Course: Adsorption Science and Technology: Fundamentals and Applications

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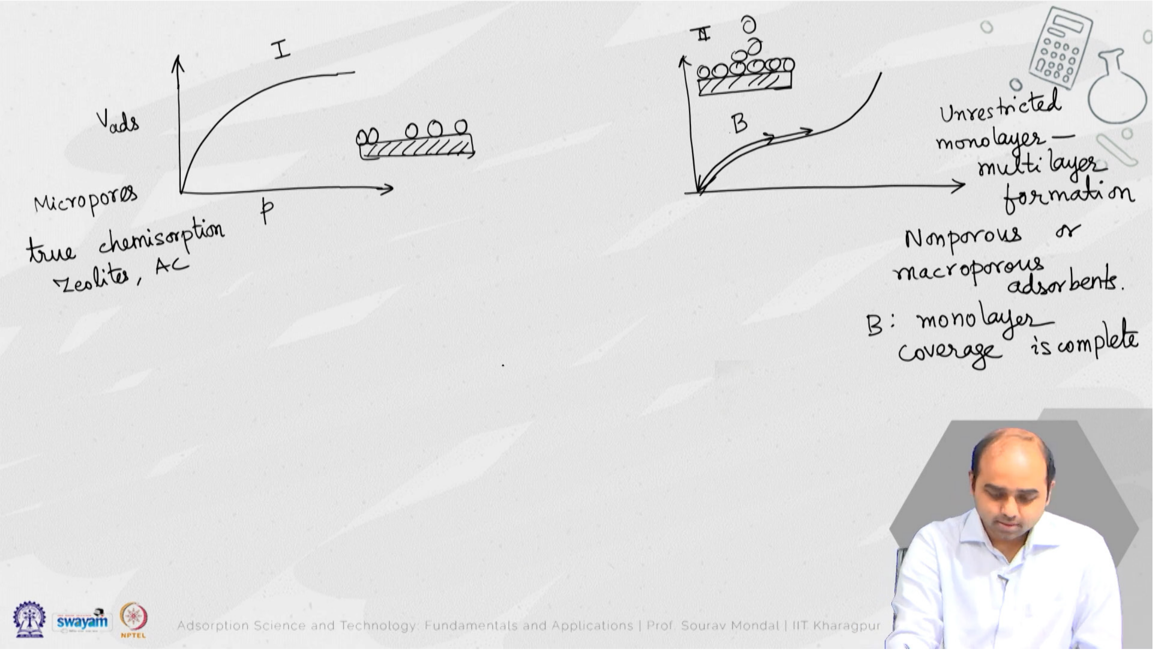
Week 03

Lecture 11 | BET Analysis

Hello everyone, welcome to this third week of this course. In this week we are going to talk about the particularly focusing on this BET you know adsorption. So, BET there is also an equipment in the name of the BET. So, this BET is actually a multilayer adsorption model it can I mean the isotherm model explains the multilayer phenomena or the physics. And this model was originally developed by three researchers, Brenor, Emanet and Taylor. So, this BET principle is used or essentially the adsorption experiments particularly for multilayer adsorption is also used in an equipment known as by the BET.

So, besides evaluating the adsorption isotherm. This equipment is used or heavily popular or widely popular for measurements of the surface pore surface area, pore size distributions, pore volume and other things. So, in the in this week itself we will talk about all of this how the background of this equipment the background of the BET isotherm in fact. The difference between chemisorption, physisorption, how the pore size analysis are calculated, what would how the you know this pore size distribution of the surface area of the adsorbent or the catalyst is evaluated for porous materials is something that we will focus in detail in this week.

So, the first lecture we will talk about mostly on the BET analysis the equipment and the background of the adsorption. So, first let us talk about the types of the adsorption that we normally encounter. So, if you recall the there are different types of adsorption patterns that is obtained moving from monolayer to you know heterogeneous multilayer, homogeneous multilayer and then you know extended multilayers where each of the multilayers can be considered to be monolayer. And finally, when there is too much of multilayer formation there is a chance of the formation capillary condensation and something that we will focus in this week itself. So, first to talk about these different you know monolayers or the multilayers operation, let us try to quickly revise or quickly catch up once again about the different types of adsorption patterns that are normally observed and this will also help us to connect the different types of adsorption behavior which is normally seen or encountered in this BET equipment too.

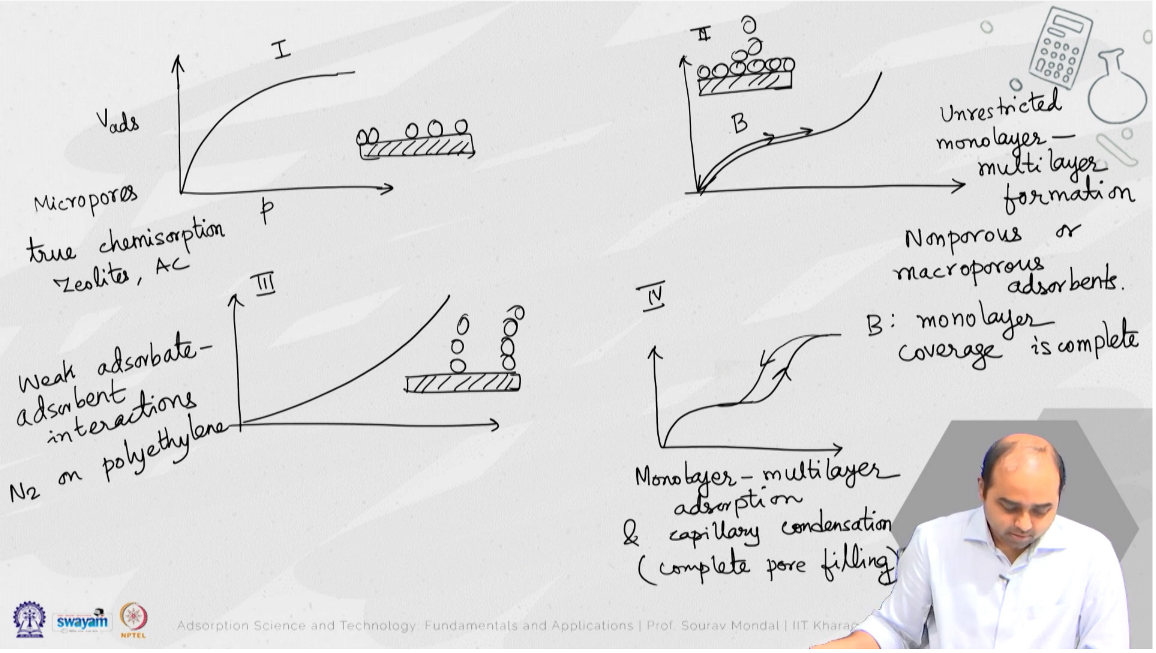


So, this was the classical type. So, here we are plotting the adsorption of the species or the adsorbate with respect to the partial pressure or the pressure. So, in this type mostly we see or mostly the micro pores are observed, as the adsorption is limited only to few layers of the adsorption. So, in this case you observe mostly a monolayer type adsorption and this is the scenario of true chemisorption. Normally zeolites activated carbon do express this kind of behavior.

The second type generally represents unrestricted monolayer to multilayer formation. So, this is the situation of non porous or macro porous adsorbents up to this part this portion B, this monolayer may be up to this part I can extend this part B suggest that monolayer is complete. So, this is the situation when one start to get you know multiple layers after the monolayers is formed. In type III here there is no formation of monolayer directly there is formation of multilayers. So, this is the scenario when one would expect this weak adsorbate adsorbent interactions a common observation of adsorption of nitrogen on polyethylene.

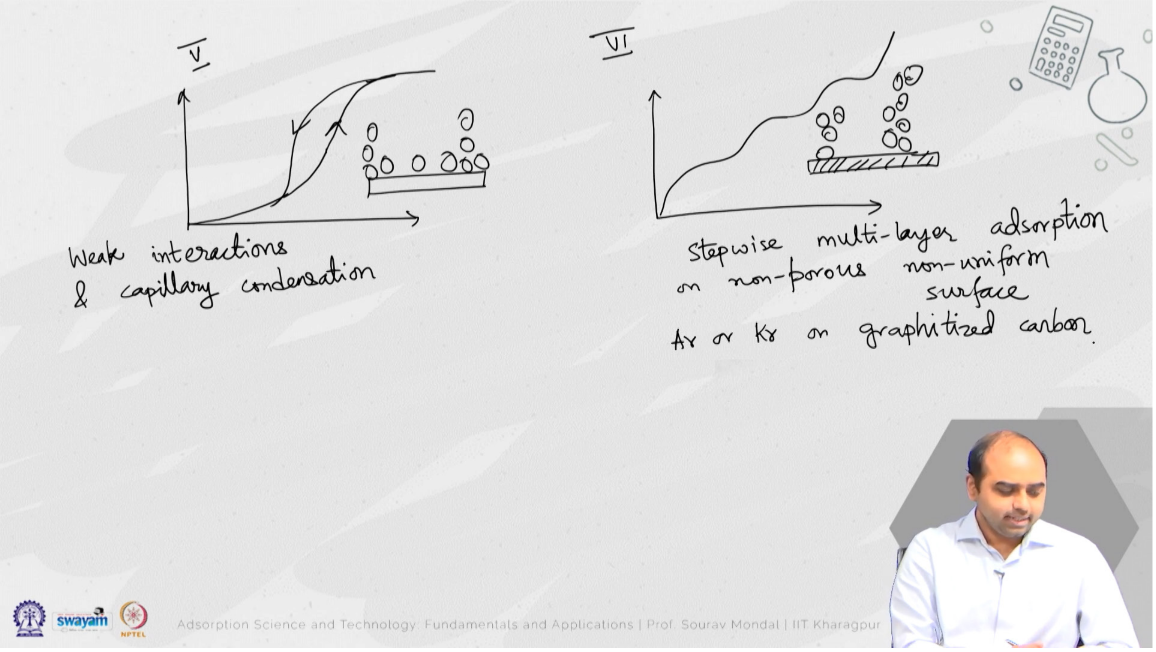
Type IV is something when we see monolayer then multilayer, even multilayers you know do saturate, and this is like the desorption profile this is the adsorption profile. So, there is a hysteresis which is also observed many times. So, this is monolayer multilayer this is the classical response monolayer multilayer adsorption and capillary condensation.

So, the presence of the hysteresis is a signature mark of the capillary condensation and in this case you can expect to achieve complete pore filling. Type V is essentially an extended version.



So, without forming the monolayer you start to form the multilayer and then the monolayer forms or the multilayer gets covered. So, initial response is like the heterogeneous multilayer then you know the multilayers start to complete the coverage. So, this is the scenario type V is the scenario when there is weak interactions and capillary condensation. Type VI is something that we have not mentioned before and this is like you know multilayer adsorptions, but without formation of any complete coverage. So, this is like step wise multilayer adsorption on non-porous non-uniform surface particularly when the surface is very rough.

This is the scenario is like you continue to have you know multilayer formations without any monolayer coverage or without coverage of the particles. This is multilayers forming fast and then slowly you are having monolayer coverage. This is the scenario when first you have monolayers then multilayers and then multilayer coverage starts to happen. So, please try to understand the difference between IV and V that in the case of the IV the the first the monolayer coverage is done then the multilayer starts and then the multilayer coverage is done. In the case of the fifth type, there is first formation of the multilayer and then the monolayer coverage takes place.



V

Weak interactions & capillary condensation

VI

Stepwise multi-layer adsorption on non-porous non-uniform surface

Ar or Kr on graphitized carbon.

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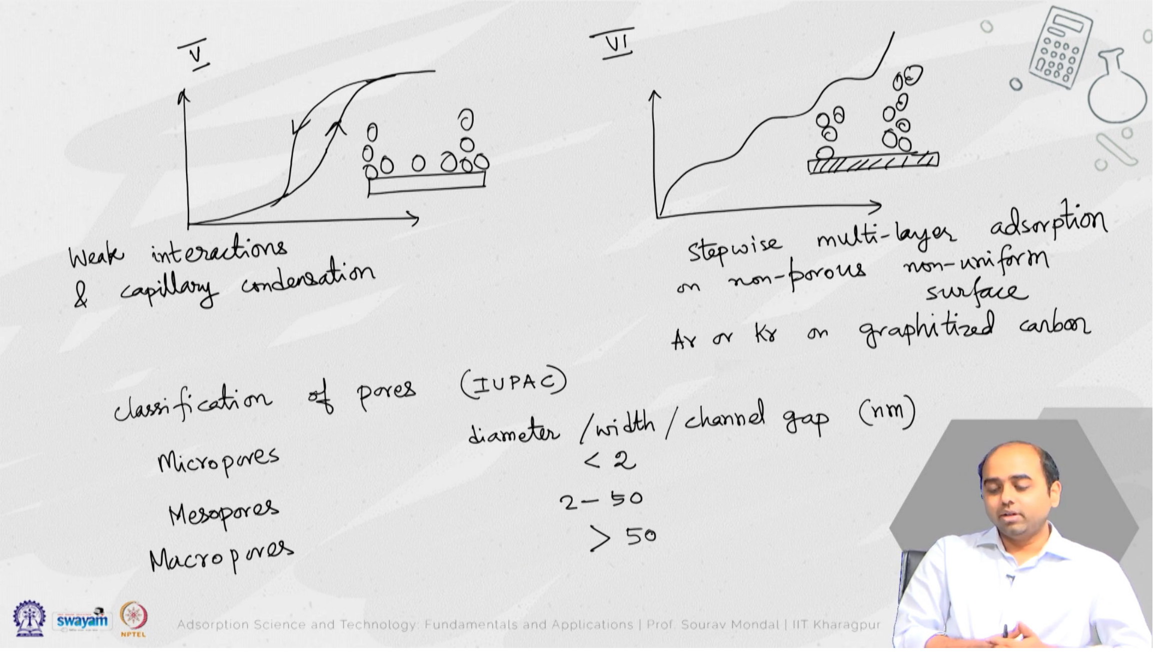
And sixth is there is no monolayer coverage you are continuously you are having multilayer absorption. So, this is the scenario when you have argon or you know other inert gases krypton for example, on graphitized carbon this kind of adsorption profile is normally observed. Now, typically this interaction typically this interaction is generally you know limited or described very nicely by the heat of the adsorption, but before going into the heat of the adsorption I just want to define the classification of mesopore micropore and macropore. So, this classification of pores as per the IUPAC you know guidelines suggest that for this diameter of the pore or the width diameter or the width of the pore it could be also the distance between two walls in a slit channel or a cylindrical wall or like the gap, sorry channel gap I can write or the slit gap depending on the geometry of the pores in nanometer. So, this is should be less than 2.

In the case of mesopores which is normally the case for most you know adsorbents or catalyst this is in the range of 2 to 50 and macropores is something which is classified if the pore size is greater than 50 nanometers. Very micropores like they are defined as ultra micropores or super micropores, they are actually sub nanometer level for example, in the range of 0.7 or 8 to 2 nanometers is generally described as super micropores or ultra micropores. I would like to emphasize that this capillary condensation is an important phenomena. The capillary condensation that we have already described before this capillary condensation is very strong within micropores and it is generally not so popular in macropores.



Weak interactions
& capillary condensation

Stepwise multi-layer adsorption
on non-porous non-uniform
surface
Ar or Kr on graphitized carbon

classification of pores (IUPAC)

	diameter / width / channel gap (nm)
Micropores	< 2
Mesopores	2 – 50
Macropores	> 50

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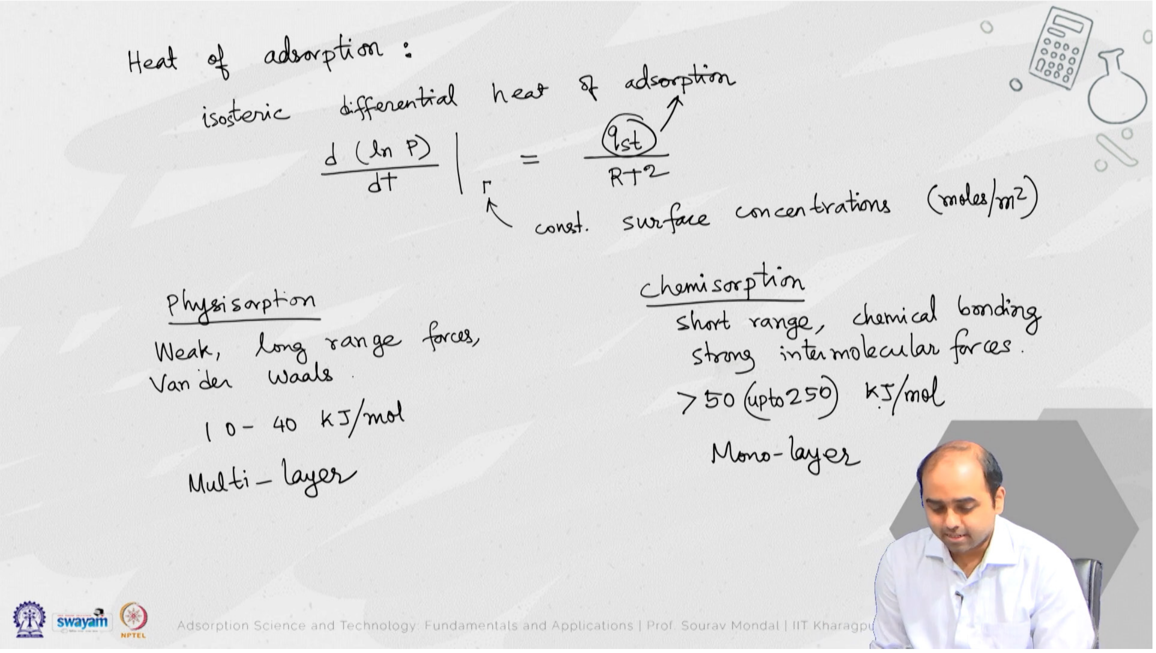
So, the presence of capillary condensation or hysteresis is also an example or also a signature mark on the presence of the micropores or to some extent low level mesopores. Now, coming to the heat of the adsorption because the heat of the adsorption is naturally generally used or generally considered to identify the nature of the interaction in this you know multi layers or single layer meso micro adsorbate adsorbate interactions and all. The heat of adsorption is very important. So, generally the you know isosteric isosteric differential differential heat of adsorption is represented from the thermodynamics of the adsorption from the free energy equation and coupling it to the Clausius-Clapeyron equation. It stands something like this, at constant.

So, this represents the constant surface concentration something like moles per meter square. Now, the constant surface concentration this differential of del del t of ln p and this is the isosteric heat of adsorption. So, typically depending on the value of the heat of adsorption the nature of the you know this adsorption profiles is generally distinguished. So, typically the if the value of the this heat of adsorption is very large we generally consider that there is you know chemisorption which is happening and if this value is low then there is a chance of this physisorption. Now coming to this aspect of chemisorption and physisorption let us try to you know distinguish or try to list down the different aspects of chemisorption and physisorption.

So, as you know by the name that in physisorption there is no formation of chemical bonds whereas, in chemisorption there is a formation a strong interaction between the molecules. So, the type of bonding that we have in physisorption is weak generally long range forces are dominant or a plays a role van der Waals type interaction is expected. Whereas in chemisorptions it is mostly short range interaction, chemical bonding and the forces are very strong. Typically the enthalpy change in this this is option or the heat of adsorption, I would say is in the range of 20 to 40 kilo joule per mole or better to say from 10 to 40 10 to 40 kilo joule per mole whereas, chemisorption is definitely greater than 50 and it can go all the way up to 250 kilo joule per mole. So, this clearly suggest that the energy involved in the chemisorption process is much much higher than the physisorption suggesting the you know strong interaction between them.



Heat of adsorption :

isosteric differential heat of adsorption

$$\left.\frac{d(\ln P)}{dt}\right|_{\Gamma} = \frac{q_{st}}{RT^2}$$

const. surface concentrations (moles/m²)

Physisorption

Weak, long range forces,
Van der Waals.

10 - 40 KJ/mol

Multi-layer

Chemisorption

short range, chemical bonding
strong intermolecular forces.

> 50 (upto 250) KJ/mol

Mono-layer

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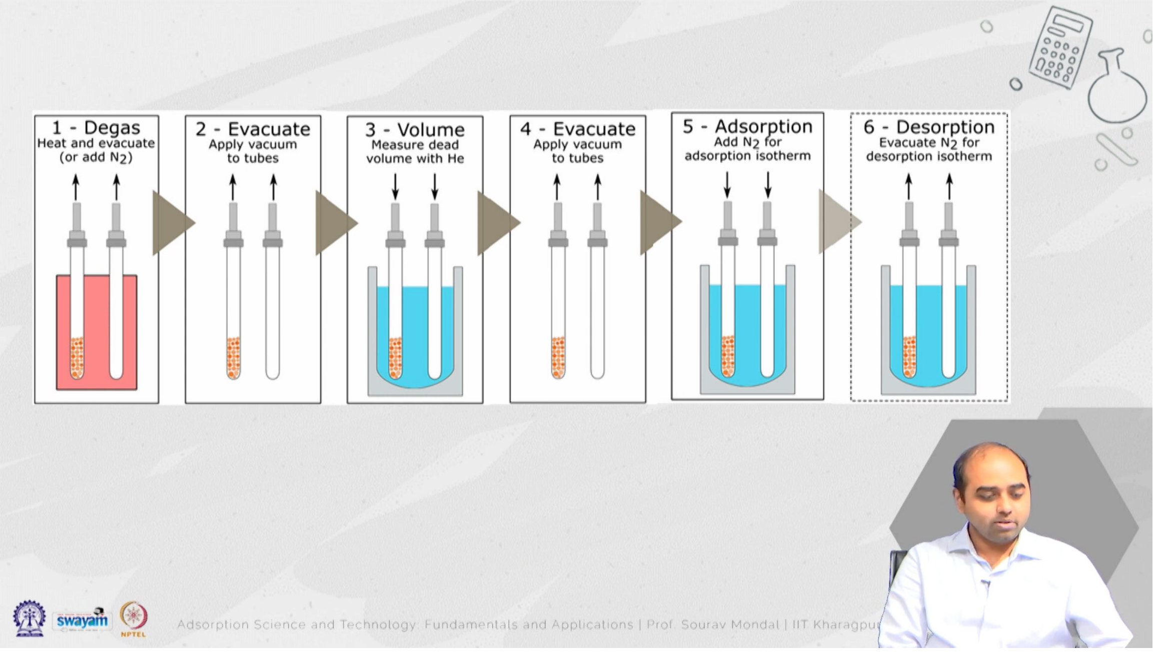
In the case of physisorption it is generally multilayers which is possible, but chemisorption it is mostly monolayer in nature. This adsorption profile also suggest that there is a possibility of formation or or there is a possibility of you know this capillary condensation phenomena more in the case of the physisorption than in chemisorption. Finally, surface specificity or the role of the surface whether it is surface energy, surface roughness plays a big role in chemisorption than in physisorption. So, these are generally generally the different you know the distinction points for chemisorption and physisorption. So, now it is time to look into the you know this equipment details about this BET analysis.

So, in this BET analysis what is generally done is first the sample and that is placed into this you know this glass or the quartz cuvette is heated and degassed or dried up to remove all residual air molecules if at all it is present. So, the idea is that this consists of a of a system where essentially you have a cell which holds the sample and you try to use you know this nitrogen gas at very low temperature to adsorb onto the you know this this adsorbent. And then in the process you try to evaluate the amount that is absorbed with respect to the pressure of your nitrogen and develop the equilibrium isotherm profiles and from there you work out the multilayer isotherm BET model to discuss or to describe the different features patterns and we will talk about and and also the surface area pore size and all those things. So, how it works out? The first step is to do a degassing, you heat and evacuate all the you know the residual you know gas that is present in your sample. The next step is to apply vacuum to these tubes or to these system, so that further there is no possibility of any residual gas.

In the next step, you measure the volume or the dead volume of your sample with the help of the helium gas. Then once again you remove the helium gas from the system. Next step you start this is actually the main step you start the adsorption or you add nitrogen to your system. In that case the nitrogen starts to adsorb and you work out or you measure the amount that is adsorbed right. And in the next case you find out the desorption profile or you decrease the pressure to work to estimate the amount that is released from the system.



1 - Degas
Heat and evacuate (or add N_2)

2 - Evacuate
Apply vacuum to tubes

3 - Volume
Measure dead volume with He

4 - Evacuate
Apply vacuum to tubes

5 - Adsorption
Add N_2 for adsorption isotherm

6 - Desorption
Evacuate N_2 for desorption isotherm

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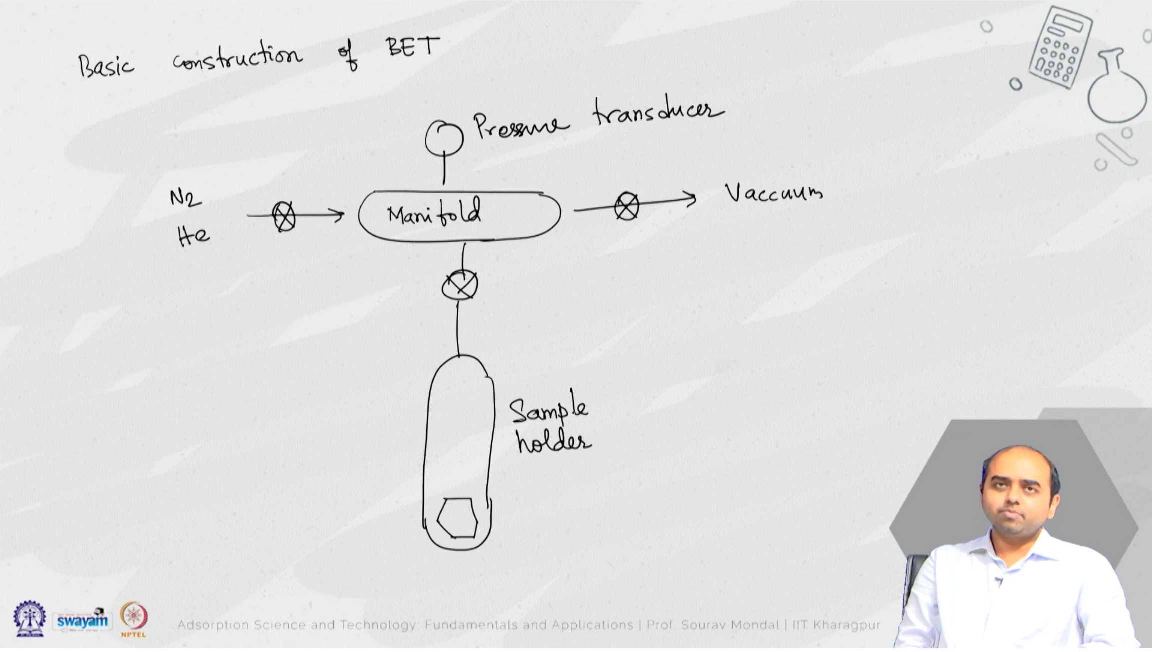
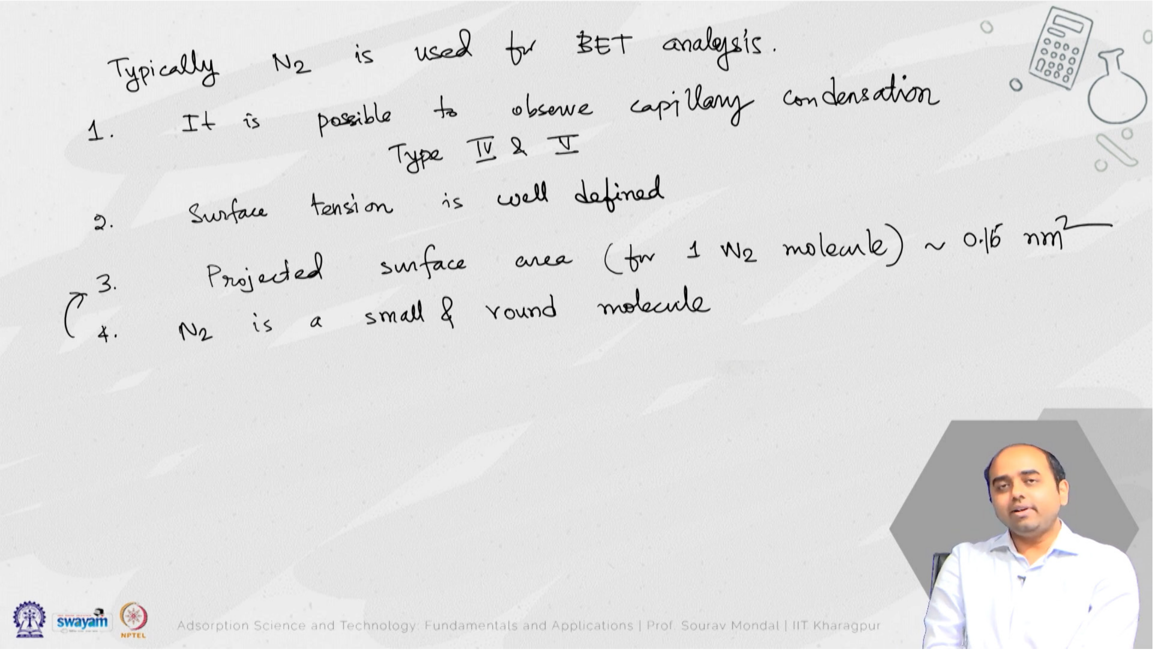
So, from here the isotherm profile is constructed in this case. Now, just to give you a quick overview about how does the system looks like in reality, I will just quickly draw a schematic. So, generally it involves you know few valves then you have this setup of the valves, sample holder and then there are some controllers to control the pressure as well as the temperature in the system. So, the basic construction of this equipment. So this is like a manifold of different gas lines.

Whether you have this nitrogen, then you have helium, vacuum systems are there, pressure transducer. You have the valves in between and then it goes to the sample holder. The sample holder is generally preserved in a constant temperature bath. So, the typical things that are involved is the thermostat, then you have a dewar to hold the you know sample to hold the you know low temperature cell. Then there is a you know the level sensor temperature sensors as well as a lot of these pressure sensors to accurately measure the you know pressure profiles during this adsorption phenomenon now typically nitrogen nitrogen is used for the analysis so typically nitrogen or essentially liquid nitrogen is used for BET analysis, the primary reason is that it is possible to observe capillary condensation.



So, physisorption using liquid nitrogen. So, it is mostly type IV and type V, where you see capillary condensation. The surface tension of nitrogen is very well defined and this property is well defined since this is very important as the surface tension of the sample with respect to air if since that value is known and air contains mostly nitrogen the surface tension of this particular solute or this gas, is very important and very necessary to work out this you know pore size and pore size distribution using Kelvin equation which we will see later on in the upcoming lectures. So, the knowledge of the surface tension is very important for nitrogen this can be easily used the value of the air. Another important point why nitrogen is used is that the projected surface area.



Typically N_2 is used for BET analysis.

1. It is possible to observe capillary condensation
   Type IV & V
2. Surface tension is well defined
3. Projected surface area (for 1 N_2 molecule) ~ $0.16\ nm^2$
4. N_2 is a small & round molecule

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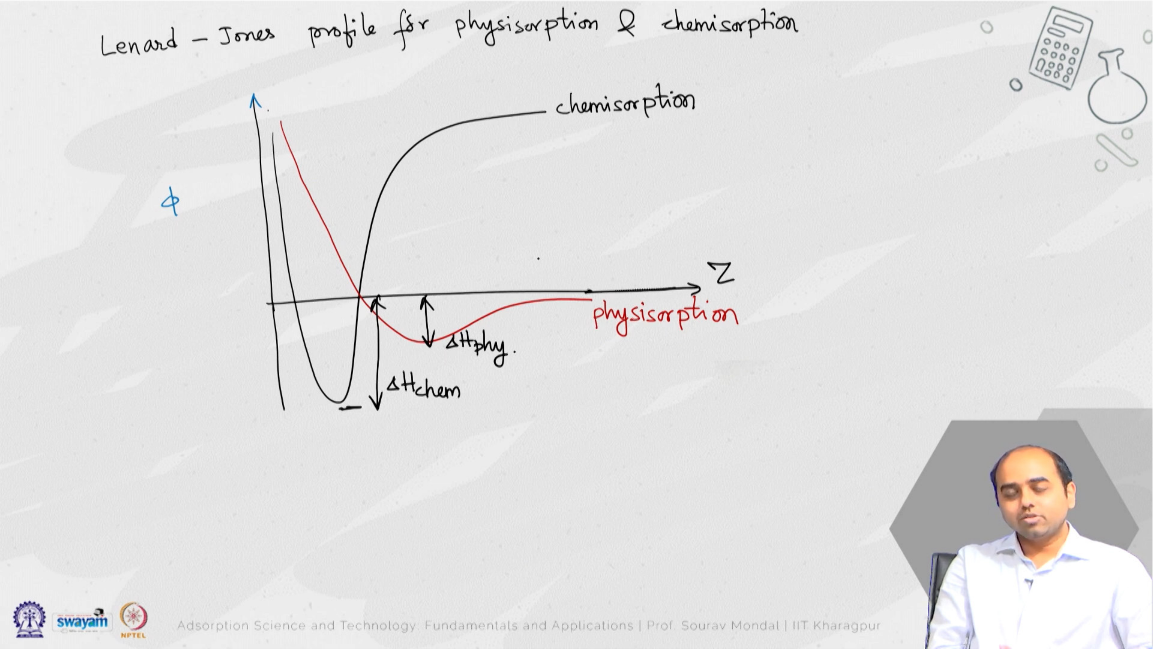
So, this you will see again in the surface area calculation that why it is important for one nitrogen molecule is again very well defined and it is typically around 0.16 nanometer square. So, this is important to work out that how much of the pore surface area is available by calculating exactly the number of nitrogen molecules you know adsorbed per meter square or per centimeter square of the sample or the exposed surface area and from the projected area of each nitrogen molecule you can work out the pore surface area and finally nitrogen which is again in collaboration with point you know this three that nitrogen is a small and round molecule. So, its surface area coverage is very well defined and the projected surface area from where we are calculating the surface area for the sample or the pore surface area is generally less erroneous and this is very since the volume of each nitrogen molecule is very small is also suitable for micro porous or micro porosity measurements. I will quickly explain the difference of the you know this energy diagram in the case of the physisorption and the chemisorption.

So, in the case of the physisorption one normally you know observes the I mean this is the Leonard Jones or the van der Waals description for physisorption, and chemisorption scenarios. So, in the case of the chemisorption this is the profile whereas, in the case of the physisorption since the interaction is very weak. So, this is the case of physisorption. So this is the potential energy function and this is the separation distance from the from the adsorbate molecules to the adsorbent phase. So typically it can be understood that the delta H or the energy drop in the case of chemisorption is much higher compared to the drop in the case of physisorption.



Lenard – Jones profile for physisorption & chemisorption

Of course, this part where it is above the baseline represents the activation energy for that system. But typically, this is the Leonard Jones or the van der Waals interaction profile for this system or in the case of physisorption and chemisorption scenarios. Typically, the BET isotherm which of course, we will talk about in the next lecture has a lot of assumptions and the important assumption includes that there is no adsorbate to adsorbate interactions. And, the multilayer formation which happens assume that there is monolayer or monolayer to each of these multilayer which does exist. So, all the you know in different multilayers have the same level of the heat of adsorption. So, with this I will close this lecture in the next class we will talk about the sorption profiles particularly focusing on the BET isotherm. Thank you hope you found this lecture useful.