Physico-Chemical Processes for Wastewater Treatment
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Lecture 35
Adsorption V

Good day everyone and welcome to these lectures on adsorption units operations which are used in the physico-chemical processes for water or wastewater treatment. So, in the previous lecture with respect to adsorption, we studied adsorption kinetics, adsorption isotherm. And in the adsorption kinetics we found that there are different types of kinetic models which can be used to represent the kinetic data.

Similarly, in the adsorption isotherm we studied, there are different types of isotherm equations like Freundlich, Langmuir, Redlich-Peterson, Temkin, etcetera, which can be used to represent the equilibrium data under those conditions. So, Freundlich and Langmuir isotherms are one of the basic isotherm equations which are used and there are like two parameter model equation that means, only two parameters are unknown in those equations.

Now, continuing further, one of the equations which is commonly used is called BET. So, before going to BET we will try to understand what is monolayer and multilayer adsorption. And after that we will try to discuss how the BET theory has been developed and how the BET theory has been applied for determining the important adsorption characteristics using the isotherm equation.

So, this we are going to learn today. So, surface area pore, surface area, pore size which are determined for any adsorbent they are used determined by understanding the liquid nitrogen adsorption studies or any other inert gases studies adsorption studies on various types of adsorbent. Before going towards that, let us understand the monolayer and multilayer adsorption.

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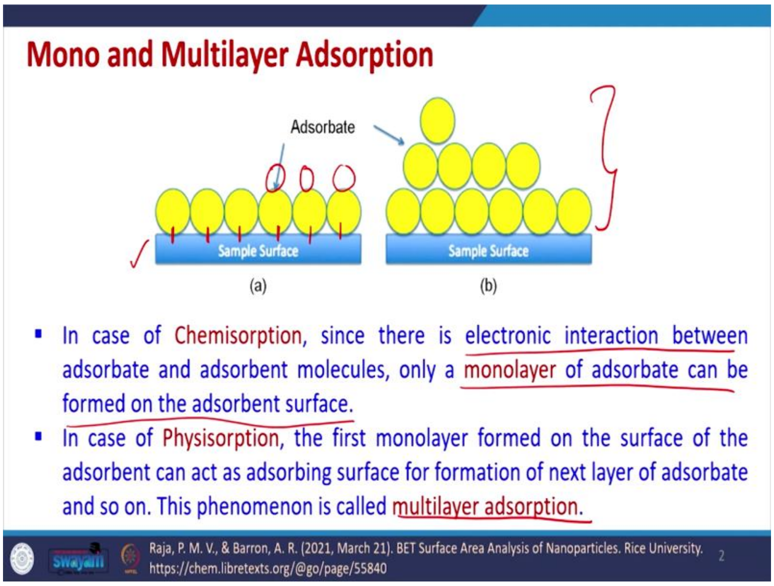

Mono and Multilayer Adsorption

- In case of Chemisorption, since there is electronic interaction between adsorbate and adsorbent molecules, only a monolayer of adsorbate can be formed on the adsorbent surface.
- In case of Physisorption, the first monolayer formed on the surface of the adsorbent can act as adsorbing surface for formation of next layer of adsorbate and so on. This phenomenon is called multilayer adsorption.

Raja, P. M. V., & Barron, A. R. (2021, March 21). BET Surface Area Analysis of Nanoparticles. Rice University. https://chem.libretexts.org/@go/page/55840

So, in the chemisorption in which there is electronic interaction between the adsorbate and adsorbent molecules, only a monolayer of adsorbate can be formed on the adsorbent surface. So, this is there because there is a bond which is occurring. Now, and that bonding is not possible for the second layer, if any second layer will happen that will not be bonded by any electronic interaction, it will be only physical in nature and that will be by van der Waal force of attraction. So, this is for chemisorption only single layer is possible.

Now, for physisorption where van der Waal forces of attraction are important only the first monolayer formed on the surface of the adsorbent can act as an adsorbent surface for next layers. So, in this way, we can have a multilayer adsorption which is possible because only van der Waal force of attraction is operating. So, in chemisorption only monolayer adsorption is possible, in physisorption multilayer adsorption is possible if any multilayer adsorption is occurring.

So, there are only two possibilities one possibility is that all the layers are multiple only physisorption is occurring. In the second case, the first layer may be chemisorption and a subsequent layer if formation occurs will be physisorption but these can be determined only from experimental data. And for analyzing these multilayer adsorption BET is one of the common isotherm which is used for determining this.

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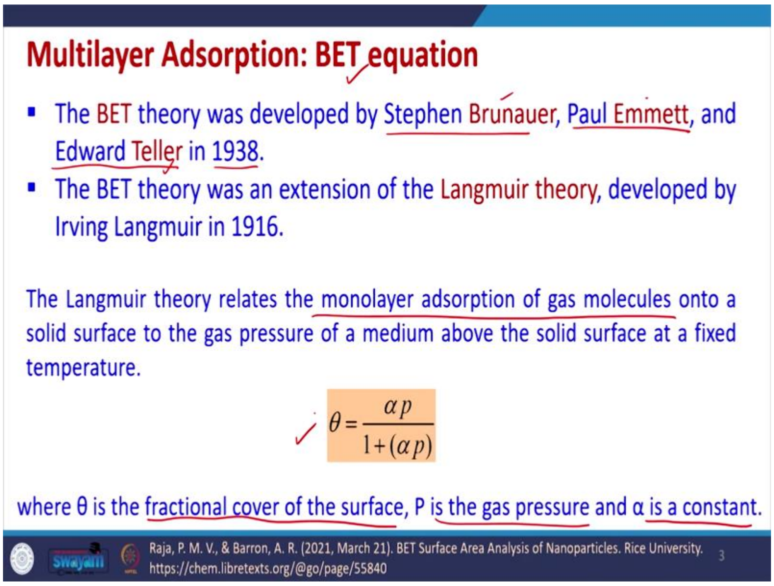

Multilayer Adsorption: BET equation

- The BET theory was developed by Stephen Brunauer, Paul Emmett, and Edward Teller in 1938.
- The BET theory was an extension of the Langmuir theory, developed by Irving Langmuir in 1916.

The Langmuir theory relates the monolayer adsorption of gas molecules onto a solid surface to the gas pressure of a medium above the solid surface at a fixed temperature.

$$\theta = \frac{\alpha p}{1+(\alpha p)}$$

where θ is the fractional cover of the surface, P is the gas pressure and α is a constant.

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where θ is the fractional cover of the surface, P is the gas pressure and α is a constant.

So, what is BET? So, for multilayer equation we have BET equation. So, BET equation BET theory was given by Stephen Brunauer, Paul Emmett and Edward Teller in 1938. So, that is why Brunauer Emmett Teller theory. So, this is BET theory or BET equation. It was further extended by, it was, extension of Langmuir theory, which was developed in 1916.

So, as per Langmuir theory, the monolayer adsorption of gas molecules onto a solid surface to the gas pressure of a medium about the solid surface at a fixed temperature is given by this equation, where theta is the fractional cover, P is the gas pressure and alpha is the constant. We are discussing this equation in particular, because any of that adsorbent properties with respect to the specific surface area, pore size, etcetera can be determined using the nitrogen adsorption. So, nitrogen is a gas. So, that adsorption is generally done under adsorbent surface and for analyzing the data this equation is used. So, that is why this discussion is being done.

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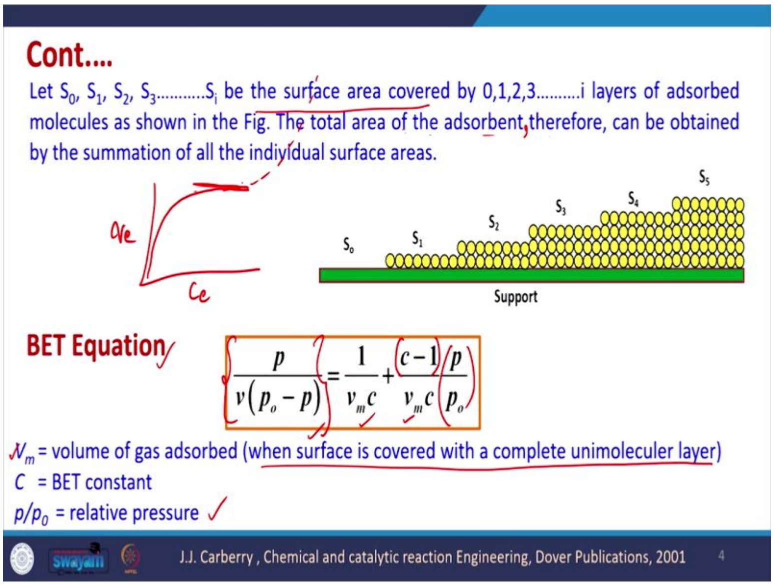

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Let S_0, S_1, S_2, S_3...........S_i be the surface area covered by 0,1,2,3..........i layers of adsorbed molecules as shown in the Fig. The total area of the adsorbent, therefore, can be obtained by the summation of all the individual surface areas.

BET Equation

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{(c-1)}{v_m c}\left(\frac{p}{p_o}\right)$$

V_m = volume of gas adsorbed (when surface is covered with a complete unimoleculer layer)
C = BET constant
p/p_0 = relative pressure

J.J. Carberry , Chemical and catalytic reaction Engineering, Dover Publications, 2001

BET Equation

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c-1)}{v_m c}\frac{p}{p_0}$$

V_m = volume of gas adsorbed (when surface is covered with a complete unimoleculer layer)

C = BET constant

p/p_0 = relative pressure

Now, suppose S0, S1, S2, S3, etcetera are the surface area covered because of different layers of adsorbed molecules as shown in figure. So, the total area of the adsorbent, therefore, can be obtained by summation of the individual surface area. Now, the BET equation is given by this particular expression which is given here. And in this case, the relative P by P0 which is called as relative pressure is important.

So, here the equation has been converted in such a form that it is linearized already. So, what does it mean here that generally all these parameters will be known and these P by P0 will be known, so slope will be this and intercept will be this. So, from this we can determine a number of parameter. Now, in between this equation Vm represent the volume of gas adsorbed when the surface is covered with a complete uni-molecular level.

So, we try to analyze the data with respect to monolayer only, but we extend it for multilayer. So, this is there. And for Langmuir theory, the saturation is if we plot Kv versus Ce data as per Langmuir theory the saturation will occur. So, this is like a monolayer. So, this is first, but if the extension is there, so we will analyze the data only up to this point. So, this is the first monolayer formation has already occurred.

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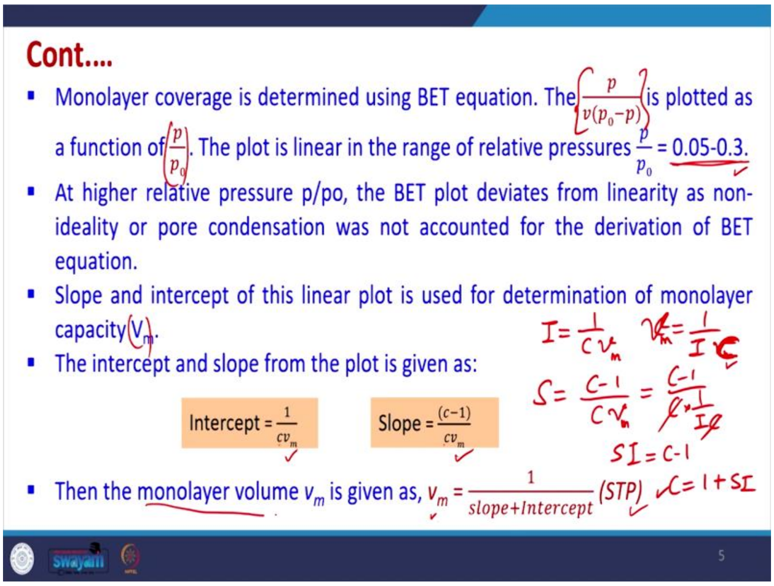

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- Monolayer coverage is determined using BET equation. The $\frac{p}{v(p_0-p)}$ is plotted as a function of $\left(\frac{p}{p_0}\right)$. The plot is linear in the range of relative pressures $\frac{p}{p_0}$ = 0.05-0.3.
- At higher relative pressure p/po, the BET plot deviates from linearity as non-ideality or pore condensation was not accounted for the derivation of BET equation.
- Slope and intercept of this linear plot is used for determination of monolayer capacity(V_m).
- The intercept and slope from the plot is given as:

Intercept = $\frac{1}{cv_m}$ Slope = $\frac{(c-1)}{cv_m}$

- Then the monolayer volume v_m is given as, $v_m = \frac{1}{slope+Intercept}$ (STP)

$I = \frac{1}{CV_m}$ $V_m = \frac{1}{IC}$

$S = \frac{C-1}{CV_m} = \frac{C-1}{\cancel{C}\frac{1}{I\cancel{C}}}$

$SI = C-1$

$C = 1+SI$

Now, monolayer coverage is determined using the BET equation. So, this particular thing is plotted as a function of P by P0 and the plot is linear in the range of, generally it will be in the range of this it may vary also, but we use the only the linear range data. At higher relative pressures, the BET plot may deviate from linearity as non-ideality and pore condensation etcetera may start occurring at those conditions for gas phase adsorption.

So, we do not consider, we only consider data to the range where the linearity is more and generally it will be up to the relative pressure range of 0.3. Now, slope and intercept from this plot can be used for determination of monolayer capacity, which is Vm. And then the intercept and slope can be determined. So, this we can see here the intercept and here the slope. So, and then the, if we actually little bit manipulate, so we can find out the value of Vm from combining these two equations.

So, this is possible. So, from one we can find out the value of C and if we keep it in this, like we can keep that intercept suppose it is I. So, I by C Vm and from here the C value is 1 upon I Vm. And in the second equation slope S is equal to C minus 1 upon C Vm. And we can keep the C values here or we can directly keep the, in place of C we can keep the Vm values from here, so this is, because we need to find out the Vm.

So, if we keep Vm here C minus 1 and C and Vm is equal to 1 upon I C, C C goes off, and S into I is equal to C minus 1. So, C is equal to 1 plus SI. So, this is the expression and if we keep here and solve it, we will get this equation that Vm is equal to 1 upon slope plus intercept at STP values. So, we can find out the Vm values whatever is the monolayer volume which is there.

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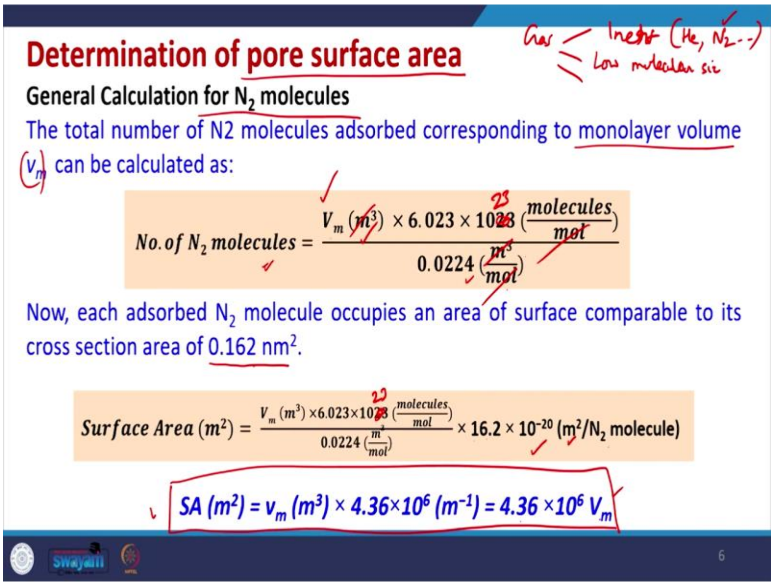

Determination of pore surface area

Gas < Inert (He, N_2 - -)
Low molecular siz

General Calculation for N_2 molecules

The total number of N2 molecules adsorbed corresponding to monolayer volume (v_m) can be calculated as:

$$No. of\ N_2\ molecules = \frac{V_m\ (\cancel{m^3}) \times 6.023 \times 10^{23}\ (\frac{molecules}{\cancel{mol}})}{0.0224\ (\frac{\cancel{m^3}}{\cancel{mol}})}$$

Now, each adsorbed N_2 molecule occupies an area of surface comparable to its cross section area of 0.162 nm^2.

$$Surface\ Area\ (m^2) = \frac{V_m\ (m^3) \times 6.023 \times 10^{23}\ (\frac{molecules}{mol})}{0.0224\ (\frac{m^3}{mol})} \times 16.2 \times 10^{-20}\ (m^2/N_2\ molecule)$$

$$\boxed{SA\ (m^2) = v_m\ (m^3) \times 4.36 \times 10^6\ (m^{-1}) = 4.36 \times 10^6\ V_m}$$

So, this is, this can be, this expression can be used for finding out the pore surface area. Now, first for determining the adsorbent property like pore surface area, we, first thing that why we use any gas and which gas is preferred. So, what we do that, there are few options first thing for determining surface area we should select the gas, we should have some properties one thing is that it should be inert, inert that, so that there is no chemical reaction occurring and we are going, we can, it does not reacts with the absorbent.

So, inert gases can be used. Now, inert gases can be helium, nitrogen and other. Now, among it should be having lower possible molecular size. So, lower molecular size is preferred. So, and if this is there we can determine more accurately the surface area. So, this molecular size should be lower possible, lowest possible. Now, the lowest possible will be helium, but with helium there is a problem that the gas separation from the atmosphere will be difficult. So, this gas is costlier.

Second thing is that we have to generally the apparatuses are determined with respect to liquid nitrogen condition where we can adsorb maximum amount of nitrogen. So, what we do is that we take that temperature to a certain level where nitrogen is in the liquefied form. So, for this nitrogen, so that the maximum nitrogen adsorption may occur.

So, generally nitrogen gas is preferred because it is easily available, it is inert also and it can, it says pore size is good enough for analyzing any gas separation or otherwise. So, this is possible, most of the gases which are there have higher molecular size. So, generally it will be good enough for gas phase separation for liquid phase separation always it will be good enough. So, now the total number for suppose we are performing calculation using N2 molecules.

So, the total number of N2 molecules adsorbed corresponding to monolayer volume Vm can be calculated using this equation. So, number of molecules is equal to Vm, Vm will be in meter cube. Now, the molecules what we do is that we know that any, at any standard temperature pressure conditions, so any 1 mole of gas occupies 22.414 liter of volume so that 22.4 has been converted into meter cube.

So, we have 0.0224 meter cube per mole. So, this meter cube meter cube go off only mole is remaining. Now, each mole we know occupies 6.023 into 10 raised to 23 molecules per mole. So, this mole mole also goes off, so we can determine the number of N2 molecules which have been adsorbed if we know the Vm. So, this Vm can be determined from the BET equation.

And once Vm is known, we can determine the number of N2 molecules which have been adsorbed on the adsorbent surface. So, this can be determined. Now, each adsorbed N2 molecule occupies surface comparable to its cross section and that cross section is 0.162 nanometers square. So, this is there. So, that is how if each of the N2 molecule occupies this and from that data we can determine the surface area, so surface area will be Vm, what we do is that we multiply for each of the molecule.

So, the each N2 molecule occupies this surface area. So, what we do is multiply here 16.2 into 10 raised to minus 20. So, once we get this, we can use this particular equation to find out the surface area for any adsorbent, only thing is that we should know the Vm, what is the monolayer volume, which has been adsorbed and that data can be obtained from the BET equation. So, this is possible. So, all the calculations etcetera have been performed here, the 4.36 into 10 raised to 6 into Vm and this Vm should be in meter cube, this we have to take care.

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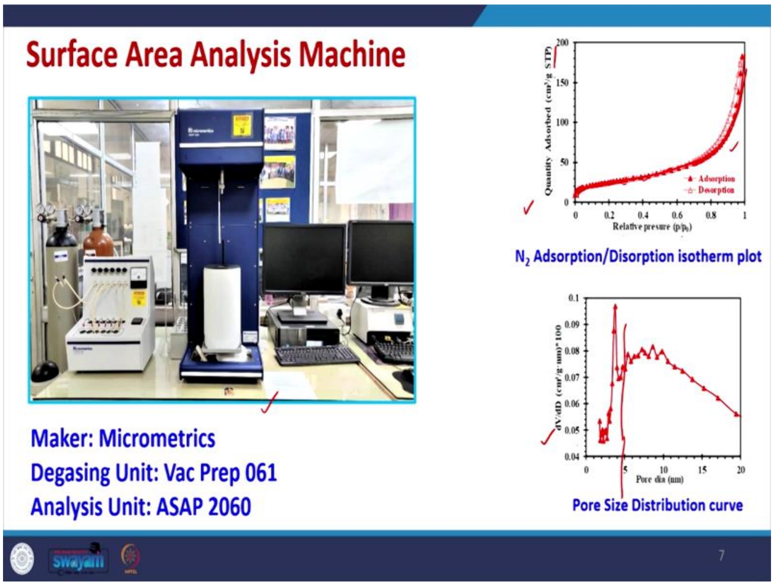

Surface Area Analysis Machine

Maker: Micrometrics
Degasing Unit: Vac Prep 061
Analysis Unit: ASAP 2060

N_2 Adsorption/Disorption isotherm plot

Pore Size Distribution curve

Now, this is the apparatus which has been used. So, this is available with us also. So, this is from Micrometrics, there are many other companies also. And what we get the data, we generally what we do is that we get this type of data quantity adsorbed centimeter cube per gram of adsorbent at STP.

So, for gas phase separation we always, whenever gases are involved and whenever we are reporting any volume, we should always report the temperature and pressure also. So, common thing is use standard temperature and pressure. So, triple point of water conditions have been used for reporting the quantity adsorbed, now and relative pressure is in the range of P by P0. And so, this type of apparatus can be used for performing this test.

And in this we get, what we do is that first we adsorbed the molecules and then we dissolve the molecule. So, adsorption is represented by this curve you can see here and then dissolve. And not only we can use the adsorption and desorption data for calculation of surface area, we can interpret many of the things using this particular curve which you like Kv versus P by P0 curve, and how, what is the behavior of this isotherm, what is the hysteresis type, they give a lot of information. So, many people work upon this.

And from this data we can get this type of data also dV by dD, I will not go in that much detail in this lecture, this is another topic but we can get the data that okay that how much surface area is available with respect to up to 5, suppose 5 nanometer we can see up above that. So, any of this size range we can select to know that how much surface area is because of mesopores, how much surface area is because of micropores, so, all those analysis can be performed.

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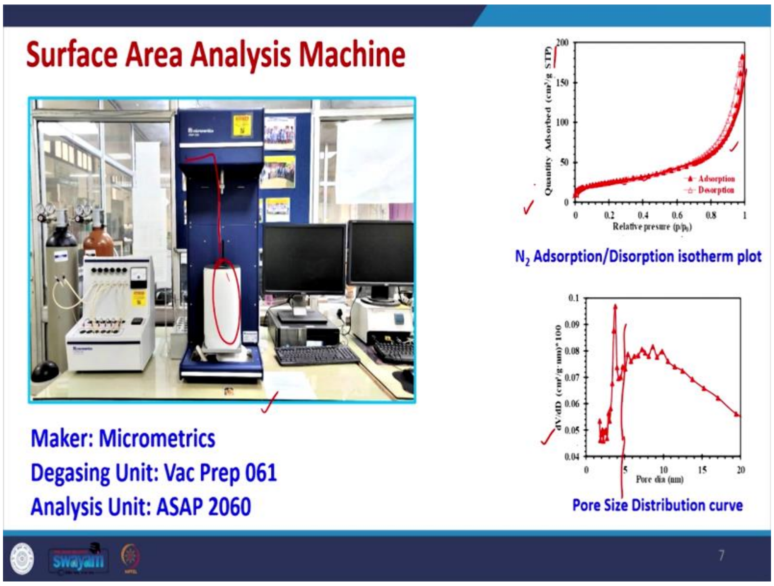
Liquid Nitrogen

Cryogenic Container

N_2 Plant



Surface Area Analysis Machine

Maker: Micrometrics
Degasing Unit: Vac Prep 061
Analysis Unit: ASAP 2060

N_2 Adsorption/Disorption isotherm plot

Pore Size Distribution curve

Now, this is the cryogenic container which is used for filling this liquid nitrogen and this liquid nitrogen is filled here. So, that we can keep the temperature up to liquid condition and then nitrogen is, nitrogen is flown. And so, that the maximum amount of adsorption may occur and after that desorption studies are also performed and the quantity adsorbed or desorbed are measured at various conditions using the calculations are already there in the software itself.

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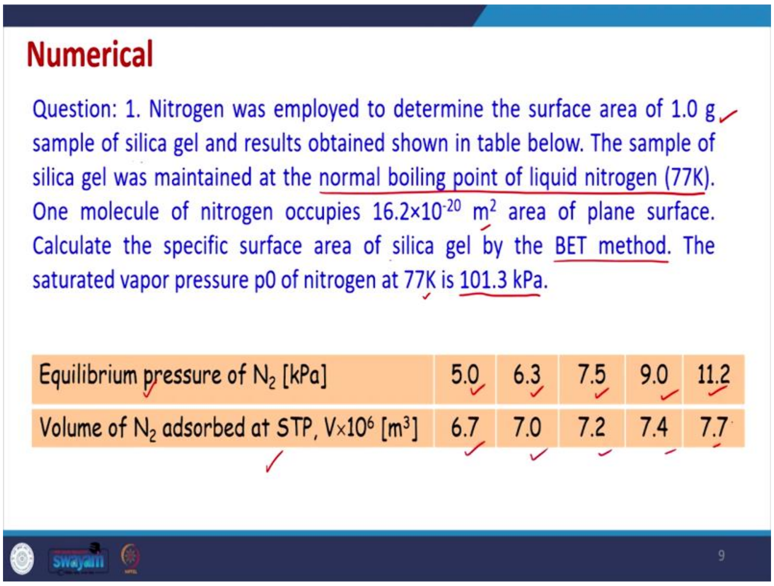

Numerical

Question: 1. Nitrogen was employed to determine the surface area of 1.0 g sample of silica gel and results obtained shown in table below. The sample of silica gel was maintained at the normal boiling point of liquid nitrogen (77K). One molecule of nitrogen occupies 16.2×10^{-20} m^2 area of plane surface. Calculate the specific surface area of silica gel by the BET method. The saturated vapor pressure p0 of nitrogen at 77K is 101.3 kPa.

Equilibrium pressure of N_2 [kPa]	5.0	6.3	7.5	9.0	11.2
Volume of N_2 adsorbed at STP, $V\times10^6$ [m^3]	6.7	7.0	7.2	7.4	7.7

So, let us takes some numericals related to this. So, as to understand. Now, nitrogen was employed to determine the surface area of 1 gram of sample of silica gel and results obtained are shown in table here. The sample silica gel was maintained at the normal boiling point of liquid nitrogen. So, we always maintained the temperature of 77 Kelvin in this unit, so it is very, very less.

Now, one molecule of nitrogen occupies 16.2 into 10 raise to minus 20 meters square of area of plane surface. So, this already we have learned previously, Now, calculate the specific surface area of silica gel using the BET method and the saturated vapor pressure of nitrogen at 77 Kelvin has been given to be this and the equilibrium pressure at different conditions are given at 5, 6.3, 7.5, 9, 11.2.

And here, actually the data points may be large number, only for numerical only few data points are given. And then the volume of N2 adsorbed at this condition has been given like this. So, this data is available.

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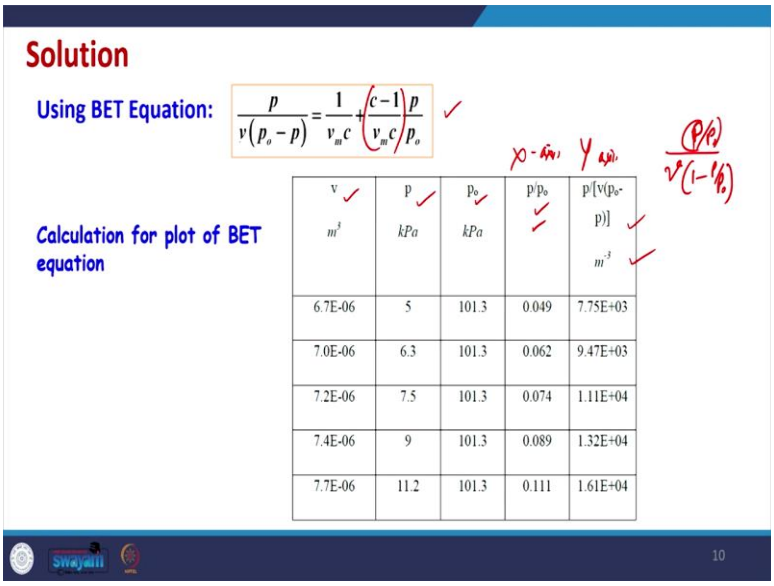

Solution

Using BET Equation: $\frac{p}{v(p_o-p)}=\frac{1}{v_m c}+\left(\frac{c-1}{v_m c}\right)\frac{p}{p_o}$ ✓

Calculation for plot of BET equation

x-axis y axis $\frac{(P/P_0)}{V(1-P/P_0)}$

v ✓ m^3	p ✓ kPa	p_o ✓ kPa	p/p_o ✓	$p/[v(p_o-p)]$ ✓ m^{-3} ✓
6.7E-06	5	101.3	0.049	7.75E+03
7.0E-06	6.3	101.3	0.062	9.47E+03
7.2E-06	7.5	101.3	0.074	1.11E+04
7.4E-06	9	101.3	0.089	1.32E+04
7.7E-06	11.2	101.3	0.111	1.61E+04

Now, what we do is that this is the BET equation, so we perform the calculation first. So, volume is already given, pressure is given, P0 is known, it is given so we determine P by P0. Similarly, we can determine P by divided by V into P0 minus P. So, this can also be written as 1 upon V or P by P0 this is there and 1 minus P by P0. So, this equation can also because P by P0 is already known V is known we can determine this, so this is this is y axis data, this is x axis data. So, this is there. So, we perform we plot this data.

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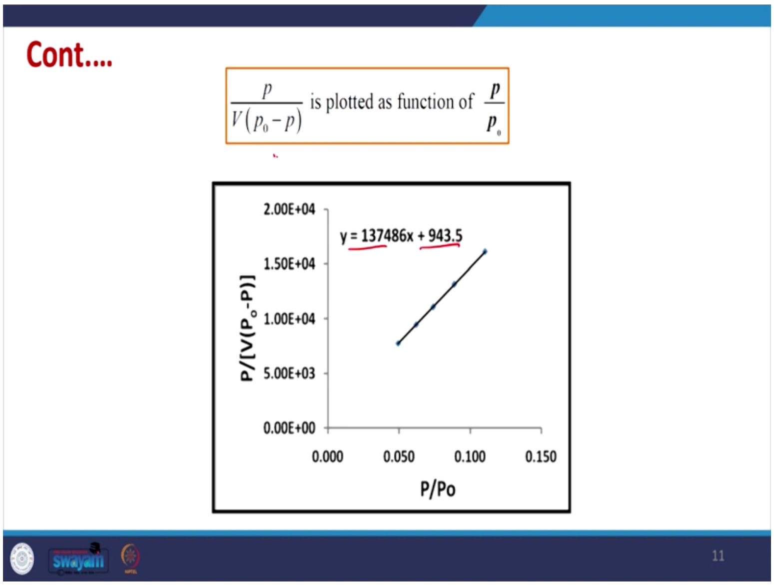

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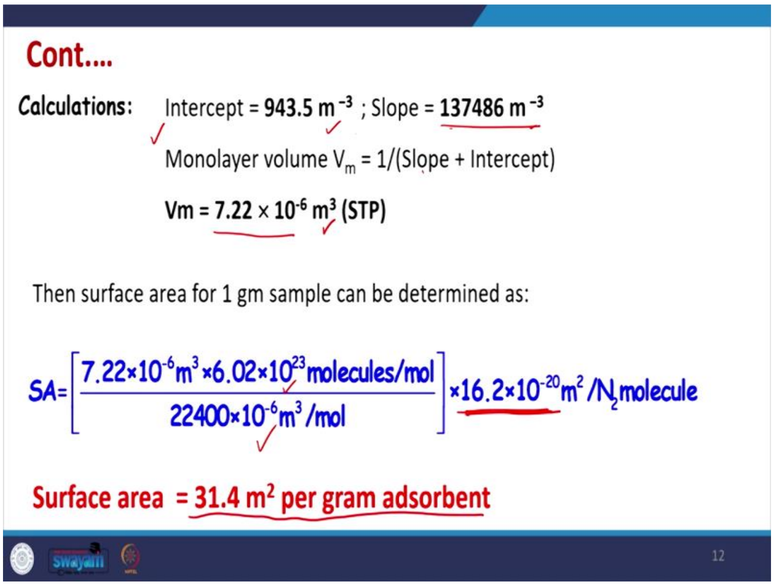
$\frac{p}{V(p_0-p)}$ is plotted as function of $\frac{p}{p_o}$



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Calculations: Intercept = **943.5 m^{-3}** ; Slope = **137486 m^{-3}**

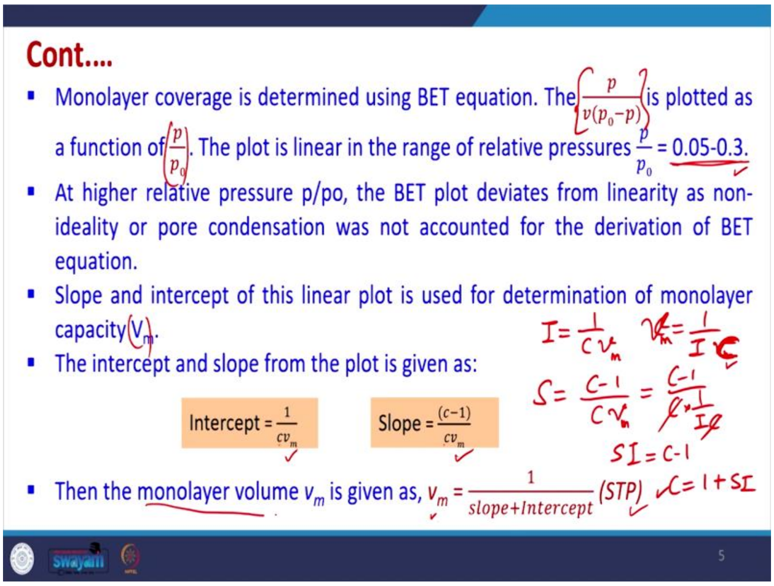
Monolayer volume V_m = 1/(Slope + Intercept)

Vm = 7.22 × 10^{-6} m^3 (STP)

Then surface area for 1 gm sample can be determined as:

$$SA=\left[\frac{7.22\times10^{-6}m^3\times6.02\times10^{23}\,molecules/mol}{22400\times10^{-6}m^3/mol}\right]\times16.2\times10^{-20}m^2/N_2\,molecule$$

Surface area = 31.4 m^2 per gram adsorbent



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- Monolayer coverage is determined using BET equation. The $\left\{\frac{p}{v(p_0-p)}\right\}$ is plotted as a function of $\left(\frac{p}{p_0}\right)$. The plot is linear in the range of relative pressures $\frac{p}{p_0}$ = 0.05-0.3.
- At higher relative pressure p/po, the BET plot deviates from linearity as non-ideality or pore condensation was not accounted for the derivation of BET equation.
- Slope and intercept of this linear plot is used for determination of monolayer capacity (V_m).
- The intercept and slope from the plot is given as:

Intercept = $\frac{1}{cv_m}$ Slope = $\frac{(c-1)}{cv_m}$

- Then the monolayer volume v_m is given as, $v_m = \frac{1}{slope+Intercept}$ (STP)

$I = \frac{1}{Cv_m}$ $v_m = \frac{1}{IC}$

$S = \frac{C-1}{Cv_m} = \frac{C-1}{C\cdot\frac{1}{IC}}$

$SI = C-1$

$C = 1+SI$

So, this type of equation will be there and equations are given. So, this is plotted as a function of P by P0 and this is given. Now, once this is given, what we do is that we use this data with respect to performs other calculations. So, what are those calculations? We know that intercept is 943.5. So, this will be there and slope is this value. Now, monolayer volume, if you remember, it was given here that it is equal to 1 by slope plus intercept.

So, this is the same is being done here. So, 1 by slope plus intercept because both are having the same unit per meter cube. So, because 1 by this is being done, so, overall unit will become meter cube, so, Vm is 7.2 into 10 raise to 6 minus meter cube minus 6 meter cube. The surface area can be calculated.

It was already done previously, so, this data has been used here and since each of the molecule is having this much area, we can perform the calculation and surface area is to be for this particular condition it is 31.4 meter square per gram of adsorbent. So, this is the surface area which has been obtained for this. So, this way we can determine the surface area, we can determine the average pore size, etcetera also using this equation.

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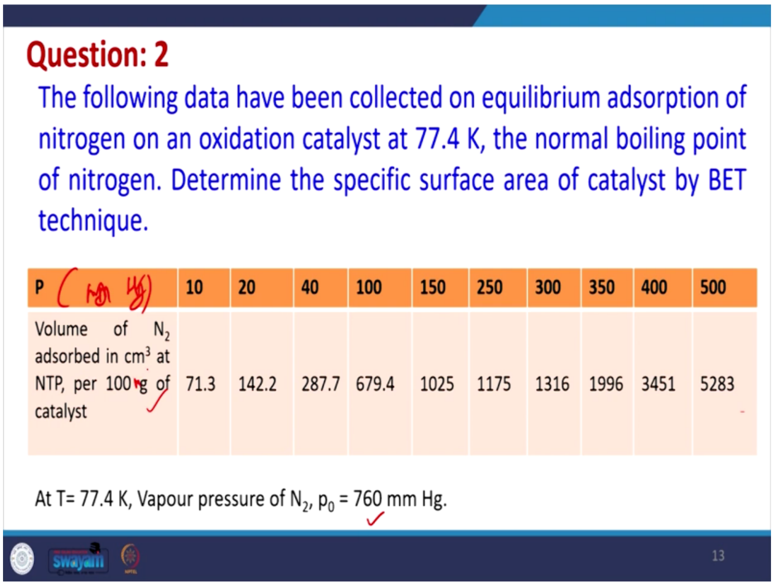

Question: 2

The following data have been collected on equilibrium adsorption of nitrogen on an oxidation catalyst at 77.4 K, the normal boiling point of nitrogen. Determine the specific surface area of catalyst by BET technique.

P (mm Hg)	10	20	40	100	150	250	300	350	400	500
Volume of N_2 adsorbed in cm^3 at NTP, per 100 mg of catalyst ✓	71.3	142.2	287.7	679.4	1025	1175	1316	1996	3451	5283

At T= 77.4 K, Vapour pressure of N_2, p_0 = 760 ✓ mm Hg.

But, now, another data has been given where at different pressures for a catalyst, this data has been given and the vapor pressure has been taken here in millimeter Hg. So, these values are also in millimeter Hg, so any of the units may be there and these values are there and volume of N2 adsorbed in centimeter cube at NTP per 100 grams of catalyst are given here. So, the catalyst is 100 milligram it must be of the catalyst.

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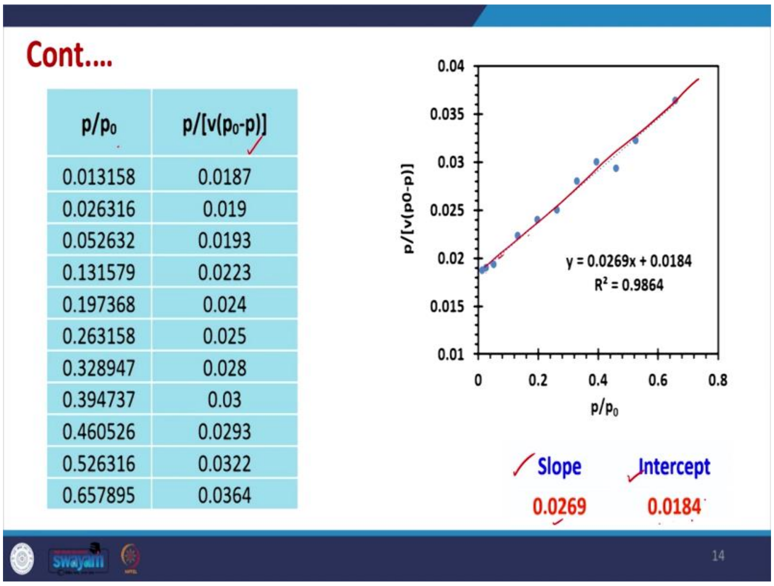

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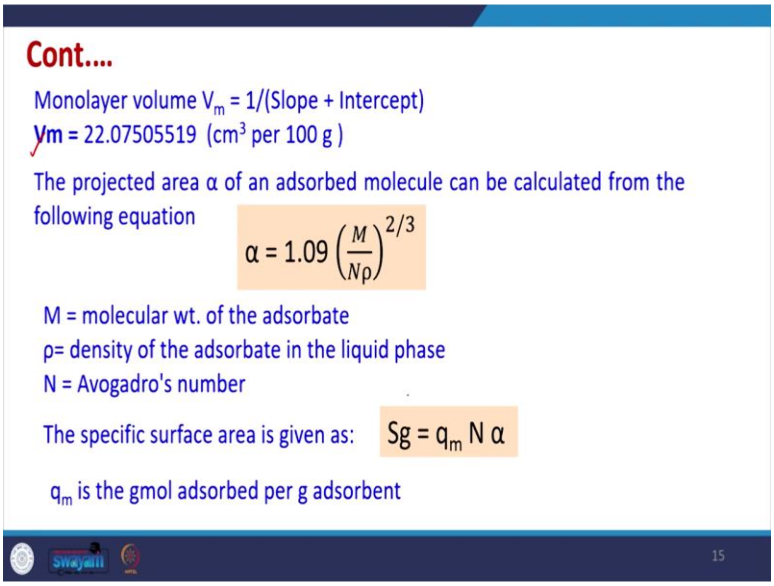
p/p_0	$p/[v(p_0-p)]$
0.013158	0.0187
0.026316	0.019
0.052632	0.0193
0.131579	0.0223
0.197368	0.024
0.263158	0.025
0.328947	0.028
0.394737	0.03
0.460526	0.0293
0.526316	0.0322
0.657895	0.0364

Slope	Intercept
0.0269	0.0184



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Monolayer volume V_m = 1/(Slope + Intercept)

Vm = 22.07505519 (cm³ per 100 g)

The projected area α of an adsorbed molecule can be calculated from the following equation

$$\alpha = 1.09\left(\frac{M}{N\rho}\right)^{2/3}$$

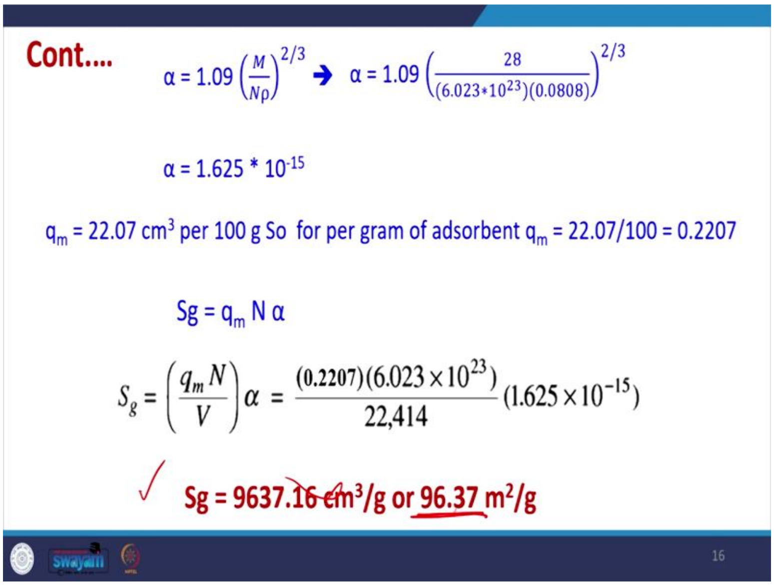
M = molecular wt. of the adsorbate

ρ= density of the adsorbate in the liquid phase

N = Avogadro's number

The specific surface area is given as: $Sg = q_m N \alpha$

q_m is the gmol adsorbed per g adsorbent



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$$\alpha = 1.09\left(\frac{M}{N\rho}\right)^{2/3} \rightarrow \alpha = 1.09\left(\frac{28}{(6.023*10^{23})(0.0808)}\right)^{2/3}$$

$\alpha = 1.625 * 10^{-15}$

q_m = 22.07 cm³ per 100 g So for per gram of adsorbent q_m = 22.07/100 = 0.2207

$Sg = q_m N \alpha$

$$S_g = \left(\frac{q_m N}{V}\right)\alpha = \frac{(0.2207)(6.023\times10^{23})}{22{,}414}(1.625\times10^{-15})$$

✓ **Sg = 9637.16 cm³/g or 96.37 m²/g**

So, this P by P0 data again P by V into P0 minus P data has been determined, we can plot this data and we draw a linear line on this. So, slope of this curve is 0.0269, intercept is 0.0184 and both can be used together to find out the volume and once the volume is known, because the surface area is known, we can determine the calculation and the overall surface area will be 9637 centimeter cube per gram and sorry this can be used by directly determining this value 96.37 meter square per gram, this is there. And through this we can determine the surface area.

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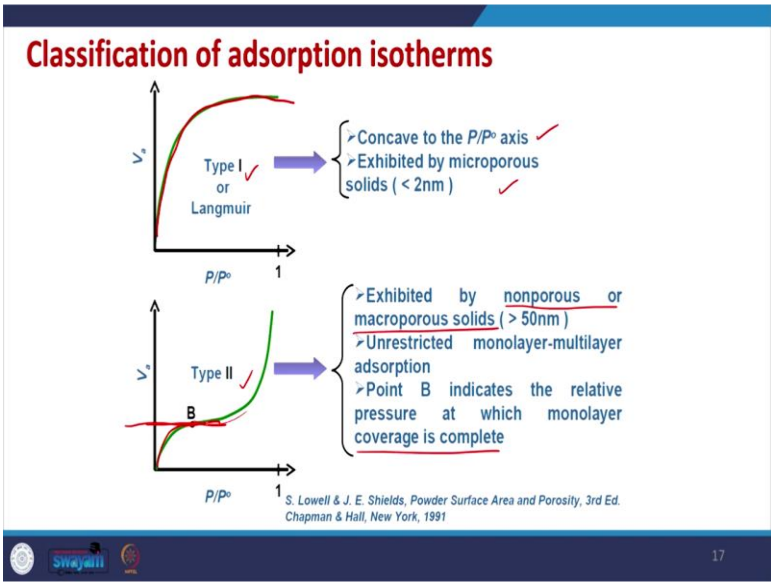
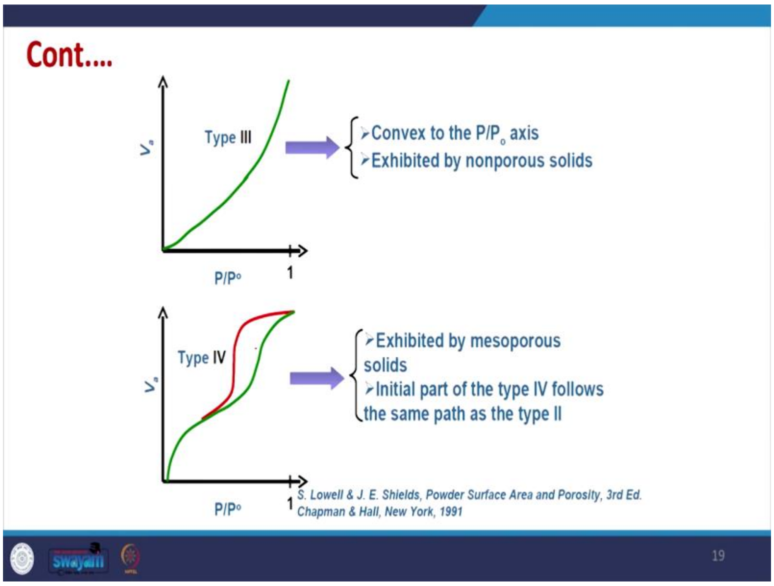


Classification of adsorption isotherms

- Concave to the P/P° axis
- Exhibited by microporous solids (< 2nm)

- Exhibited by nonporous or macroporous solids (> 50nm)
- Unrestricted monolayer-multilayer adsorption
- Point B indicates the relative pressure at which monolayer coverage is complete

S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991



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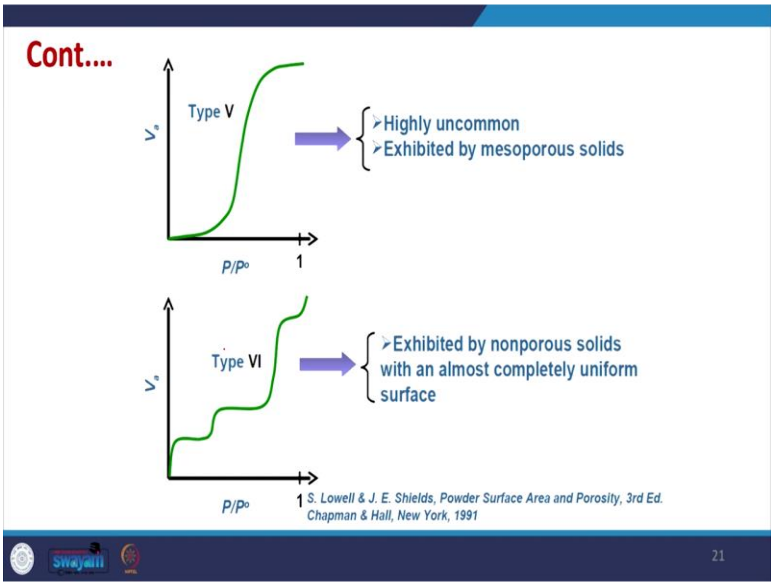
- Convex to the P/P_o axis
- Exhibited by nonporous solids

- Exhibited by mesoporous solids
- Initial part of the type IV follows the same path as the type II

S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991



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- Highly uncommon
- Exhibited by mesoporous solids

- Exhibited by nonporous solids with an almost completely uniform surface

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Now, along with the surface area there are different classification of adsorption isotherms in particular for gas phase adsorption. And they have different characteristics and they have, we can interpret lot of data out of them. And there are different classifications, classification like type 1, type 2, you can see here type 3, type 4, type 5 and type 6. So, there are three classifications which have been given for different types of isotherms which can be observed for any gas phase. And they give a lot of data for gas phase or liquid phase also.

The first is type 1, which you will be like very similar to Langmuir. So, here the saturation is being this, so this is called type 1 isotherm, it is concave to P by P0 axis and if it is there it will exhibit that this particular thing has more microporous structure. Now, there is a possibility that the curve may go up to saturation up to this and again it is going up, so this is called type 2nd.

So, this is also very common. So, this is exhibited by nonporous or microporous solids, they have unrestricted monolayer or multilayer adsorption which is occurring. Point B indicates relative pressure at which monolayer coverage is complete. So, this is there. So, this is possible for any gas.

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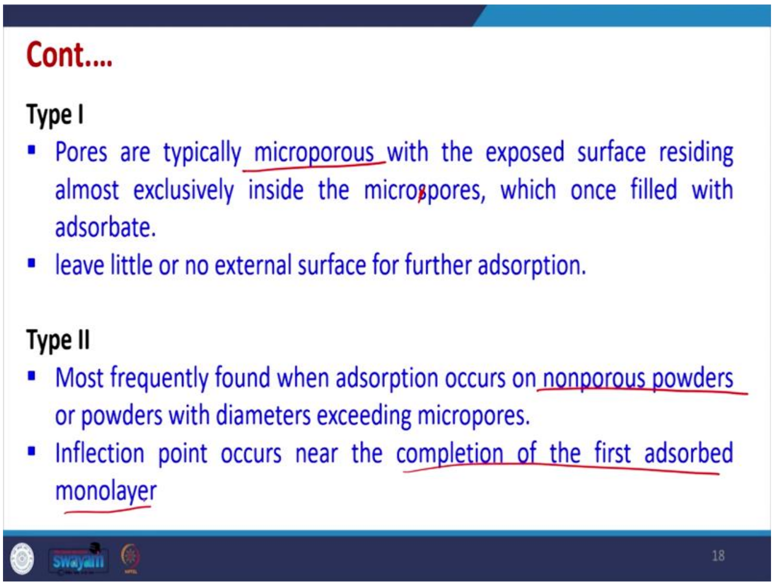

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Type I

- Pores are typically microporous with the exposed surface residing almost exclusively inside the micro~~s~~pores, which once filled with adsorbate.
- leave little or no external surface for further adsorption.

Type II

- Most frequently found when adsorption occurs on nonporous powders or powders with diameters exceeding micropores.
- Inflection point occurs near the completion of the first adsorbed monolayer

So, pores are for type 1, pores are typically microporous with the exposed surface residing on almost exclusively inside the micropores and which ones filled with adsorbate there is saturation. So, this is there. And they leave little or no external surface area for further adsorption. In type 2nd, it is most frequently found when adsorption occurs on non-porous powders. So, this is possible and it is like multilayer it is happening, it is like van der Waal forces of attraction. Inflection points occur to the under completion of first adsorbed monolayer, so this is there.

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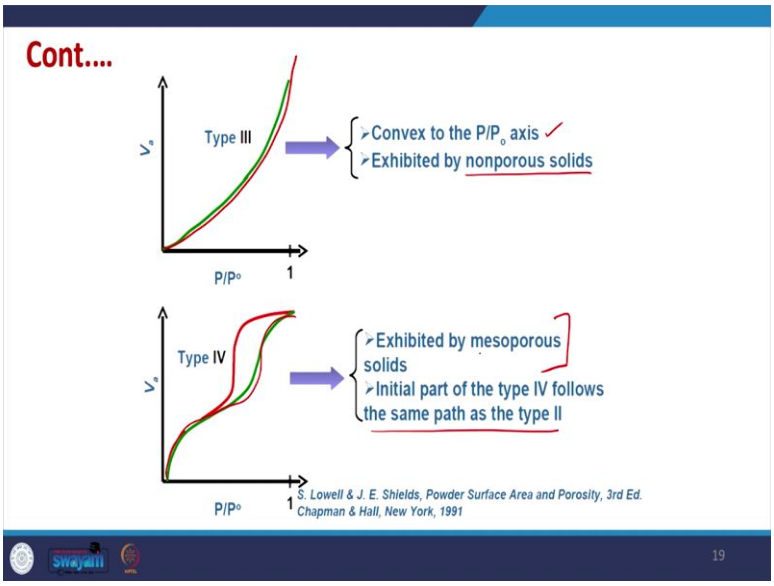

Cont….

- Convex to the P/P_o axis ✓
- Exhibited by nonporous solids

- Exhibited by mesoporous solids
- Initial part of the type IV follows the same path as the type II

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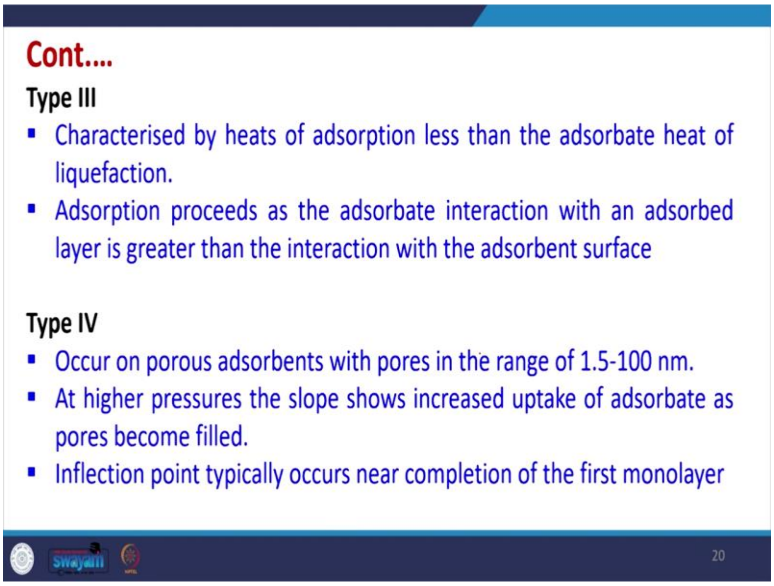

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Type III

- Characterised by heats of adsorption less than the adsorbate heat of liquefaction.
- Adsorption proceeds as the adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface

Type IV

- Occur on porous adsorbents with pores in the range of 1.5-100 nm.
- At higher pressures the slope shows increased uptake of adsorbate as pores become filled.
- Inflection point typically occurs near completion of the first monolayer

Then there is a type 3rd which is convex to the P by P0 axis we can see here it is going up. So, it is again for non-porous solids. Type 4, we will have again it is starting to go up then saturate and again go up. So, initial part of the type 4 follows the same path as type 2nd, but later on it varies. So, it is more exhibited by mesoporous solids. So, this we can see. Similarly, type 3rd already we have discussed.

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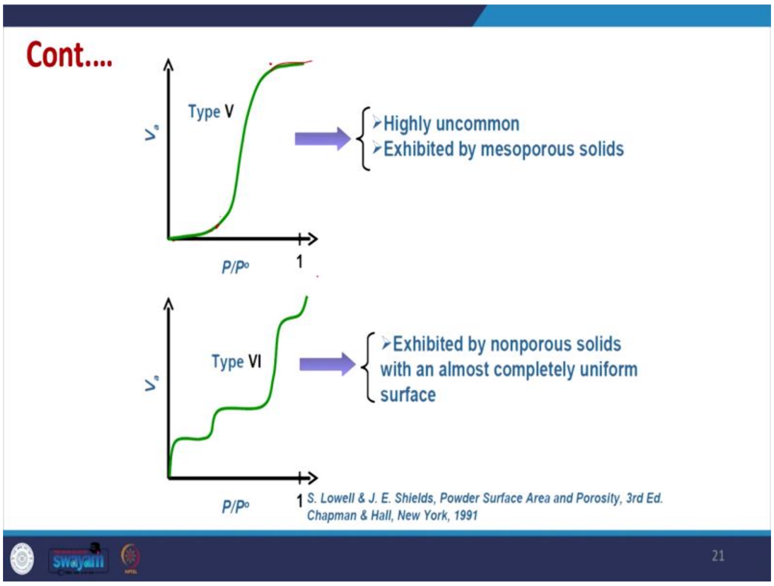
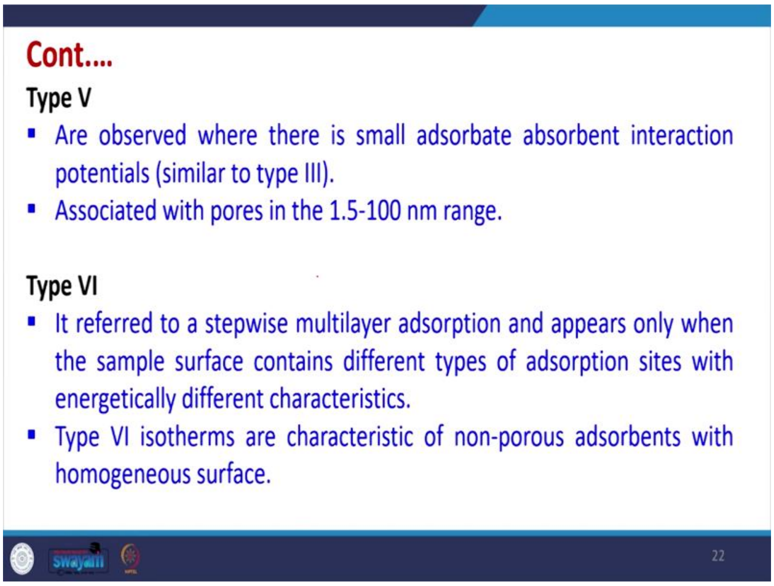


Cont….

- Highly uncommon
- Exhibited by mesoporous solids

- Exhibited by nonporous solids with an almost completely uniform surface

S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991



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Type V

- Are observed where there is small adsorbate absorbent interaction potentials (similar to type III).
- Associated with pores in the 1.5-100 nm range.

Type VI

- It referred to a stepwise multilayer adsorption and appears only when the sample surface contains different types of adsorption sites with energetically different characteristics.
- Type VI isotherms are characteristic of non-porous adsorbents with homogeneous surface.

For type 4, this is the type of they will reach some saturation and again increase very quickly from near to it and again reach the saturation. So, this is not commonly observed, it will be exhibited by mesoporous solid, but generally not very common. And type 6 is also not very common, but it may have multiple saturation levels which are there. So, this is there. And from these type of curves, we can get the idea that, okay, which type of isotherm is there.

And from that also, we can interpret a lot of things using whether it is porous, non-porous, what is the tentative whether it is microporous or mesoporous. So, some idea can be obtained from initial curve itself without performing the calculation. And few of the curves are not very common like type 5 and 6, but initial curves are 1st, 2nd, 3rd, 4 are common more.

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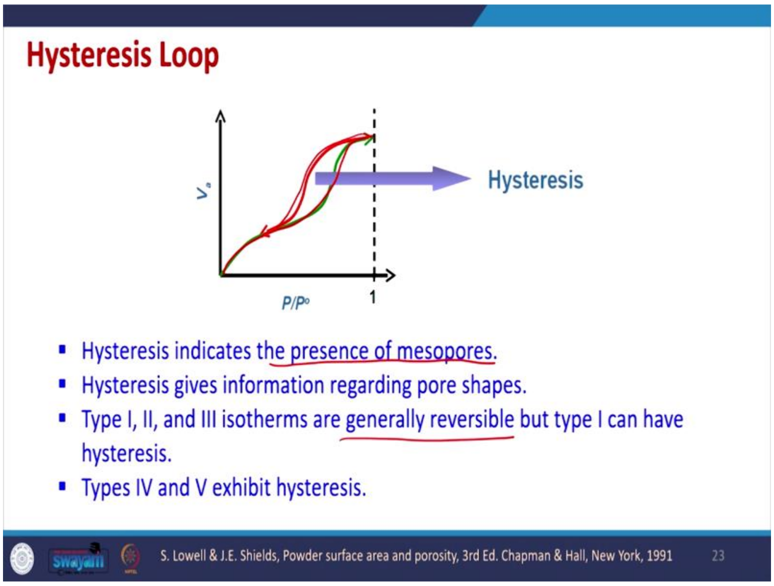

Hysteresis Loop

- Hysteresis indicates the presence of mesopores.
- Hysteresis gives information regarding pore shapes.
- Type I, II, and III isotherms are generally reversible but type I can have hysteresis.
- Types IV and V exhibit hysteresis.

S. Lowell & J.E. Shields, Powder surface area and porosity, 3rd Ed. Chapman & Hall, New York, 1991

So, and also because we perform the adsorption and desorption. So, during adsorption it will go like this, but in during desorption it will hysteresis will be there. So, hysteresis if any of the system or adsorbent shows hysteresis it means that there are more mesopores. Hysteresis gives information regarding the pore shapes also which will be shown in the next slide. Type 1, 2nd, 3 type of isotherms they are like generally reversible, but type 1 can have more hysteresis. And type 4 and 5 always exhibit hysteresis. So, this is possible.

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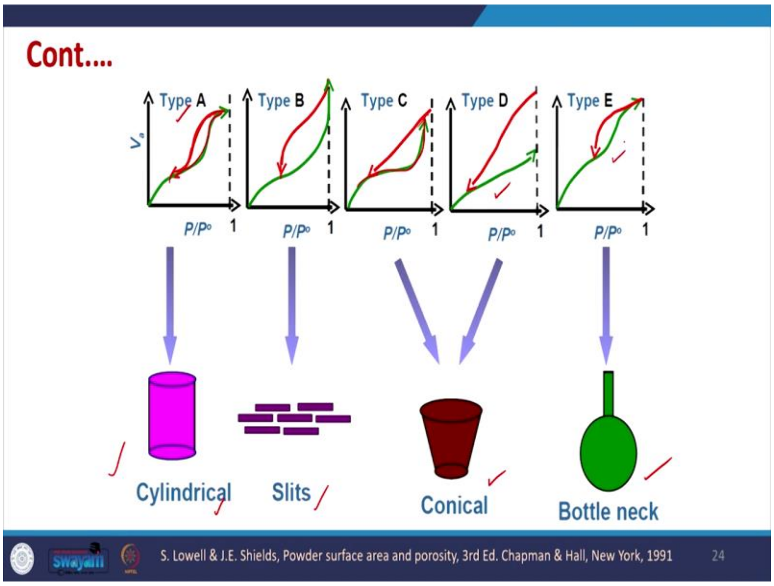

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Now, depending upon the type of hysteresis and type of curve, different types of pores are possible. So, earlier we had discussed there are different types of pores possible like cylindrical, conical, bottle neck, slits shaped. And different types of hysteresis behavior, type A hysteresis behavior, you can see the difference is coming. And this will sluggish, so there is a S sub, S shape is there.

For Type B there is not a very pronounced S shape it will diminish very quickly. For Type C there is more linear type and this is the shape here. Similarly, for type D there is a difference, type E. So, each of the curves show different types of hysteresis and from hysteresis data, we can interpret a lot of the pore type which may be available.

So, they may be cylindrical, slit, conical. I suggest that you can read any of the references which are given here for better understanding this hysteresis and different type of isotherms shapes, because they give a lot of information, but we need to study them in more detail for understanding. This is only a basic information has been given. If you are interested, you can go on reading these literature for better understanding.

So, this will now close today's lecture and from today's lecture we found that okay, nitrogen adsorption is one of the common methods which is used. And we get lot of data with respect to how much volume of nitrogen has been adsorbed at different relative pressures. So, once that data is available, we apply the BET equation to determine the surface area of the adsorbent.

There are many other possible calculations which are beyond the scope of this lectures and which are possible and those data can be used for performing the, determining the pore size whether they are micropores, mesopores, macropores, how much percentage of those pores are there this is also possible.

We can use that same data to determine the heterogeneity of the absorbent surface, that information can also be collected, but these can be determined using, these can be understood by reading different literatures which are there. So, with this we will end today's lecture. Thank you very much.