend the on were the particular specious is if have a surface particular attracting specious for the absorb it out here. Then the absorb it instead of sitting are in to form go on see this locations and form a chemical bond.

So, we can see specifically that this particular atom will try to go on form sit out here and form a chemical bond and release in release it energy. So, thereby lowering the overall energy of the system, so second atom is it will try to go here now and form a chemical with the targeted specious as well. So, again it can also lead to changes in the internal bonding because of that it might tend to these stabilize at and it might tend to lower its energy.

And again, because of this it is also to the point of approach so that is what we just discuss that. Because, this particular specious is now much more comfortable or much more attractive to the this particular approaching specious this becomes a highly sensitive to the point of approach or the absorb absorptions type. So, that is what happening with the chemise option part.

So, this is how it becomes that it becomes orientation of the molecule; it might also be case that the particular molecule coming like this. And my sight is out here, and which can accept this particular molecule then I really this part has to come down here and sit more light this. That is the reason this 1, because much more 2 also to the orientation. It is not, because also to the orientation of the particular molecule and again that type of bonding which generate out of it it again is of much more sensitive to that particular thing.

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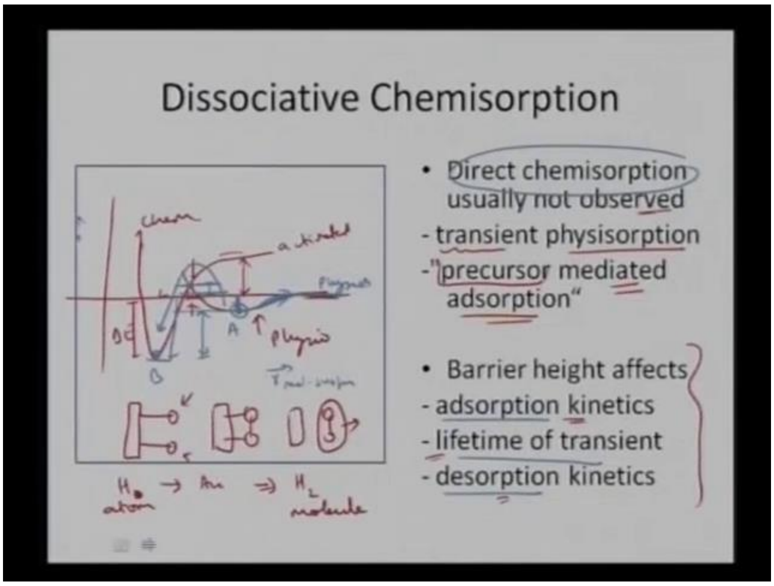

Dissociative Chemisorption

- Direct chemisorption usually not observed
- transient physisorption
- "precursor mediated adsorption"

- Barrier height affects
- adsorption kinetics
- lifetime of transient
- desorption kinetics

Then, again we can also see dissociative chemise option and generally the direct chemise option is generally not observed. Because, it is basically being followed by the Physiorption; so Physiorption is this so of transient face and which mediate the absorption. So, it's of the precursor to mediate the absorption at a for a Chemisorption. So, in this particular case what we can see is once we have a particular potential out here, and then we tried to have a Physiorption.

Then, we did see that of a sometime depending on how the potential curve is we might have some certain barrier to it. It this is for the Chemisorption and this for the Physiorption**.** So, we can see that this is 0 potential and it might happen that our surface in much more activated. So, what we can see that the initial potential is now much higher at much higher level, but by lowering energy it can lower down its energy by so much extra.

So, Physiorption will definitely try to go and jump into this particular well that is what we can see here. That once I am here, that once a particular specious come here and it wants to lower its energy it has to cross this particular barrier and then jump on to the lower energy well. So, it can lower its energy were this particular extent. But to overcome this particular to basically, attain this particular much of stability it has overcome this much of a barrier.

So, that can happen that also is required to happen that this barrier height will affect the overall absorption kinetics. Because, depending on the height what is the overall probability that will define is the lifetime of transient. Because, it has transient state and it has to jump to the low state so this is nothing, but the transient time. And also these option kinetic that might happen that this, jump from here to this from point a to point b is such that it is long enough.

So, what can happen it can basically get these on to the surface, because this much energy it can take or it can basically go back or it can get deserve from the surface itself. The overall transient time is very important, these also kinetic is also very important and the overall lifetime also of the transient also very important; for the transition from Physiorption to Chemisorption.

So, generally we see that direct Chemisorption does not occur, and then this is a potential out here. This is overall this is of the molecules surface interface, which the overall distance and that is what we are seeing here. So, in this particular case we can see that we need to first 1 the molecule has to go under Physiorption**,** and then basically it has to cross this barrier at this particular junction. And then, come back to chemise out state lower its energy.

So, Physiorption basically serves as the pre curser to mediate the Chemisorption, and then again the barrier heights are basic factors and terms of detecting the absorption kinetics. Or define the lifetime of the transient or the desorption kinetic, it in detected by the particular barrier height. And some time it might also happen that Physiorption to chemisorptions may not be freezable at all.

Let me, go back to it chemise option can happen like that that we have a particular entity; which now can go and saw go and basically sit on the sub straight. But later on what can happen is that it can now start chemically reacting with the itself and it can leave the surface as a molecule. So, initially atoms they come they go and sit on the surface and the basically get dissociated by forming a molecule.

That is what is happening this what is what is called a Dissociative Chemisorptions. That we have specious arriving having as a atom and then it stays on the surface. And then , lives out depending on chemical stability. This can happen is that that stop it can basically sit on gold surface, but once it is desorbs it the Hydrogen atom is basically coming and sitting on the gold surface. But it goes or does a hydrogen molecule so Hydrogen atom is coming, but it leaving as a hydrogen molecule.

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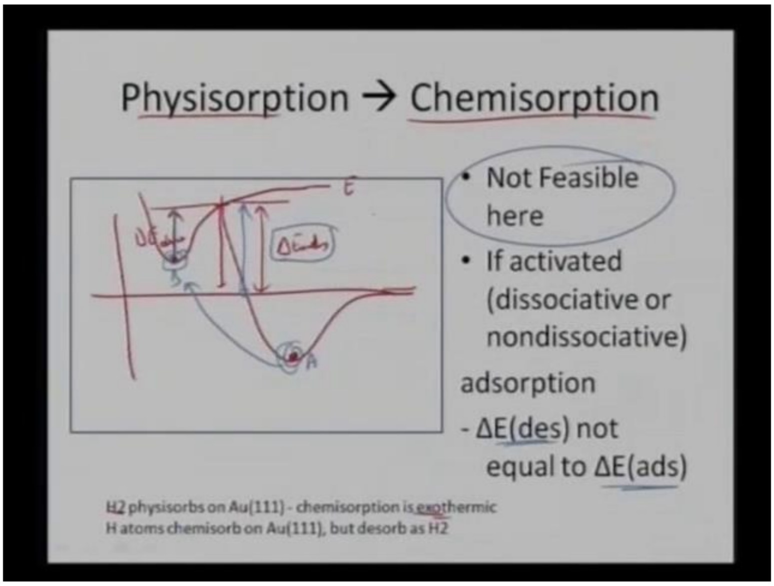

Physisorption → Chemisorption

- Not Feasible here
- If activated (dissociative or nondissociative)

adsorption

- $\Delta E(des)$ not equal to $\Delta E(ads)$

H2 physisorbs on Au(111) - chemisorption is exothermic
H atoms chemisorb on Au(111), but desorb as H2

That is what basically can happen, but in some cases like it can happen that once Hydrogen is absorb preserving on the gold surface chemisorptions is exothermic. So, again that may not assist the formation of Hydrogen Physiorption on the gold surface at all. In that particular case, we can see that in some cases Physiorption to chemisorptions may not be visible in certain cases.

Because, in certain cases like a Hydrogen wants to Hydrogen molecule wants to absorbs on gold surface. Chemisorption becomes basically it is not becoming usable, because it requires very high energy to get on the gold surface. So, in that particular case we can see the transition will be more like this that we have Physiorption which can occur like this.

There may be chemise option, but in chemise option we have more like this a kind of pattern. So, we have certain energy much higher so we have this height which is again pretty high. So, we have this particular these option energy is from here to here chemise option these option will basically happen here this for these option. But whereas, for the option we require such in such a high energy data e absorption, but my molecules is sitting here or the atom sitting here.

Then, it may not freezable for it to basically go from this state the lower energy state like a to b. We can see, that in certain cases once I do not have this thing adsorption our my delta it is also is not equal to the delta e adsorption. Generally we I can expect that, this might once it is point b when chemise option is occurring. Once it is lowering the energy, that it make sense were the jump of atom for the particular point for a particular specious to go from point a to point b.

Because, it is lowering its energy but in certain cases, when there is particular these option thing is pretty high you know and again my delta a option even higher. So, in that particular case it will remain adsorb, because it is much lowering of the energy like here. So, we have our delta a adsorption and the better height is pretty high in this particular case we can see delta e adsorption is pretty high.

So, for these option it is again lower, but it will it will better height itself so high that the point a may not want to go to point b. And in that case the Physiorption to chemisorptions may not be possible at all.

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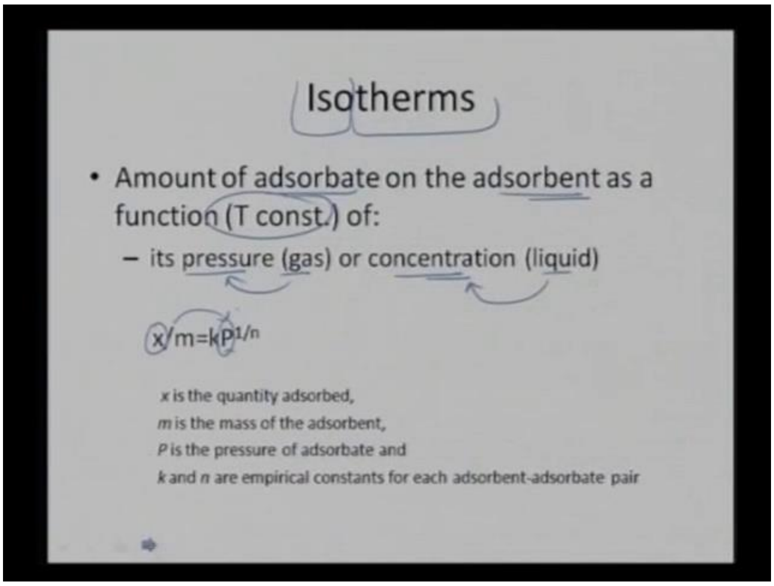

Isotherms

- Amount of adsorbate on the adsorbent as a function (T const.) of:
  - its pressure (gas) or concentration (liquid)

$x/m=kP^{1/n}$

x is the quantity adsorbed,
m is the mass of the adsorbent,
P is the pressure of adsorbate and
k and *n* are empirical constants for each adsorbent-adsorbate pair

So, define that how this particular thing how the adsorption is occurring. We can define the in terms how what is the amount of adsorb it on the adsorbent as a function of consent temperature that is how we get the term Isotherm. So, we defining this particular relationship at a constant temperature you define how much amount of adsorb it is sitting on the adsorbent. And that can be define by the pressure or the concentration of the specious on a particular adsorbent.

So, if it is a gas we define it by pressure; if it is liquid we define it by pressure; if it is a liquid we define it by concentration. So, we can define it by the quantity which is being adsorb on the particular mass of adsorbent. So, to basically we can normalize it and that thing is been defined by the pressure of the adsorbent the k n and being the constants for the adsorbent which is means specific for a particular adsorbent.

So, in this particular case we can see that higher the quantity being adsorb I can get higher amount of pressure which can be or which can pressure of the adsorb it which can be render. So, higher quantity of adsorbent my pressure is not now much higher. So, that is how it basically this particular relationship comes about.

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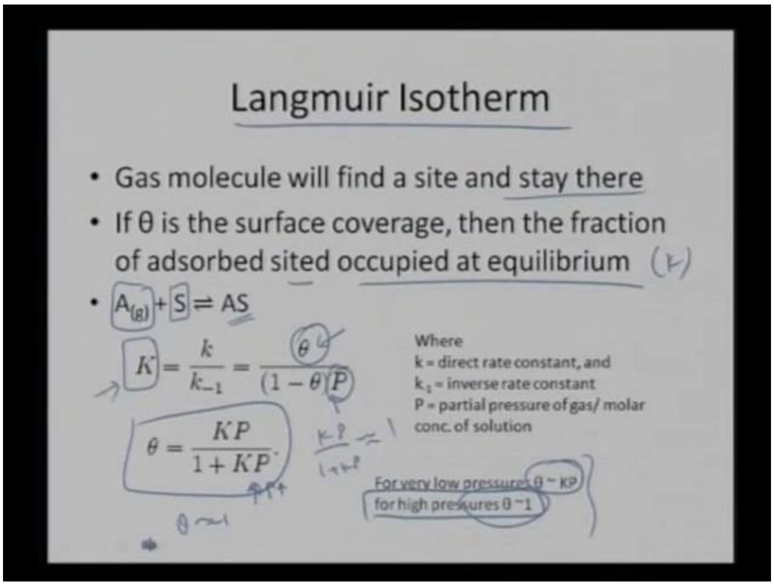

Langmuir Isotherm

- Gas molecule will find a site and stay there
- If θ is the surface coverage, then the fraction of adsorbed sited occupied at equilibrium (k)
- $A_{(g)} + S \rightleftharpoons AS$

$$K = \frac{k}{k_{-1}} = \frac{\theta}{(1-\theta)P}$$

$$\theta = \frac{KP}{1+KP}$$

Where
k = direct rate constant, and
k_{-1} = inverse rate constant
P = partial pressure of gas/ molar conc. of solution

For very low pressures θ ~ KP
for high pressures θ ~1

But again in this particular case we can also define at using a Langmuir Isotherm that gas molecule will and it will stay there. Because, there are certain assumption which are required and again, and a once we have theta is a surface coverage in the fraction of adsorb it which is now sited it basically now occupied the equilibrium. So, that is what we can see here the overall equilibrium fraction. It can be basically, being defined by the specious of which are the direct constant and with the inverse rate constant.

So, that eventually come out to be the overall coverage so this is the overall free space which are the available though the particular specie. And this is the overall partial pressure of the gas or molar of solution. So, though this from this we can see what is the overall fraction of the adsorb sight which is now occupied at particular equilibrium. So, that is been given by k so again we can see.

So, this k can be defined as the equilibrium number of fraction of the fight which are now occupied this is defined by k. So, we have particular specious of a which is gas and is going an sitting on a particular surface S to form AS or it is occupying a particular surface and equilibrium. You can define the overall fraction of the adsorb sight, by the overall surface coverage and the overall partial pressure which is being generated.

So, from this we can directly see is a very low pressure when I have p very very low, I get overall theta which is becomes equal to the KP. Because, once were this term is very very low and this becomes KP by 1 and this is again nothing, but equal to KP, but 1 for very high pressures once a pressure very very high. Then, what happens is my this term domination and then KP were 1 plus k p it becomes eventually to be 1. So, my theta come becomes approximately 1 for high pressures.

So, this is what the this is how it is defined by the that we have finding fraction of adsorb sights which are being occupied equilibrium that is being defined by the overall surface coverage. And the overall pressure of the gas which is now main generated or the concentration of the solution. And from that we can defined the overall coverage and for a very low pressures my theta is equal to KP. For high pressures my theta is equal to approximately 1.

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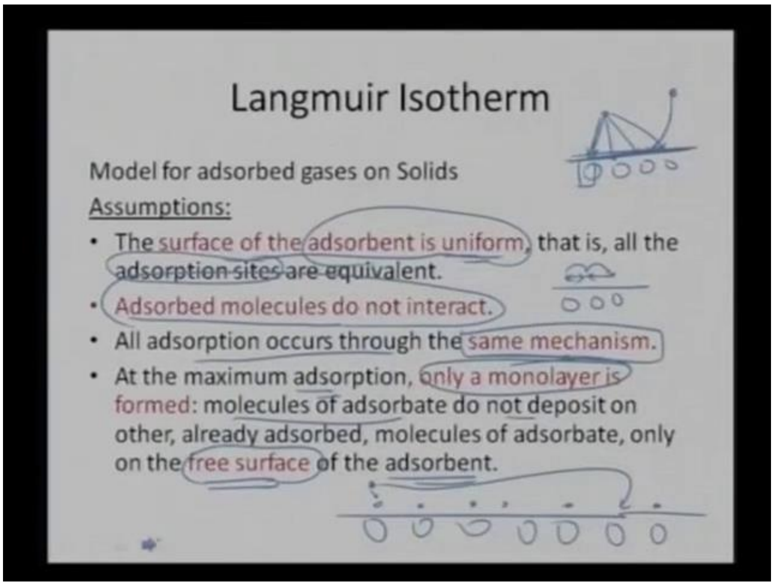

Langmuir Isotherm

Model for adsorbed gases on Solids

Assumptions:

- The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
- Adsorbed molecules do not interact.
- All adsorption occurs through the same mechanism.
- At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

And is now, base on certain assumptions and this assumptions are very they require to be out here. Because, this is this is also modeling for doing the particular defining the particular in terms of deciding its coverage. So, as assumptions are it is surface of the absorbent is uniform it means, that all sights which are required for adsorption that the equivalent.

So, if I particular surface coming here it has a equal it have going setting on any of the sights. So, this is what is being defined that the surface of the adsorbent is usually form this surface adsorbent is uniform and all adsorption sights are equivalent. Secondly, it says that adsorb molecules do not interact, so once have a particular specious which has now adsorb on the surface it does not react or interact amount 1 another.

So, adsorb molecule they are no interacting and again, all adsorption is occurring through the same mechanism. That is 1 more feature of it that, the way this particular specious will go and sit on this particular sight. The similar manner, another specious will go and sit on some other sight. So, they are being detected by the same mechanism for this particular adsorption and at the maximum adsorption, only a monolayer is forming.

But that again becomes a limitation for this, because generally we defined for Physiorption more than 1 layer can a practically form. But for in this particular modeling model we can take it only is the single monolayer or keeping the simplicity. Because, the way we are defining the coverage that is again dependent on the kind of pressure which is naming generated by the surface.

So, that become a limitation for defining the isotherm so molecules of adsorb at they do not deposit on the already adsorb molecules of adsorb it. And be deposit only on the free surface of the adsorbent. So, if I have a particular surface were I have see that deposition of already certain molecules or irons or atoms out here second atom it may not see and may not sit here it might go to some available sight.

Then, it can follow in sit here that is the deal about the adsorption of particular molecules on a free surface. This we can see, that it has certain limitations that we are assuming that surface of adsorbent is uniform and adsorb molecules they do not do interact whereas, practically these adsorb molecules again start interacting with one another that again is a possibility. But again, we are saying that adsorption is occurring to the same mechanism and it forms only a mono layer and then newly arriving specious can sit only at a free surface.

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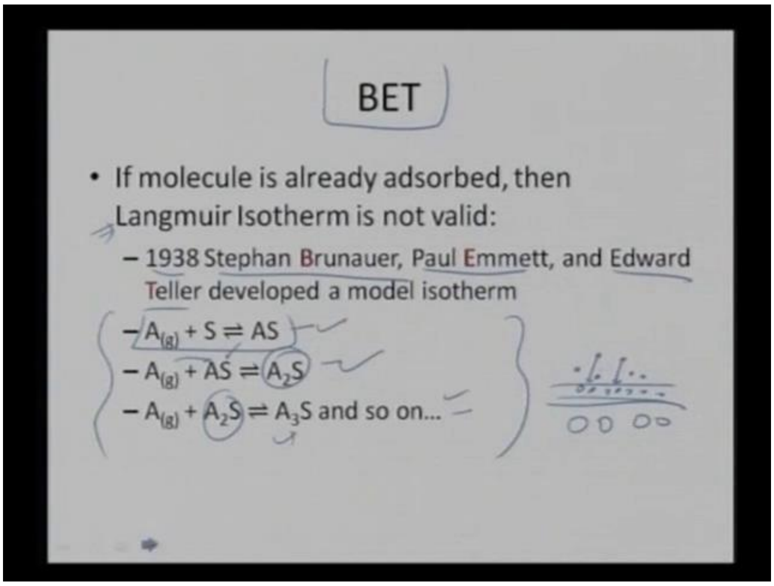

BET

- If molecule is already adsorbed, then Langmuir Isotherm is not valid:
  - 1938 Stephan Brunauer, Paul Emmett, and Edward Teller developed a model isotherm
  - $A_{(g)} + S \rightleftharpoons AS$
  - $A_{(g)} + AS \rightleftharpoons A_2S$
  - $A_{(g)} + A_2S \rightleftharpoons A_3S$ and so on…

So, to define that we have method of seeing how much coverage is being done by particular specious. So, we can defined that by a BET a technique that is called Brunauer Emmett technique and this is name on the who basic the defined particular. In 1938 those are Stephen Brunauer, Paul Emmett and Edward Teller who has basically developed model Isotherm.

So, as we see in the previous assuming only a single monolayer to be getting adsorb as a monolayer. But in this case, we can see we can basically classify as a network or a sub routine of it that we can see that first we are forming a monolayer and then we firming a bio layer and then we firming a trio layer. So, we can see is molecules already on a surface then we cannot extend the isotherm.

Once a molecules is already now adsorbed, so BET technique now comes into picture it can define. Then, as the multiple layer which we can see that there are multiple levels of the absorbent of the surface forms of monolayer. Then, that monolayer comes sense it and next specious at set on surface the form bio layer and keep some going so on.

And that is what has more practical, because it might be happen that specious they can come and find this surface we more and start sitting on the surface of already adsorb specious. So, that is how it is firming the bio layers that multiple surface layers.

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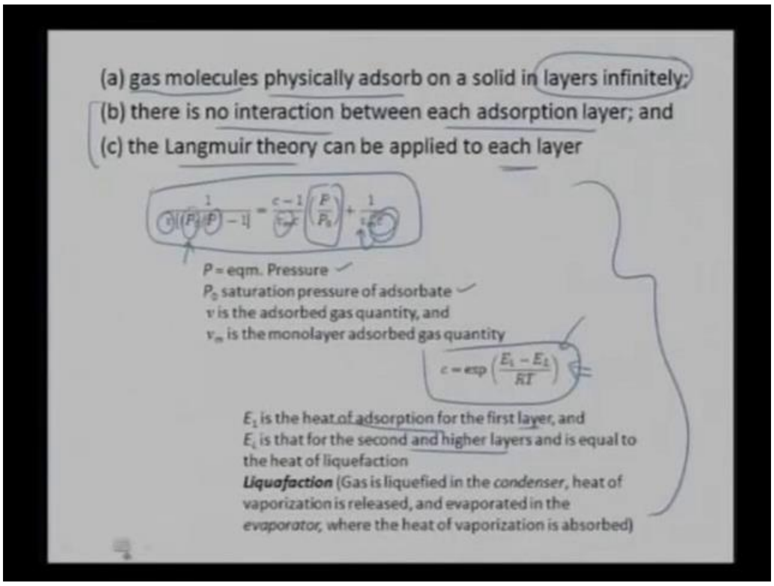

(a) gas molecules physically adsorb on a solid in layers infinitely;

(b) there is no interaction between each adsorption layer; and

(c) the Langmuir theory can be applied to each layer

$$\frac{1}{v[(P_0/P)-1]} = \frac{c-1}{v_m c}\left(\frac{P}{P_0}\right) + \frac{1}{v_m c}$$

P = eqm. Pressure

P_0 saturation pressure of adsorbate

v is the adsorbed gas quantity, and

v_m is the monolayer adsorbed gas quantity

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

E_1 is the heat of adsorption for the first layer, and

E_L is that for the second and higher layers and is equal to the heat of liquefaction

Liquafaction (Gas is liquefied in the *condenser*, heat of vaporization is released, and evaporated in the *evaporator*, where the heat of vaporization is absorbed)

So, basically may be assume that gas molecules they are getting physically adsorb on a surface and firming an infinite layers. So, deepening on how many grass molecules come there is no limitations that day by to certain mono layer or a bio layer. So, in this particular assumptions we are making a practical case that gas molecules can come and sit on a already adsorb surface as well.

It can form infinite layer or the same time this 1 more limitation and that we are also assume in a there is no interaction between the each adsorb layer. And again, we can assume we are also assuming that Langmuir through we can again be applied to each layer. So, this is again limitations of that, but we are limiting, we are eliminating 1 limitation by making it making it a multiple layer or a infinite layer adsorption on the surface.

But, we are assuming that these all layer their independent in the they do not interact with 1 another and the same time we can apply this Langmuir to each adsorb layer. So that, is the advantage of this particular BET theory and it basically comes out to be a formula like that that our adsorb gas quantity. It has some relation with the equilibrium pressure a equilibrium pressure and a saturation pressure.

So, this is a saturation pressure on the equilibrium pressure with respect to the monolayer which is not being adsorb on the on the surface. So, that is how it basically comes an in this seek is nothing, but the constant which is which arise on the a liquefy action. And it is given by, the exponential of e1 minus el that is nothing, but the heat of adsorption which is now first layer to lower the energy and el is for the second and higher layers.

So, how much energy is reduced by the adsorption of all these specious; this is more like a reduction in the energy of a particular surface by the adsorption that is being accounted by the term c. And that is how it is now associate with the how the monolayer at the option will occur with respect to the pressure it is forming that is now giving by the equilibrium pressure to saturation pressure of the adsorbent.

Saturation pressure of the adsorbent is basically, the maximum pressure it can an is the pressure is at the equilibrium conditions. So, this is how which can be utilize for defining the BET in this case we are doing it like that we are defining a dependence of this monolayer with respect to multiple layer. And be able to overall a saturation pressure with more and more number of atomic specious.

So, for a particular specious were getting certain equilibrium pressure and hence we have more and more number of adsorb specious it will start increasing the overall saturation pressure. So, in that particular manner we can eventually find out what is the overall compulsion or then overall concentration of a or the overall coverage of a particular specious.

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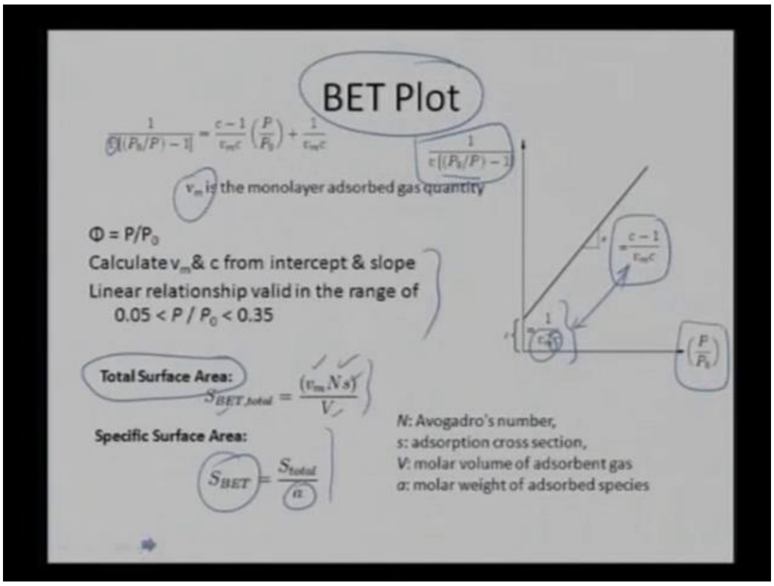

BET Plot

$$\frac{1}{v[(P_0/P)-1]} = \frac{c-1}{v_m c}\left(\frac{P}{P_0}\right) + \frac{1}{v_m c}$$

v_m is the monolayer adsorbed gas quantity

$\Phi = P/P_0$

Calculate v_m & c from intercept & slope

Linear relationship valid in the range of

$0.05 < P/P_0 < 0.35$

Total Surface Area:

$$S_{BET,total} = \frac{(v_m N s)}{V}$$

Specific Surface Area:

$$S_{BET} = \frac{S_{total}}{a}$$

N: Avogadro's number,

s: adsorption cross section,

V: molar volume of adsorbent gas

a: molar weight of adsorbed species

So, basically see is from the basically form the adsorb quantity; adsorb quantity of the grass on the particular subs aright is the define quantity. It kind of pressure it is generating in the saturation pressure, in the equilibrium pressure that particular also known. So, a relationship between them we can provide us a particular slope and a particular interest. And from a inter set and the particular slop we can always calculate what is overall gas quantity which is no adsorb as a monolayer.

Then, again the concentration which is now basically being the arrived from the a initial part of the e1 and el that is the heater adsorption, so the first layer and from the higher layers. So, from that we can always calculate the overall reduction and energy and also the overall adsorb all of particular surface. And again, from this you can basically calculate the overall surface area and we can also surface area from this particular technique.

But the idea is that now we can from can be very useful, because it will tell us what is a overall side available in a particular volume. That is thing define by the BET Isotherm and from that we can eventually calculate was the overall porosity of particular material. So, once we know what is overall free volume of available in a particular material. To this particular technique, we can using a particular equation of the total surface are by the monolayer which is adsorb on a these overall volume of the adsorb gas. And is the number and is the absorption cross section. So, from that we can always what is the total surface area and if we divided by the overall molar weight we can also get the specific surface area for a particular specious as well.

You can define what is overall specific surface area, which is now available for a particular material. So, BET comes a very in terms of defining the overall porosity the in terms of its volume as well as. So, in this particular case we can see BET plot is very critical tool in terms of able to define a particular total of surface area, as well as the specific surface are to be able to calculate overall porosity of a particular material.

Or define what is the overall area available or a particular entity or a gas specious to react with the particular surface. It is very which critical in terms of defining catalyses, because we want a particular gas or any entity to form in that adsorb an a particular surface. And surface area the adsorption in the and that will define in the available porosity volume or the overall surface area available for the reaction.

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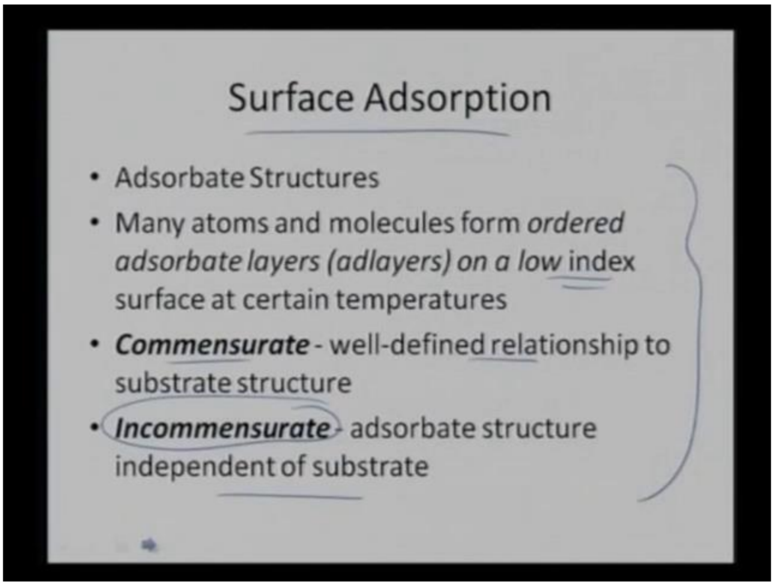

Surface Adsorption

- Adsorbate Structures
- Many atoms and molecules form *ordered adsorbate layers (adlayers) on a low* index surface at certain temperatures
- ***Commensurate*** - well-defined relationship to substrate structure
- ***Incommensurate*** - adsorbate structure independent of substrate

So, coming to the surface adsorption many atoms basically return from ordered adsorb a bit layer on a basically lower index plains. It can again, have a very defined relationships that is commensurate or it can have just random structure which independent of the structure, in which confirm incommensurate structure as well.

Again, they might have dependence on the that temperature, it might have to depends on the which is available on the surface. So, it has certain criteria which is available which can happen items of define in the surface adsorption.

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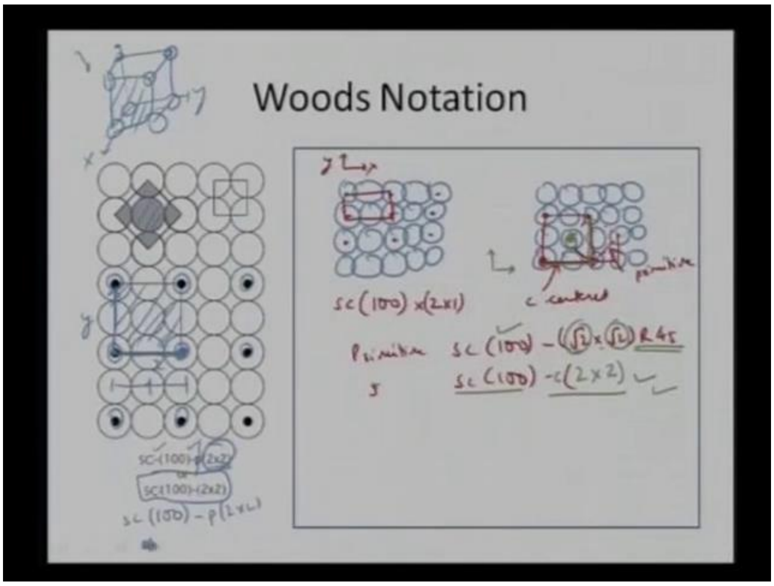

Woods Notation

SC-(100)-p(2x2)

or

SC-(100)-(2x2)

So, there are certain rotations which are now being develop, so 1 is called Woods Notations. So, if we take a particular crystal of a simple cubic this showing a 1 0 0, so we have particular unit cell of 1 0 0 we can see a simple cubic has certainly 8 atoms on the corners of a particular crystal. So, we can see a 1 of its surface if we take 1 0 0 and define it by x y and z we can see that 1 of its specious look more like this.

So, that little atoms along x and y more like this, so it can be defined like that. But once we have once we starts seems some adsorb it or it surface, we might have certain symmetry to it. So, this can again defined using the Wood Notation that in this particular case we are taking this 1 as the unit cell to it, can also have we take this particular entity is the unit cell for the adsorb it.

So, this is what we require for the sub straight this grace portion this what we require for the defining a particular sub straight. For defining the orientation of the adsorb it we have to take a unit cell and from that we can see that, it is define by a simple cubic it is more like a simple cubic structure with a 1 0 0 surface. And is a privative letters, which is now 2 by 2 of the original of the original letters length.

But, we can see it is starting from here is going to 1 and 2 letters point 2 atomic position to set out here. So, we have this atom which is now 2 atoms a part is forming 2 by 2. It is define by simple cubic, which is sitting at the 1 0 0 plane of the initial sub straight it is forming a primitive letters which as a length of 2 by 2 it is going to in the x side and 2 in the y side.

So, it is going 2 unit vectors in the x side and 2 unit y direction that is why it is forming simple cubic 1 0 0. And it we can just eliminate the primitive p and we can define it by simple cubic 1 0 0 and into 2 by 2. In case, we had certain letters like that we could also have something like this. We 1 atoms, third atoms, fourth atoms, fifth atoms like this, and then we can also see that the the if were adsorb it they are more like this.

Then, this particular case we have to take the this 1 is units cell and that will be define by a simple cubic sitting on a 1 0 0 surface. And now, it is 2 unit factors in x direction and 1 unit rector in the y direction. So, this is how it is to be defined like that in some other case, if we can go back and say that if my atomic like this for a simple cubic 1 0 0. And see if I had something like this, if I add something like this 1 atom adsorb it 1 out here, 1 out here, 1 out here, 1 out here.

I can take either this is a primitive letters or I can also take this is a primitive letter. I will definitely take this as a primitive letters, which is dotted because this 1 is forming my c centered and this 1 is now a primitive. So, I can define it 2 manner I can say it is a simple cubic first I am taking only primitive case it is simple cubic. Now, it is it has travel route 2 distance; this is 2 travel route 2 by route 2 at 45 degree.

So, I am defining it as again let me define as a primitive I take it as simple cubic sitting on the 1 0 0 surface. Now, it is a route 2 by route 2, because I am travelling at the travels in route 2 on this side on the x side and route 2 on the. y side to reach the second adsorb it specious or I can also define it as a the non primitive simple cubic 1 0 0 sub straight surface.

Now, what am doing I am now, from here I am going to this particular sight. So, what I am doing I am from here to here, and then from here to here it is more like the previous case some 2 by 2. But now, this particular specious become it has 1 more atom at the 1 more adsorb at the center. So, I make it c centered so I can define it by simple cubic 1 0 0 c center and I am 2 by 2 or it is simple cubic 1 0 0 plane. And I have to travels route 2 by route 2 x direction and in the y direction, I can refer at by factors of route 2 by route 2 at angle of 45 degree that is how am defining my adsorb it using the routes rotation.

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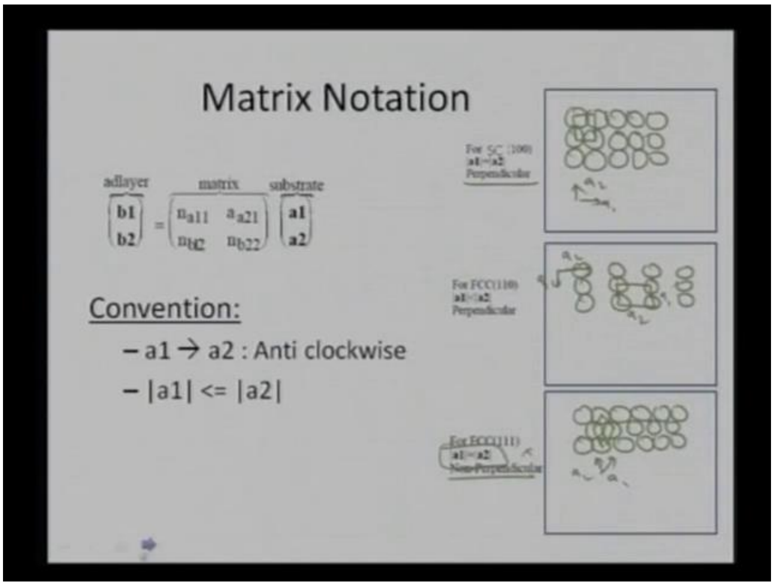

Matrix Notation

$$\underbrace{\begin{pmatrix} b1 \\ b2 \end{pmatrix}}_{\text{adlayer}} = \underbrace{\begin{pmatrix} n_{a11} & a_{a21} \\ n_{b12} & n_{b22} \end{pmatrix}}_{\text{matrix}} \underbrace{\begin{pmatrix} a1 \\ a2 \end{pmatrix}}_{\text{substrate}}$$

Convention:

- a1 → a2 : Anti clockwise
- |a1| <= |a2|

I can also define them using a Matrix Notation, so I have the similar arrangement of them. So, I can take a simple cubic 1 0 0. And in this particular case, I can have a1 equal to a2 in this particular case I can a1 equal to a2 more like that. So, my a1 direction and a2 direction they are basically equal as well as there to each other. So, that particular case I can defined them using like that.

Then, alternately I can also, some other surface like I can see I can take a 1 0 0 surface. So, my atoms in the x direction are much further apart as compare to my y direction, so I can see more like this. So in this case, I have see that my a1 is much smaller as compare to the a2 direction I am a2 like this a1 like this.

So, I am seen this my a2 this my a1, so I am seeing that 1 0 0 letters my a1 is much smaller than a2 at the same time they are perpendicular. But the we can be again, 1 more case that in some other location at can have some different arrangement of FCC. I can have a kind of structure, so I can see more like this suppose structure my a1 is like here, a2 is out here. And now, a1 and a2 they not perpendicular, but they are equals. So a1 is equal to a2, but they are not perpendicular.

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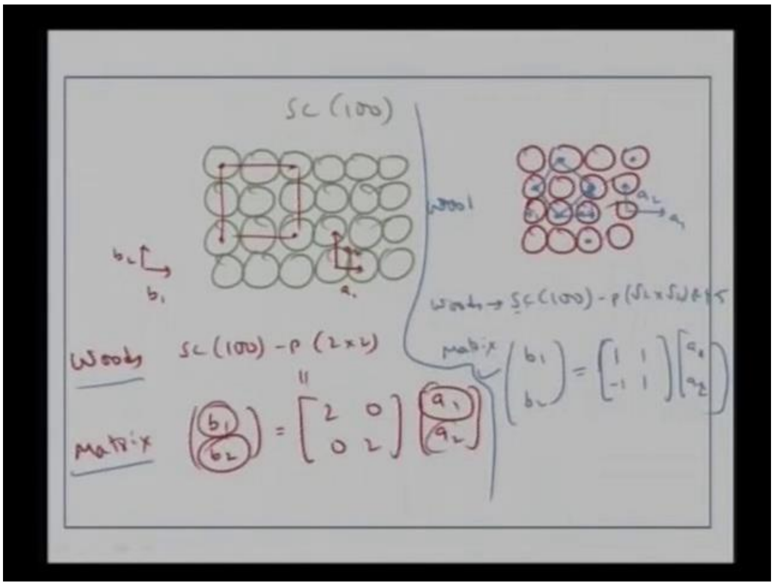

So, again I had to define the a1 a2 based on that so if I take particular I can define, I can correlate basically the words notation and the matrix notation more like this. So I am just defining the initial substrate at will be simple cubic 1 0 0 surface. And if I go back and take my adsorbed specious more like this out here a define it like that. So, in this particular case I know that it is forming a simple cubic 1 0 0 surface I am defining my primitive of 2 by 2.

So similarly, what am doing here I am if I define them as direction give a and direction b 2 and the initial direction b a1 and a2 of the initial crystal surface of a substrate. In this case, what I am doing I know that my given b1 and b2 there are dependent on the a1 and a2 by 2 0 0 0 2 of a1 a2 for achieving b2 given I am 2 distance in a1. And I am achieving my who disturbs in a2 so that is how it is equivalent to this a metric notation.

So, this is the Woods Notation and I had some other some other geometry, so in case I have some other geometry so I had at particular different geometry. So let me, take it more like this so same adsorbed atoms out here, out here, out here they place like that. So, how define I can define them b1 b2, but in this case my a1 and a2 are again the same direction is a1, this in my a2 direction.

So, this would I would have define by utilizing primitive letter of defining them as simple cubic 1 0 0. And again, it must firming my primitive route 2 by route 2 are 45 now, I can define that through my notation more like that that. In case, my b1 and b2 now what I am doing in 1 distance in the x 1 distance in a1 and 1 distance in the a2 as well. So I am defining at by 1 1 a1 a2 similarly, for the reaching I am minus 1 in the a1 so minus 1 in the a1 and 1 in the a2.

So, this is what is the Metric Notation for this particular system and this is the Wood Notation of this particular system out here. Some or the matrix notation for defining the way adsorb it is on the adsorbing and of that we can use a very simple Woods Notation or Matrix Notation. So, we can player on the we can see how it is to be defined.

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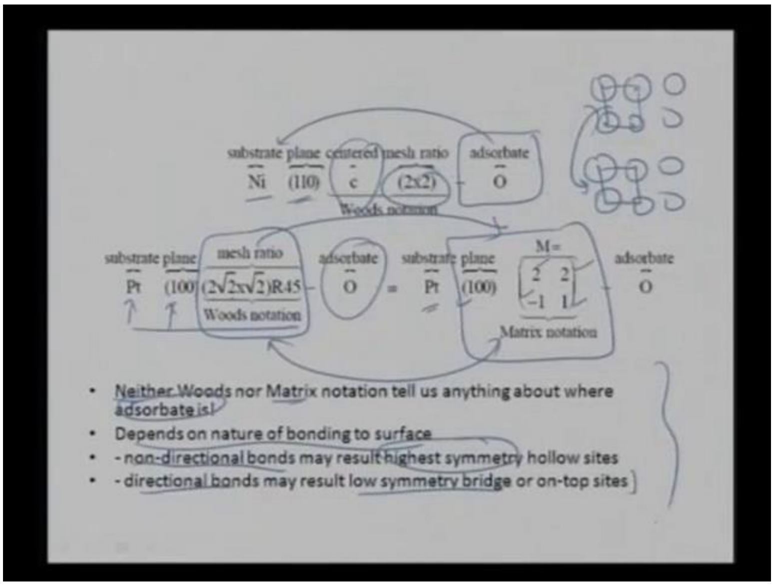

substrate plane centered mesh ratio adsorbate

Ni (110) c (2x2) - O

Woods notation

substrate plane mesh ratio adsorbate substrate plane M= adsorbate

$\text{Pt}\ (100)\ (2\sqrt{2}\times\sqrt{2})\text{R}45 - \text{O} = \text{Pt}\ (100)\ \begin{bmatrix} 2 & 2 \\ -1 & 1 \end{bmatrix} - \text{O}$

Woods notation Matrix notation

- Neither Woods nor Matrix notation tell us anything about where adsorbate is!
- Depends on nature of bonding to surface
- - non-directional bonds may result highest symmetry hollow sites
- - directional bonds may result low symmetry bridge or on-top sites

So, just to give a equivalent a taking of play 1 1 0 it can be c center and the defining the which how much this type travel to 2 in a1, 2 in a2 and we calls be define a adsorbate sitting on the substrate. So, again just to give equivalence I can towards more like that that I am defining a platinum surface of plane 1 0 0 I travels 2 root 2 a next an root to n y at a angle of are 45. And the adsorbate again Oxygen; that means equally I am in metrics Wood Notation similar plane.

But now, I define this particular of part as towards in to distance in x to distance in y an minus 1 in x minus in y so these terms become equivalent. But 1 very important criteria which the separate with basically is not at all in we can to thing that days that neither the Woods Notation all not the Matrix Notation. They will tell us anything about where to the actual adsorbate it is.

So, this tell us how this adsorbate now oriented had a head adsorbate like here follow the like here. I would know how what is the difference these 2, that will defined both the what notation as well as the matrix notation will defined as the was the same. It wood differentiate whether it is on a particular or exact location.

So, again a depends on the nature of the bonding to the surface it might happen that the non directional bonds; they may results highest symmetry. Because, they not at all they not have a certain direction so atom can go an sites an were an because of certain reposition along itself little time to a achieve a highest symmetry. But in 1 case of direction of the bonding it might need to go on sit exactly at particular location.

So, it will limit basically this some restriction so that is what it will it might create a low symmetric wages on the top site. And that is overall deal with definition of the absorption on a particular substrate. So, in this particular lecture we did see that how we define isotherm that we keep very initially we assume it to be a monolayer. But then, we can go on defining in terms of by layers and tri layers.

So, exceed our initial isotherm to making it multi layer and then assuming that it is the thin layer, which are now multi layer they do not interact which is with each other. And they have basically, form uniform layers and then they go on to forming multi layer. And from that we can also that, how Physiorption, Chemisorptions tense to basically effect how this now getting dissociative, how it is getting attached to a particular surface.

Then, we also learnt about how we can utilize this Matrix Notation and Woods Notation to basically say how where the particular where the particular adsorbent is setting on a particular adsorbents surface. And how we can play around with a with it, but these techniques do not tell us exactly where the particular adsorbate is stating. It only tells us, how they are basically setting so I end my lecture here.

Thanks a lot.