Powder Metallurgy
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Lecture – 29
BET Surface Area Analysis

Hi everyone, welcome back another lecture of this series. Right now we are talking about the surface area and the BET technique, which is used for measuring the surface area and it is based upon the adsorption of a gas on a solid surface. With regard to that we have discussed about different adsorption isotherms, and the isotherms which correspond to build up of multilayers actually correlate to the BET technique as we are going to discuss in this class.

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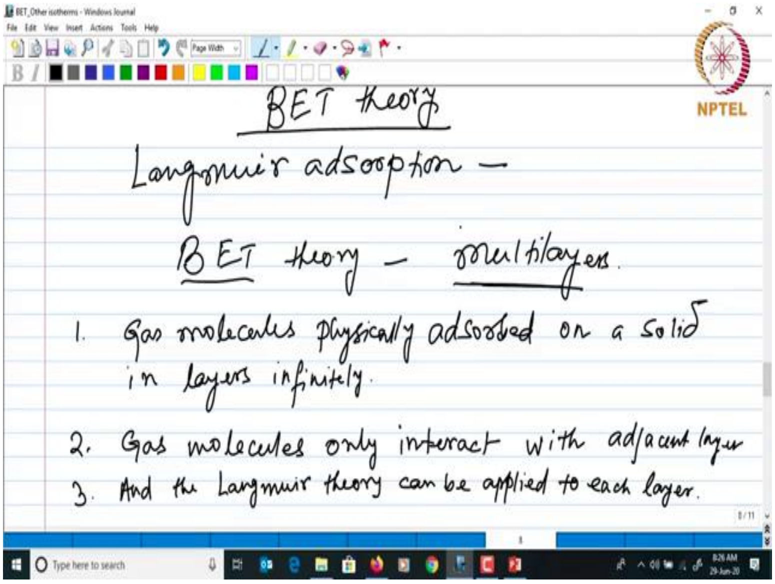

BET theory

Langmuir adsorption –

BET theory – multilayers.

1. Gas molecules physically adsorbed on a solid in layers infinitely.
2. Gas molecules only interact with adjacent layer
3. And the Langmuir theory can be applied to each layer.

BET theory is an extension of the Langmuir isotherm or the Langmuir adsorption theory, in the sense that the BET theory considers build up of multilayers, while the Langmuir adsorption theory talks about the formation of a monolayer.

So now, considering the multi layer formation in case of the BET theory, the equation for the Langmuir isotherm can be modified accordingly to obtain the BET isotherm, and in doing so, the following assumptions are made. Gas molecules physically adsorbed on a solid in layers infinitely. Then the gas molecules interact only with adjacent layer, and the Langmuir theory can be applied to each layer.

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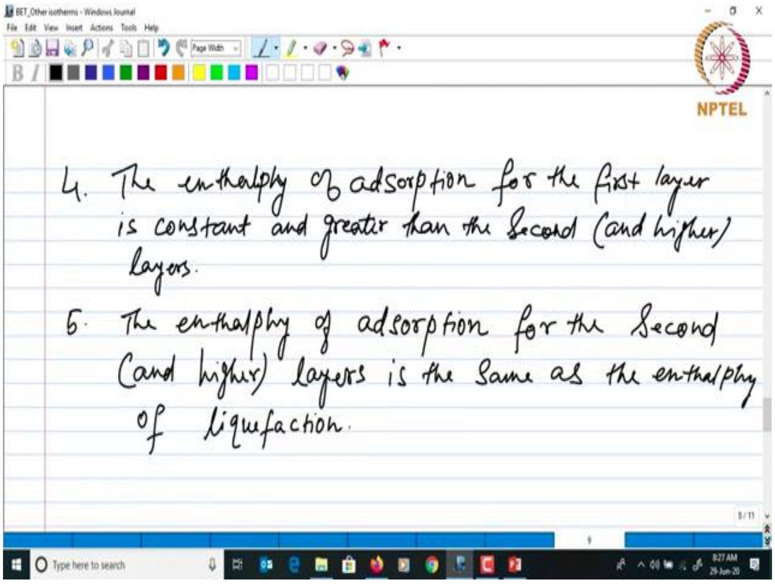

4. The enthalphy of adsorption for the first layer is constant and greater than the second (and higher) layers.

5. The enthalphy of adsorption for the second (and higher) layers is the same as the enthalphy of liquefaction.

The enthalpy of adsorption for the first layer is constant and is greater than the second and also the higher layers. Finally, the enthalpy of adsorption for the second and the higher layers also is the same as the enthalpy for liquefaction.

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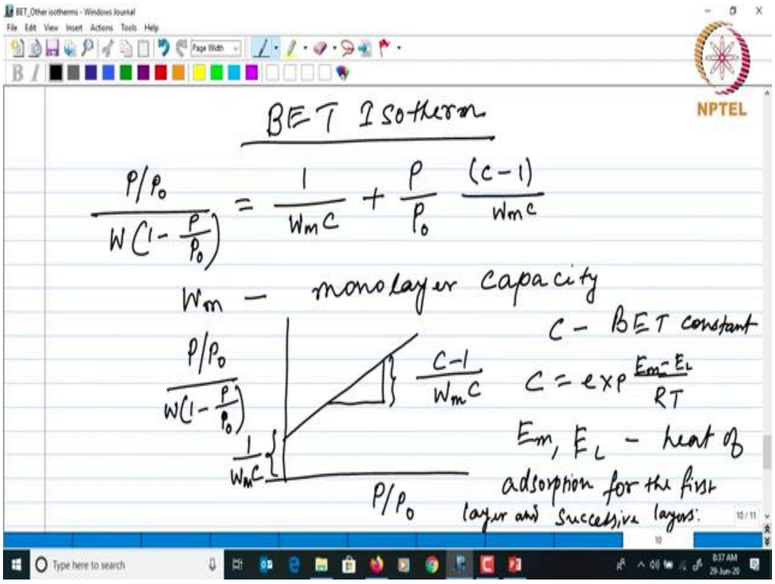

BET Isotherm

$$\frac{P/P_0}{W\left(1-\frac{P}{P_0}\right)} = \frac{1}{W_m C} + \frac{P}{P_0}\frac{(c-1)}{W_m c}$$

W_m – monolayer capacity

C – BET constant

$C = \exp\frac{E_m - E_L}{RT}$

E_m, E_L – heat of adsorption for the first layer and successive layers.

With this assumptions, Langmuir isotherm can be modified as follows to obtain the BET isotherm.

$$\frac{P/P_0}{W\,(1 - P/P_0)} = \frac{1}{W_m C} + \frac{P}{P_0}\,\frac{(C-1)}{W_m C}$$

Where P is the partial pressure of the gas, W is the amount of gas adsorbed at pressure P, P_0 is the saturation pressure of the gas, and W_m is the amount of gas adsorbed corresponding to formation of a monolayer, and this is also known as the monolayer capacity.

From this equation you can see that, if you plot this with the relative pressure P / P_0 it will give rise to a straight line. The slope of which is

$$C - 1/W_m C$$

and the intercept is

$$1/W_m C.$$

Here C is the BET constant and this is given by the following expression;

$$C = e^{(E_m - E_L)/RT}$$

where E_m and E_L are the heat of adsorption for the first layer and the successive layers respectively. And R is the gas constant and T is the absolute temperature.

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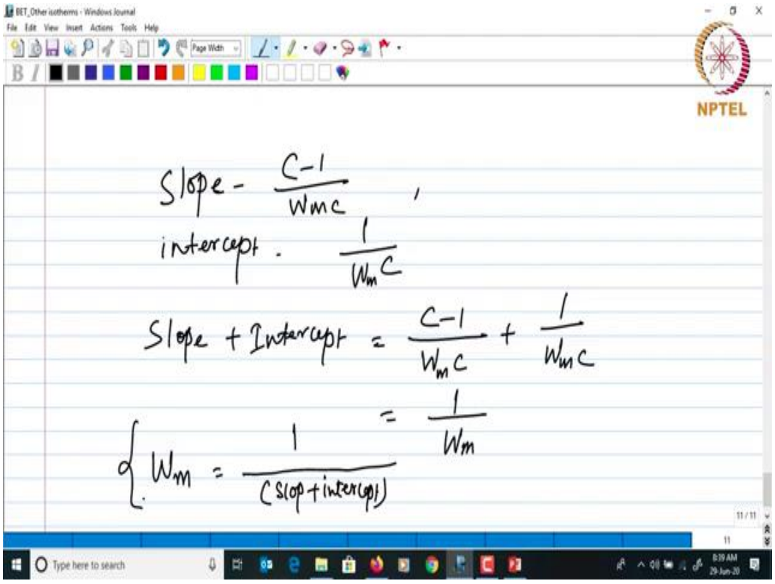

$$\text{Slope} - \frac{C-1}{W_m C},$$

$$\text{intercept} \cdot \frac{1}{W_m C}$$

$$\text{Slope} + \text{Intercept} = \frac{C-1}{W_m C} + \frac{1}{W_m C}$$

$$= \frac{1}{W_m}$$

$$\left\{ W_m = \frac{1}{(\text{slop} + \text{intercept})} \right.$$

If you add the slope plus the intercept, this is what is obtained. Therefore, W_m is simply the reciprocal of slop plus intercept. That is how we can obtain the monolayer capacity from this equation, by plotting it between these two parameters which gives rise to a straight line. So now that we have understood the basic principle behind the BET technique, it is time for us to look at the BET instrument and the actual measurement methods.

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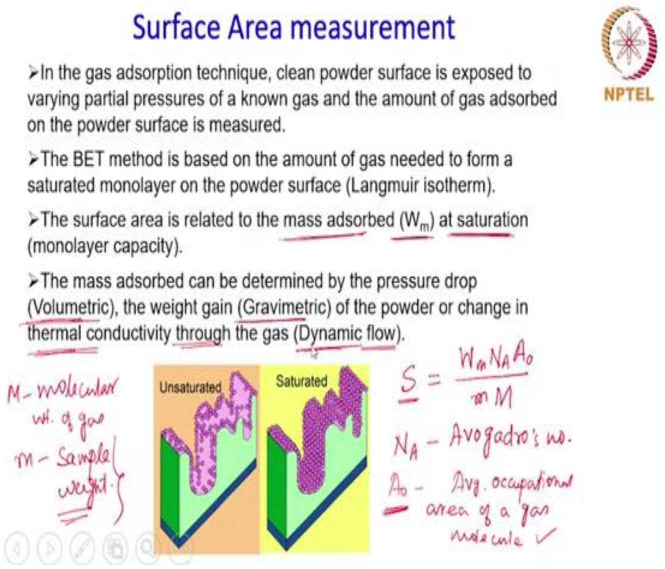

Surface Area measurement

- In the gas adsorption technique, clean powder surface is exposed to varying partial pressures of a known gas and the amount of gas adsorbed on the powder surface is measured.
- The BET method is based on the amount of gas needed to form a saturated monolayer on the powder surface (Langmuir isotherm).
- The surface area is related to the mass adsorbed (W_m) at saturation (monolayer capacity).
- The mass adsorbed can be determined by the pressure drop (Volumetric), the weight gain (Gravimetric) of the powder or change in thermal conductivity through the gas (Dynamic flow).

M - molecular wt. of gas

m - Sample weight

$$S = \frac{W_m N_A A_0}{m M}$$

N_A - Avogadro's no.

A_0 - Avg. occupational area of a gas molecule ✓

In this BET technique or the gas adsorption technique of measuring surface area, a clean powder surface is basically exposed to varying partial pressure of a known gas; the adsorbate gas, and the amount of gas absorbed on the powder surface is measured.

So, what we need to obtain from here is the mass adsorbed at saturation when the monolayer is formed. This is what we are looking for; W_m and just now we have seen how it is related to the partial pressure of the gas or the relative pressure. In order to determine this, there are various methods which can be used in this gas adsorption technique and these are as follows.

The mass adsorbed can be determined by the pressure drop which is kind of measuring the volume of gas before and after the adsorption has happened, and hence known as a volumetric method. The weight gain of the powder due to the adsorption can also be determined to get to know about the monolayer capacity W_m.

This method is known as the gravimetric method, as is based upon the weight gain which is being measured. Apart from that the thermal conductivity change due to the adsorption can also be measured and from that the amount of gas that is adsorbed can be calculated. This particular method goes by the name dynamic flow.

These are the different methods which can be used in the gas adsorption technique to measure the amount of gas that is being adsorbed at the saturation when the monolayer is formed.

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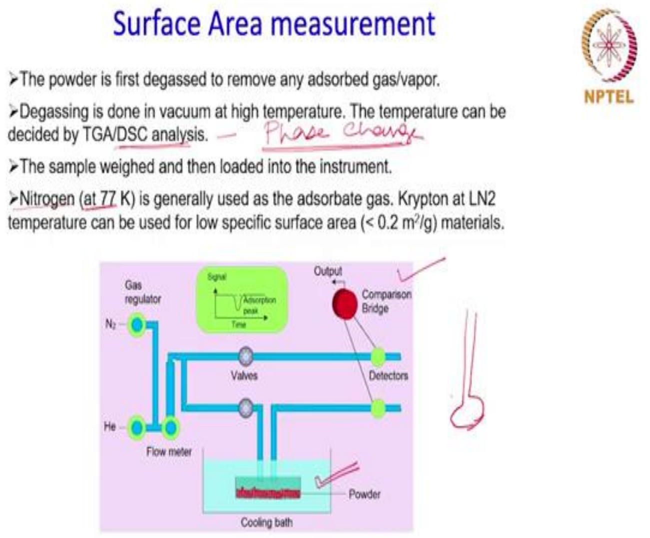

Surface Area measurement

- The powder is first degassed to remove any adsorbed gas/vapor.
- Degassing is done in vacuum at high temperature. The temperature can be decided by TGA/DSC analysis. – Phase change
- The sample weighed and then loaded into the instrument.
- Nitrogen (at 77 K) is generally used as the adsorbate gas. Krypton at LN2 temperature can be used for low specific surface area (< 0.2 m^2/g) materials.

If we look at that instrument which is being used for this, this is a schematic of the same. Here you can see a very basic parts of the instrument. As I said before, a clean powder surface has to be presented for this adsorption to happen. And therefore, the first thing which is done in this technique is to clean the powder, in order to do that it has to be degassed to remove any adsorbed gas or vapor which maybe physically or chemically adsorbed on the surface of the powder.

So, the first step is degassing and that can be done under vacuum at high temperature. And the temperature which can be used to do this degassing can be determined either by thermogravimetric analysis, TGA or differential scanning calorimetry DSC.

TGA will simply give you the mass loss of a powder sample as you heat it. So it will show up to what temperature the mass loss is happening; that means, all the adsorbed gas and the moisture is being removed. So from that we can determined as to what temperature, the powder sample has to be heated for the degassing to take place.

If there are chances of any phase changes, then DSC analysis can also be performed in order to know that, what is that temperature or the temperature range in which a different phase might form and therefore, that temperature has to be avoided during degassing of the sample.

Most of the modern instruments have a degassing chamber as an integrated part of the instrument itself. So before the sample is loaded in the sample chamber it is first sent to the degassing chamber, degassed cleaned and then cooled down and after that it is sent to the sample chamber where it is exposed to a liquid nitrogen bath to keep the sample at very low temperature, because nitrogen is generally used as the adsorbed gas and it has to be used at its boiling point which is 77 Kelvin.

Therefore, the sample is cooled down by bringing the liquid bath to the sample tube. The sample tube if you see it is basically a tube with a bulb at the end. The design of the bulb may be different depending on the type of sample. It has a tube like and then at the end there is a bulb. So the sample is loaded and kind of kept in the bulb.

This sample tube has to be exposed to the cooling bath which is basically liquid nitrogen. After the sample tube is loaded to the sample chamber this cooling bath is brought in contact with the sample tube and it is cooled down and after that the adsorbed gas which is, generally nitrogen as I said is passed through the sample at a known pressure.

And the amount which is adsorbed when the monolayer forms can be determine by the three different techniques as we talked about before, and from that the specific surface area can be calculated. Apart from nitrogen other gases also can be used for example, Krypton at liquid nitrogen temperature can be used for materials having low specific surface area in the range of less than 0.2 m^2/g.

Once the W_m or the amount adsorbed corresponding to the monolayer formation is obtained from this measurement, the specific surface area can be obtained from this equation,

$$S = W_m N_A A_0 / mM$$

where S is the specific surface area, N_A is Avogadro's number, A_0 is the average occupational area of a gas molecule, M is the molecular weight of the gas which is being used as the adsorbate. m is the sample weight. Therefore, it is also necessary to measure the sample weight before the surface area measurement is started. It has to be done carefully, because most of the time the amount which is being absorbed is very small particularly, if you are using the Gravimetric method which is based upon the weight change after the adsorption.

Since, that weight change is very small this measurement of the sample weight has to be done very carefully. In order to calculate the specific surface area from this particular equation, this property of the gas the occupational area has to be known and that is why a known gas is used so that these can be easily obtained.

So, these three methods that I mentioned will be discussed a one by one separately. And we will see how each of these methods are performed to obtain this amount adsorbed for the saturation.

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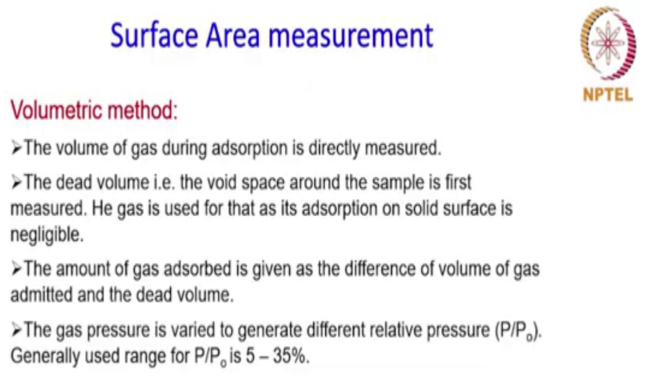

Surface Area measurement

Volumetric method:

- The volume of gas during adsorption is directly measured.
- The dead volume i.e. the void space around the sample is first measured. He gas is used for that as its adsorption on solid surface is negligible.
- The amount of gas adsorbed is given as the difference of volume of gas admitted and the dead volume.
- The gas pressure is varied to generate different relative pressure (P/P_o). Generally used range for P/P_o is 5 – 35%.

Let us talk about the volumetric method first, in this technique the volume of the gas during the adsorption is directly measured. In order to measure the gas adsorbed, first the dead volume, that is the void space around the sample is measured. Once the sample is degassed and dried and it is loaded into the sample chamber. First whatever volume is left around the sample which is known as the dead volume, that is first measured.

And this is the volume which is used to actually calculate the adsorbed gas by the difference of these volume and the actual amount of gas which is being admitted into the sample chamber. In order to measure this dead volume, helium gas is generally used, because helium exhibits negligible adsorption on solid surfaces.

As I said the amount of gas which is adsorbed is given as the difference of volume of gas which is actually admitted into the sample chamber and the dead volume. So, from this difference, the amount which is actually absorbed on to the sample surface can be calculated.

In order to generate different relative pressure to plot the isotherm the pressure can be varied, and in each case the amount of gas that is being adsorbed is calculated by this difference method. The generally used range for this measurement in terms of the relative pressure is from 5 to 35% which is basically the linear range or the monolayer coverage region of the isotherm.

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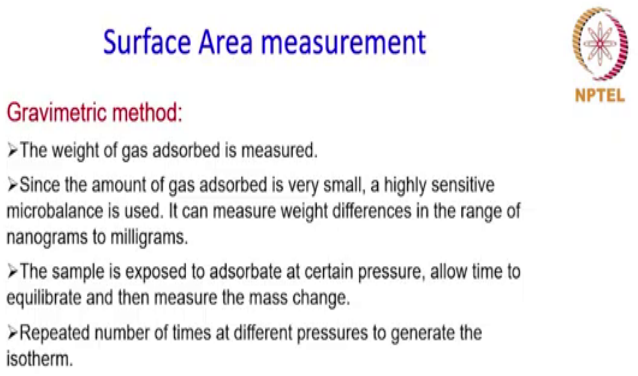

Surface Area measurement

Gravimetric method:

- The weight of gas adsorbed is measured.
- Since the amount of gas adsorbed is very small, a highly sensitive microbalance is used. It can measure weight differences in the range of nanograms to milligrams.
- The sample is exposed to adsorbate at certain pressure, allow time to equilibrate and then measure the mass change.
- Repeated number of times at different pressures to generate the isotherm.

In the gravimetric method, the weight of gas adsorbed is measured. In this case, since the amount of gas adsorbed is very small, a very sensitive micro balance has to be used. These kind of balances can measure weight differences in the range of nano-grams to milligrams.

So, it has to be that sensitive, because of the fact that the adsorbed amount is actually very small. In this case what is done is that the sample is exposed to the absorbed gas at a certain pressure, and a certain time is allowed for the equilibrium to establish and then the mass change is measured as the gas is adsorbed onto the surface of the powder particles. The experiment is repeated a number of times at different pressures to generate different relative pressures and to plot the isotherm.

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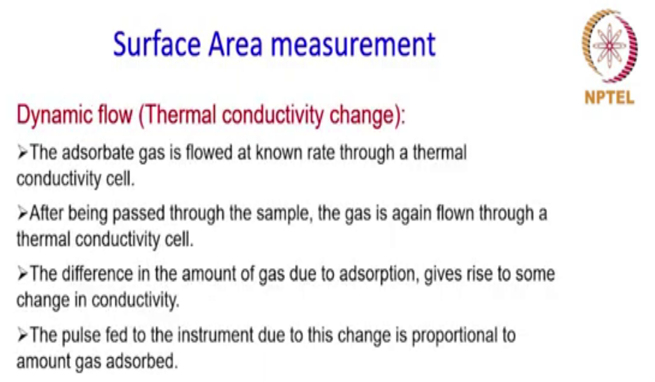

Surface Area measurement

Dynamic flow (Thermal conductivity change):

- The adsorbate gas is flowed at known rate through a thermal conductivity cell.
- After being passed through the sample, the gas is again flown through a thermal conductivity cell.
- The difference in the amount of gas due to adsorption, gives rise to some change in conductivity.
- The pulse fed to the instrument due to this change is proportional to amount gas adsorbed.

In the dynamic flow method, a parameter such as the thermal conductivity is used basically, the change in the thermal conductivity due to the adsorption process is monitored in this case.

The adsorbate gas is flowed at a known rate through the thermal conductivity cell. So here, apart from the sample cell there is a thermal conductivity cell also through which the gas will be flowed, and if there is any change in the thermal conductivity of the gas that can be captured by this thermal conductivity sensor which is there in the conductivity cell.

Now, after being passed through the sample, the gas is again flown through a thermal conductivity cell, this is to check if there is a change in the thermal conductivity as I said.

If there is adsorption of the gas on the solid surface, there will be some imbalance into the amount of gas which is flown into the conductivity cell and therefore, there will be a change in the thermal conductivity. That is how the change in the thermal conductivity can be correlated to the amount of gas which is adsorbed on the solid surface in the sample chamber.

This thermal conductivity change is fed through a pulse into the system to generate the signal. The pulse which is fed is actually proportional to the amount of gas adsorbed and that is how the amount of gas adsorbed at different pressures can be calculated, from this and the isotherm can be plotted. So, this was all about the BET surface area measurement technique.

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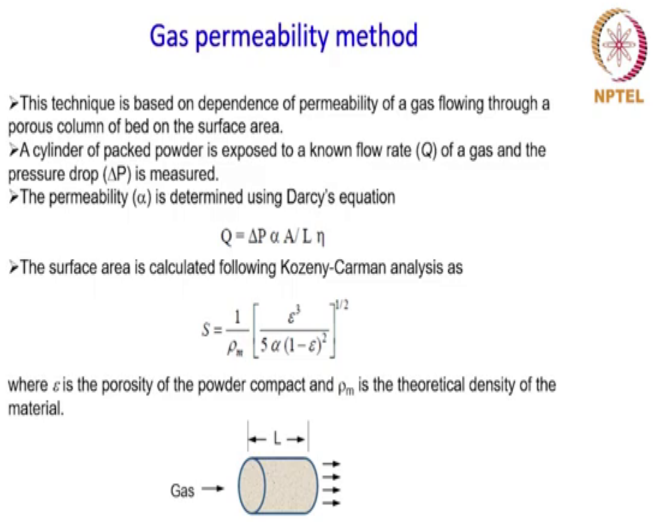

Gas permeability method

NPTEL

➢This technique is based on dependence of permeability of a gas flowing through a porous column of bed on the surface area.

➢A cylinder of packed powder is exposed to a known flow rate (Q) of a gas and the pressure drop (ΔP) is measured.

➢The permeability (α) is determined using Darcy's equation

$$Q = \Delta P \, \alpha \, A / L \, \eta$$

➢The surface area is calculated following Kozeny-Carman analysis as

$$S = \frac{1}{\rho_m}\left[\frac{\varepsilon^3}{5\,\alpha\,(1-\varepsilon)^2}\right]^{1/2}$$

where ε is the porosity of the powder compact and ρ_m is the theoretical density of the material.

Now, there is one more method which can be used to measure the surface area of powder. This is the gas permeability method. This technique is based on the dependence of permeability of a gas flowing through a porous column of bed on the surface area. From this dependence of the surface area onto the permeability, the surface area of the powder can be calculated. So, what is done here is, a cylinder of packed powder which you can see over here is first made.

This is then exposed to a known flow rate of a gas, and the pressure drop across it is measured. From that the permeability is determined using Darcy's equation which is this one;

$$Q = \Delta P \, \alpha \, A / L\eta$$

Where Q is the flow rate of the gas, ΔP is the pressure drop that is actually measured, alpha is the permeability, L is the distance through which the gas flows or the sample length a is the cross sectional area of the sample, and η is the viscosity of the gas.

Once the alpha is obtained from this equation, it is used here in another equation known as the Kozeny-Carman equation to calculate the surface area S.

$$S = \frac{1}{\rho_m}\,[\frac{\varepsilon^3}{5\,\alpha\,(1-\varepsilon)^2}]^{1/2}$$

And in this equation this ε is the porosity of the powder compact which can be measured beforehand, and ρ_m is the theoretical density of the material. So, this is before we finish this lecture, let us take a moment to summarize it.

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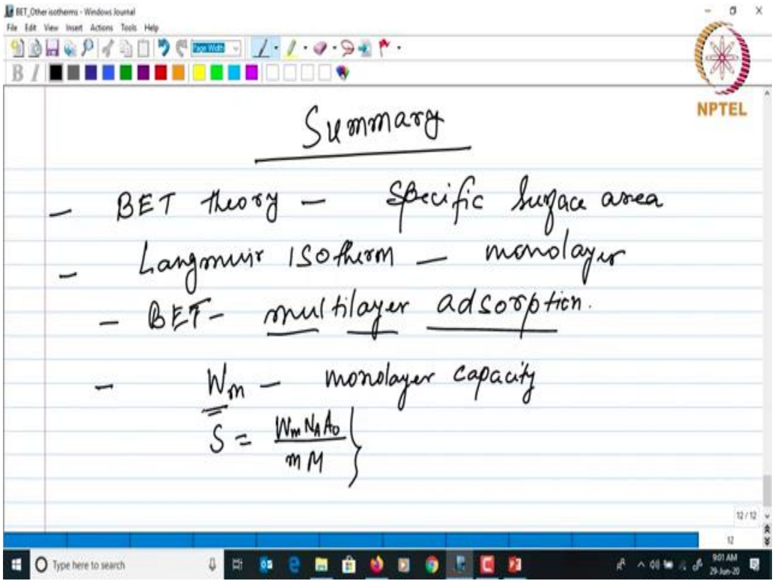

Summary

- BET theory — specific surface area
- Langmuir isotherm — monolayer
- BET- multilayer adsorption.
- W_m — monolayer capacity

$$S = \frac{W_m N_A A_0}{m M}$$

Today we talked about the BET theory and its application in measuring specific surface area. BET theory is basically an extension of the Langmuir gas adsorption theory or the Langmuir isotherm, which considers formation of a monolayer; whereas, the BET theory considers formation of multilayers with the assumption that for each of the layer the Langmuir theory can be applied.

And considering this multi layer adsorption, the Langmuir isotherm is accordingly modified to obtain the BET isotherm, and from there we can obtain the specific surface area of a powder. And in order to do that, all we need to do is basically measure this monolayer capacity or the amount of gas which is adsorbed at the monolayer coverage.

And, once it is obtained, the specific surface area can be obtained using particular equation. This we have already discussed. And in order to measure this W_m by the gas adsorption technique, there are various methods; primarily three methods can be used to do this, and those are the volumetric method where the volume of the gas is directly measured, the gravimetric method which deals with the weight change, as a result of the adsorption and this amount can also be measured indirectly by measuring a change of a particular quantity; for example, the thermal conductivity.

So those kinds of techniques are known as the dynamic flow technique, in which the gas is continuously passed over the sample. As it is being adsorbed that will be a change in a particular property. For example, the thermal conductivity which is being monitored, and from that change the amount which is being adsorbed can be calculated.

These are the methods for measuring the surface area of powders using the BET technique. With that we come to the end of this particular class, but I am going to see you soon again.

Thank you for your attention.