Course: Adsorption Science and Technology: Fundamentals and Applications

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Week 03

Lecture 13 | Surface Area Calculations

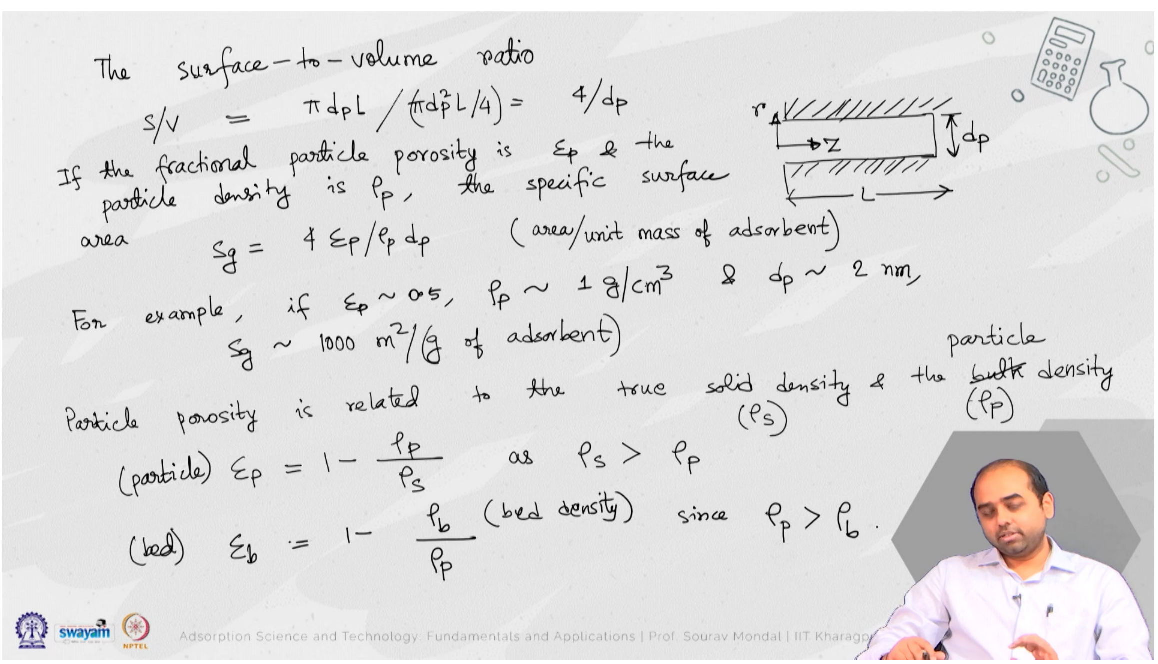
Hello everyone, welcome to this class on the adsorption. Today as you know we are going to talk about this surface area calculations. The surface area or finding out the exposed pore surface area is a very important characteristic or parameter in this characterization of the adsorption or the adsorbents. Typically this is related from the isotherm studies or the particularly the BET isotherm. So, in this class we will try to see that how the BET isotherm information can be leveraged to calculate or to estimate the pore size surface area as well as the pore size calculations. So, pore size volume or this pore size distribution is something that we will talk about in the next class, but today in this class we will talk about this pore surface area or the exposed surface area calculations.

Now, importantly in calculating the surface area it is assumed or it is considered that the pores are cylindrical in nature and adsorption happens mostly or primarily on the exposed you know the cylindrical surface area of these pores. And this is generally is quite realistic to consider. So, since the pore surface area is much much higher compared to the surface area of the catalyst or the adsorbent particles on the on the just on the surface of it. So, the pore surface area is where predominantly the adsorption occurs and that is much higher compared to the surface area of the spherical region of this catalyst.

Typically, as I have said the this pores are considered to be cylindrical in nature. So, the surface to volume ratio for these pores the surface to volume ratio for these pores is represented as this. So, this is the cylindrical surface area. We do not consider the you know top and the bottom of the cylinder because their adsorption I mean one is the so this is typically how a pore looks like and this is a cylindrical in nature. So, this is the diameter and this is the pore length.

So, we consider the pore surface area which I have shaded mostly and we are trying to calculate the pore surface area to volume and this is proportional or inversely proportional to the diameter of these pores. Now, if the fractional, if the fractional particle porosity is epsilon p and the particle density is rho p then the specific surface area. Can be I mean we can account for the porosity of the particles as well as considering its density in the specific particle surface area can be estimated from this relation. So, for example, if if epsilon p is fifty percent porous, this rho p is one gram per c c, and this diameters of this pores is 2 nanometer then if you use the above relation this will tell you that this specific surface area. So, please note that the specific surface area is defined in terms of you know area per unit mass of adsorbent.

This is how we generally define this specific surface area and that is an important characteristic here. So, this turns out to be 1000 meter square plus gram of the sorry per gram of the adsorbent. So, this is mostly what you will see that is being reported that what is the pore surface area per gram or per kg or per you know milligrams or unit mass of the adsorbent and this is a very important characteristics because higher is the you know pore surface area or the specific surface area, the better is the adsorption characteristics. Now, typically this you know porosity is defined this particle porosity is related to the through solid density and the bulk density of the bed. So the true solid density can be represented as rho s and bulk density can be represented or the particle density I would say, can be represented as rho p.

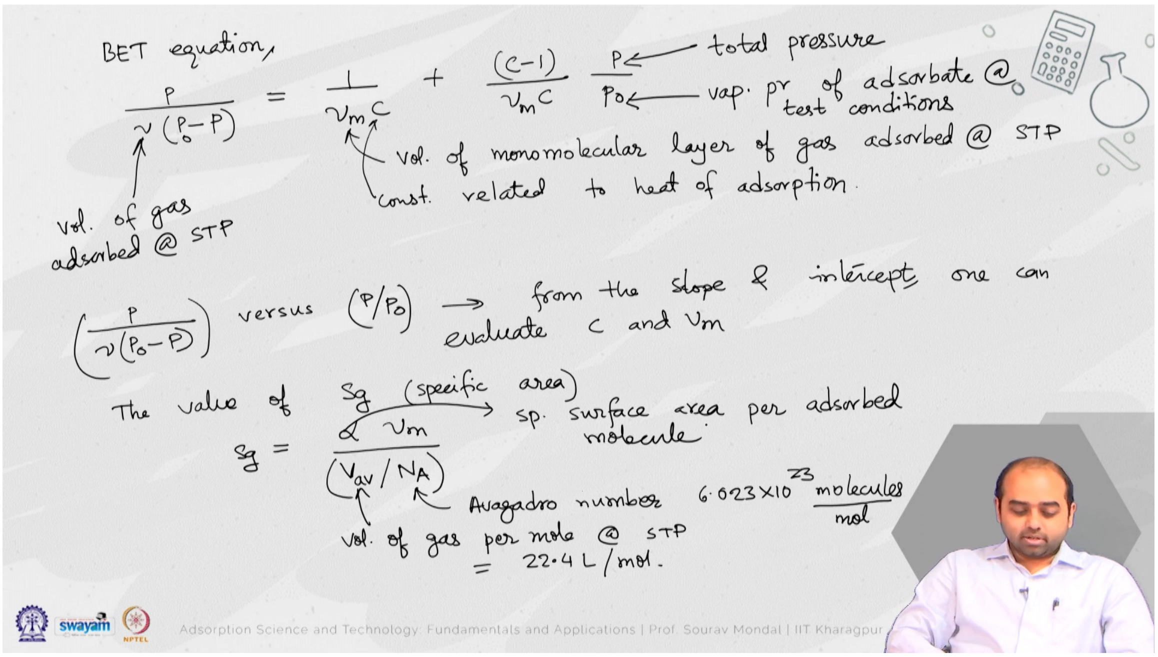


So, this epsilon p is related as 1 minus of this as the solid density is always greater than the particle density because the particle density is actually what you measure for the porous particles. Similarly, one can also define the bed porosity as something like 1 minus of this is the bulk or the bed density with respect to the particle density since you know the bed density is less than the particle density. Now this is all about how do we relate the specific surface area of the you know particles and from a purely from a microstructural geometric considerations, but this is often related to the BET isotherm how that is something we are going to talk next. So, the classical BET equation which we have already derived and comprehensively discussed in the previous class stands like this. where this Vm is the as a constant C is also constant Vm represents the you know monolayer volume.

So, here Vm represents the volume of monomolecular layer of gas. Of course, adsorbed at STP and C is of course, a constant this C is a constant which is related to the heat of adsorption and V is the volume of gas just a quick recap. of the different terms in the BET equation. P stands for the total pressure and here P0 stands for the vapor pressure of adsorbate at test conditions. So, this is the BET equation where essentially you try to make a plot of this P with respect to the V or the volume of the gas that is adsorbed from there the constants can be evaluated.

Now, if you plot this you know this P by I have intentionally written down in this linear form, so that it is much easier. If one plots these two then the slope and the from the slope and the slope and intercept one can evaluate C C and of course, this will be a straight line. So, you can straight away do a linear regression and from the slope and intercept this can be evaluated. Now, here the value of the Sg, Sg which is the specific surface area is related as alpha is a constant I will talk about it. So, this Vav is the Avogadro you know this volume occupied by 1 mole of the gas at STP conditions, NA is of course, the Avogadro number.

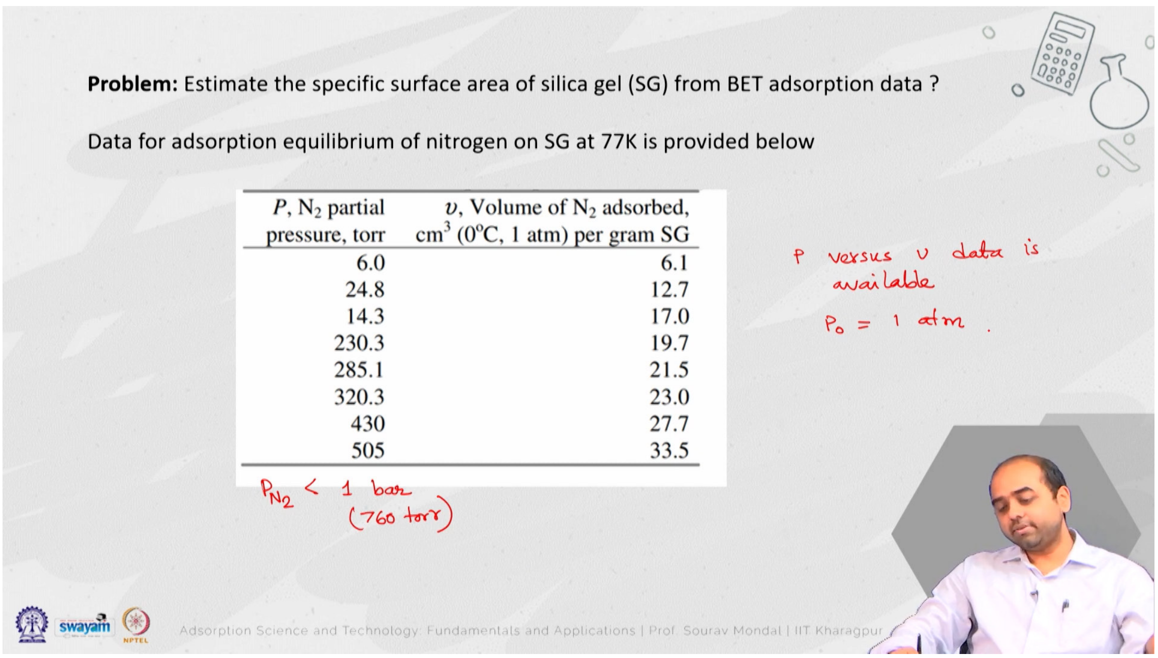
So, which is of course, something that all of you are aware of and this is the volume of gas per mole at STP and this is equal to is also something that all of you are aware of 22.4 liters per mole. Now Vm is the constant or essentially the volume of the monomolecular layer of the gas adsorbed at the STP conditions and here this alpha is essentially the surface area or I would say specific surface area or the projected surface area for adsorbed molecule. So this is a constant which is dependent on the gas and specifically as you can understand that this relates to the specific surface area per adsorbed molecule and for certain inert gases this is very well defined and generally is something that we have already talked about it before. So typically this alpha this alpha if for spherical molecules this can be evaluated analytically that for spherical molecules this projected surface area is of course if you are assuming two dimensional packing this alpha can be related as like this this is a standard expression which is available.



So where of course M is the molecular weight of the adsorbate this rho L is the density of the adsorbate which is taken as illiquid at the test conditions, and NA is something that we already know that it is the Avogadro number. So, this is how the value of alpha can be represented. So, typically this formula that I have written down here is based on the fact that one assumes how much does a single molecular layer can actually make a surface coverage. So, these factors of the you know molar volume Avogadro number is all to convert essentially the monomolecular layer volume into the number of molecules that it corresponds to and alpha represents the amount of the or the specific surface area of the adsorbed molecule and multiplying this together gives us the specific surface area per you know this gram or per this mass of the this adsorbent. Now, let us try to see one small example problem.

So, it will be clear to all of us. So, we focus on this problem. So, here is a data on the adsorption of this nitrogen on this silica gel. So, different partial pressures of nitrogen is actually varied and you can see it is moving from all the way from very small vacuum range 6 tot to considerably large values. Of course, all of this is very So, this P of nitrogen is of course, less than the 1 bar which is essentially 760 torr up to this ambient pressure continuously this is increased at 0 degree centigrade.

So, the STP condition is maintained and then the amount of the volume of the nitrogen gas that is absorbed is actually reported. So, here we have the P versus P versus V data is available. P0 here is 1 atmosphere, and from here the whole idea is to work out or to do a linear regression of this BET isotherm and work out what would be the constant. So, essentially if you use the BET equation. So, for the sake of completeness I am writing this once again.



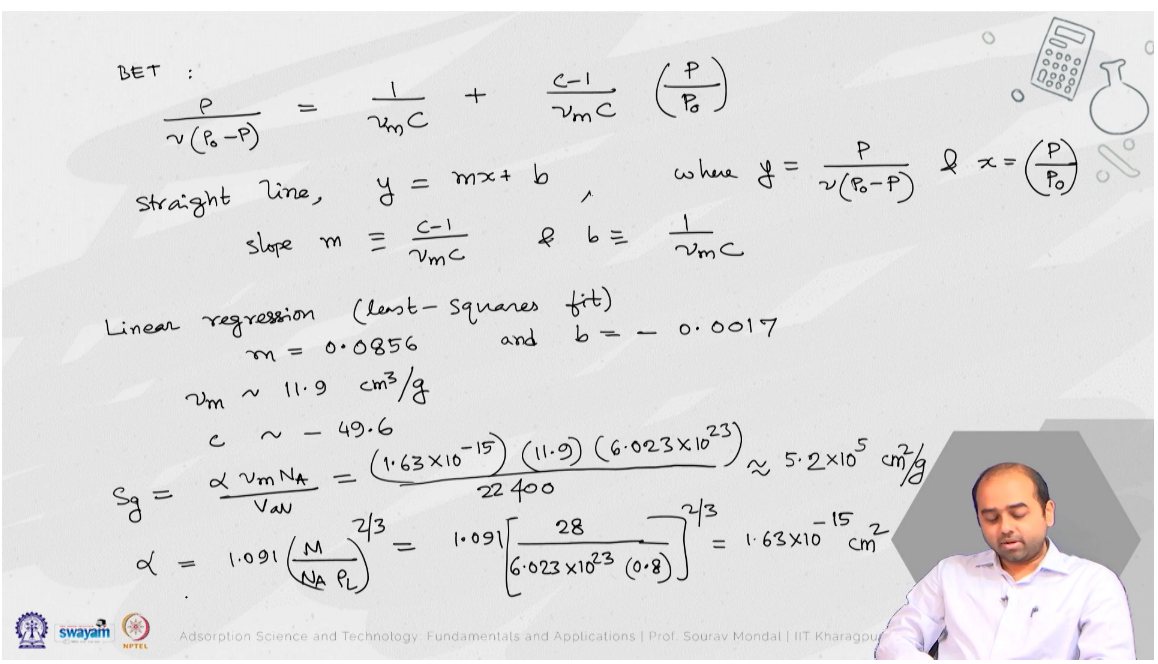
P, N_2 partial pressure, torr	v, Volume of N_2 adsorbed, cm^3 (0^oC, 1 atm) per gram SG
6.0	6.1
24.8	12.7
14.3	17.0
230.3	19.7
285.1	21.5
320.3	23.0
430	27.7
505	33.5

So, the BET equation tells us that this is the formula for the expression. So, we are supposed to work out the constants v m and c from the regression. So, here P is essentially the partial pressure of the nitrogen that is already reported in this table. P naught is the vapor pressure of nitrogen at minus 196 you know centigrade that is 760 torr and V is the volume of gas that is adsorbed at STP which is something that is tabulated in that information. And, Vm is the volume of the monomolecular layer of the gas adsorbed at STP condition.

So, that is something we are trying to find it out from the regression and c is the constant related to the enthalpy. So, if you just make a straight line and from there you know in the form of y is equal to m x plus c m x and there we can consider where y is and x is this.

So, if you do that then your slope m would turn out to be c 1 minus 1/Vm c and the intercept would turn out to be 1 by Vm c. So, if you do a least square or a linear regression least square fit you can get the slope to be 0.0856 and the intercept to be minus 0.0017. And from using this above formula of the slope and the intercept one can work out the value of Vm will come out to 11.9 centimeter cube per meter square. And the value of the constant C will come out to be minus 49.6. Now once these two constants are known now we can find out the specific surface area as using this formula.

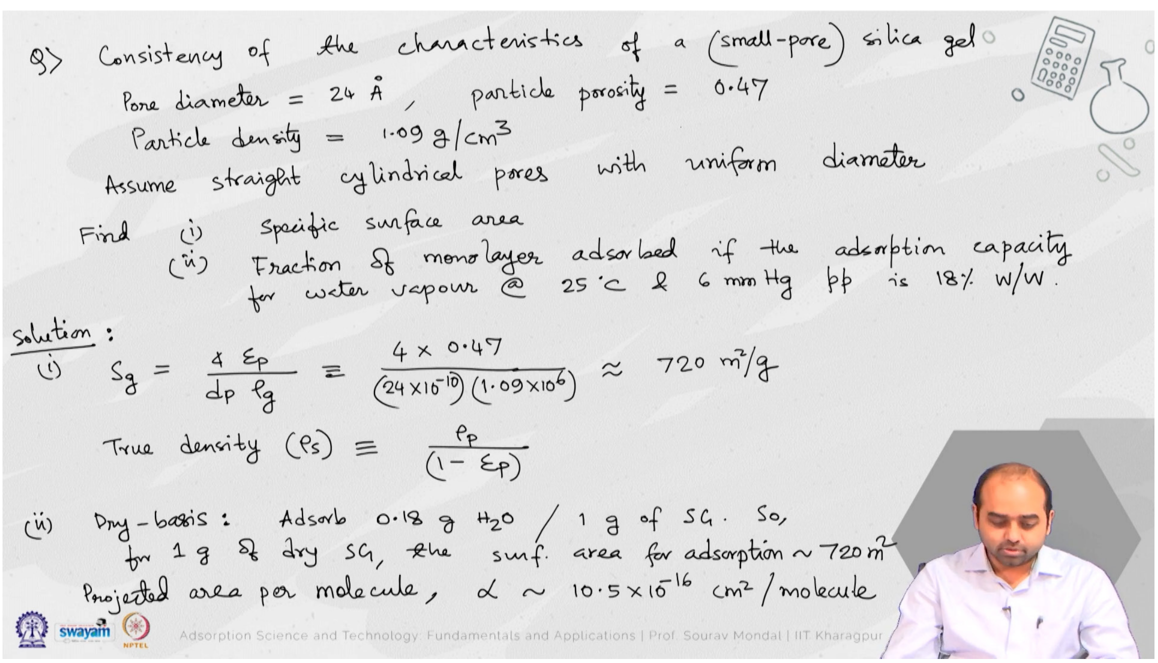
Now please note alpha has to be evaluated first. So alpha is 1.091. So, in this case the molecular weight of nitrogen is 28, Avogadro number stands at 6.023 into 10 to the power 23 and the density of the nitrogen at the liquefied conditions is 0.8. So, if this calculation is done and if you put the numbers this will turn out to be 1.63 10 to the power minus Now, if this value of the alpha is inserted here, so one can work out the value of Sg. So, Vm is already found from the regression. NA is 6.023 into into the power 23. We convert this volume from liter to centimeter cube and this will give us a value of 52 sorry 5.2 into 10 to the power 5 centimeter square per gram. And this is nothing, but around 52 meter square per gram of the you know this adsorbent surface area that is available or that this particular silica gel adsorbent use. Now, let us also try to see another problem, where already these some of these information is is provided in a different context and we have to verify whether that is you know ok or incorrect. So, here the problem is about you know checking or relating the consistency of the characteristics of a small pore again silica gel adsorbent.



So, the pore diameter this porosity etcetera are provided now it is asked to calculate what would be the specific surface area. So, the pore diameter is provided 24 angstrom particle porosity is given as 0.47 of course particle density is given as 1.09 gram per cc. Now these are assumed to be straight cylindrical pores with uniform diameter.

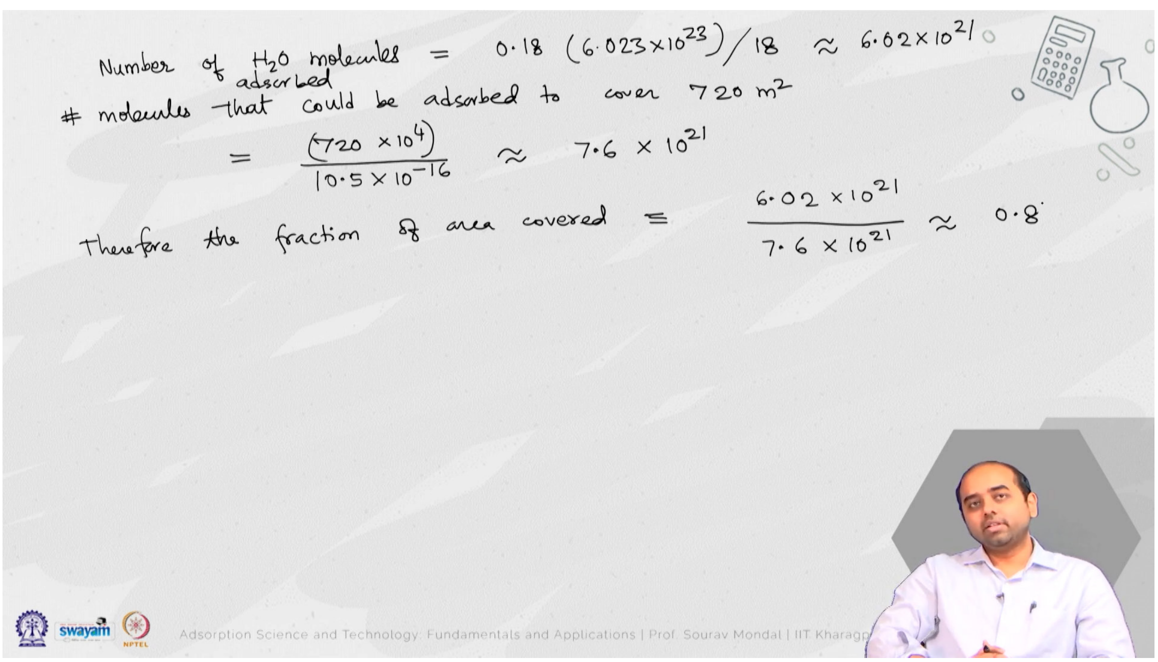
So it is asked to find out, first is the value of specific surface area. And the next thing it is asked that what is the fraction of monolayer adsorbed ? if the adsorption capacity for water vapor at 25 degree centigrade and 6 mm pressure Hg, I mean partial pressure is 18 percent weight by weight. Now for the first problem first part of this question to find out the specific surface area we can directly use the formula that we have already discussed. So, in this case it is just inserting the substituting the numbers here.

Particle porosity is 0.47, diameter is you know 24 angstrom. So, we write 24 into the power minus 10, I am converting everything to meter, meter per meter cube and this value of this particle density is once again converted from gram per centimeter cube to gram per meter cube. So, multiply with 10 to the power 6 and this gives us a value of around 720 meter square per gram. This is the true density of the you know silica gel is what is not mentioned. And if you, but this is something that one can look into this you know true density from some other resource or you can always work out I mean the true density of the silica can be worked out from the particle density sorry particle porosity that is mentioned so something like this is 1 minus epsilon p.



This would be the true density that one can work it out. So, coming to the second part of this problem which tells us that what is the fraction of the monolayer that is adsorbed. Now, here we consider for this problem for the dry basis of course, you can also work out the weight basis in the similar way. So, from the dry basis around grams water is absorbed per you know 1 gram of silica gel. So, for 1 gram of dry silica gel the surface area of adsorption is 720 meter square.

Now projected area of the molecule for this water vapor if you work out if you put the numbers of the water you will see that the projected area per molecule which is nothing but this alpha and for the water molecule if you use the formula you will see that alpha turns out to be this value. So, the number of water molecules that is absorbed can be worked out from this multiplied with the Avogadro number divided by the molecular weight and this turns out is only 18 percent is absorbed. So, number of molecules needed or molecules that could be adsorbed molecules that could be adsorbed to cover 720 meter square of area is 720 conversion of meter square to centimeter square divided by the this value now this turns out to be this. So, therefore, the fraction of area covered can be given by this value that number of water molecules that is absorbed divided by the molecules that could be absorbed to cover this 720 meter square, meter square of area is around 80 percent. So, that is the fraction of the area coverage for this monolayer adsorption.



So, I hope all of you have you know followed this lecture on the surface area calculations. See you everyone in the next class on the pore size analysis. Thank you.