# Powder Metallurgy
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## Lecture – 27
## Surface Area Analysis - 1

Hi everyone and welcome back. So, right now we are talking about the powder properties and the characterization of powder to evaluate these properties. And, we have seen one of the important properties, that is the particle size and in past few classes we have discussed about the particle size measurement and the techniques which are used to measure particle size and size distribution.

Now there is one more property of powder particles, which is very important because this property controls many of the characteristics and behavior of the powder and the material, which is ultimately made out of the powder.

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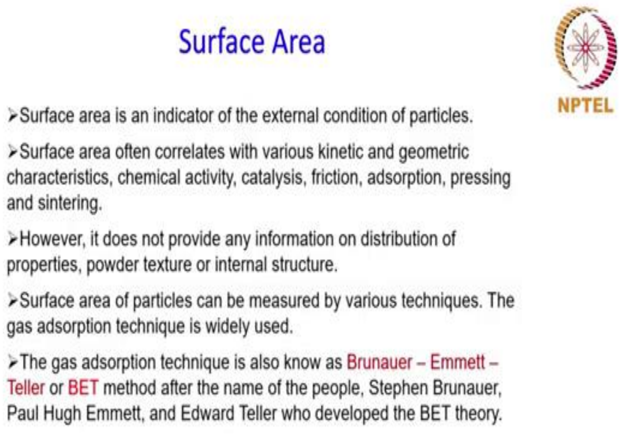

Surface Area

- Surface area is an indicator of the external condition of particles.
- Surface area often correlates with various kinetic and geometric characteristics, chemical activity, catalysis, friction, adsorption, pressing and sintering.
- However, it does not provide any information on distribution of properties, powder texture or internal structure.
- Surface area of particles can be measured by various techniques. The gas adsorption technique is widely used.
- The gas adsorption technique is also know as Brunauer – Emmett – Teller or BET method after the name of the people, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller who developed the BET theory.

It is surface area and that is what we are going to talk about in this class. How the surface area can be measured, and what are the techniques available to do this measurement?

Surface area is not only an indicator of the external condition of the particles. But, it also often correlates with various properties of the particles, such as chemical activity, catalysis, friction, adsorption, and also pressing and sintering, which are the two most important steps of the powder metallurgy process.

Surface area, however, does not provide any information on distribution of properties powder texture or internal structure. Now, when it comes to measuring surface area, there are various techniques which can be used to measure it. However, by far, the gas absorption technique is the most widely used and this gas adsorption technique is also known as the BET method, which stands for Brunauer, Emmett, Teller, after the names of the people who invented this theory.

Now, the basic principle behind this technique goes back to the Langmuir adsorption theory or the Langmuir isotherms. So, let us first talk about the Langmuir isotherms and from that we will get to understand about the basic principle behind the BET method.

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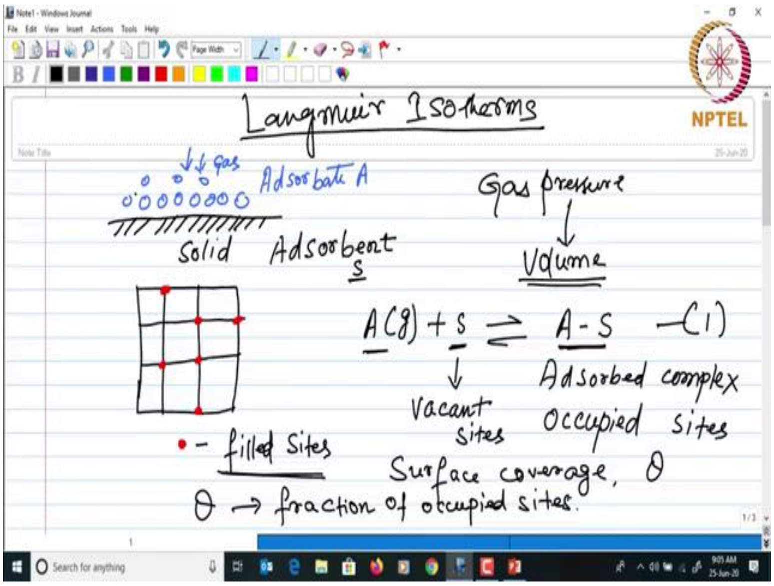

Langmuir Isotherms

gas

Adsorbate A

Solid Adsorbent S

Gas pressure ↓ Volume

$$\underline{A}(g) + \underline{S} \rightleftharpoons \underline{A\text{-}S} \quad -(1)$$

S ↓ Vacant sites

A - S: Adsorbed complex, Occupied sites

● - filled Sites

Surface coverage, $\theta$

$\theta \rightarrow$ fraction of occupied sites.

The Langmuir isotherm is about the gas absorption on a solid surface. So, let us say this is the surface of a solid (slide above) on which some gas molecules are adsorbed. So, these gas molecules, which are being adsorbed on the surface are known as the adsorbate, and the solid surface which is adsorbing them is known as the adsorbent. So, the Langmuir isotherms describe the interaction between the adsorbate and the adsorbent.

It basically describes the relation between the volume of a gas absorbed on a solid surface and the pressure of the gas at constant temperature.

Let us see how these isotherms are derived. According to the Langmuir theory of adsorption, the adsorbent or the solid surface is considered to be a homogeneous surface having specific sites in which the adsorbate molecules can bind. And, the binding of the adsorbate molecules on these sites, that means, the adsorption process is treated as a chemical reaction.

So, if you call the adsorbate as A and this adsorbent as S the chemical reaction can be written as shown below:

$$A_{(g)} + S \leftrightarrow A - S$$

So, here A in gaseous form, is the adsorbate. S basically represents the sites or the vacant sites in which A can get absorbed. And, A-S is the absorbed complex, which basically represents the occupied or filled sites.

So, in the beginning, when the gas is being absorbed on the solid surface some of the sites will be filled and some of them will be vacant which can be represented in this manner (slide above). In the slide above, the red dots indicate the filled sites. So, from here, we can define a parameter called surface coverage, which is generally written as $\theta$ and that is basically the fraction of the occupied sites.

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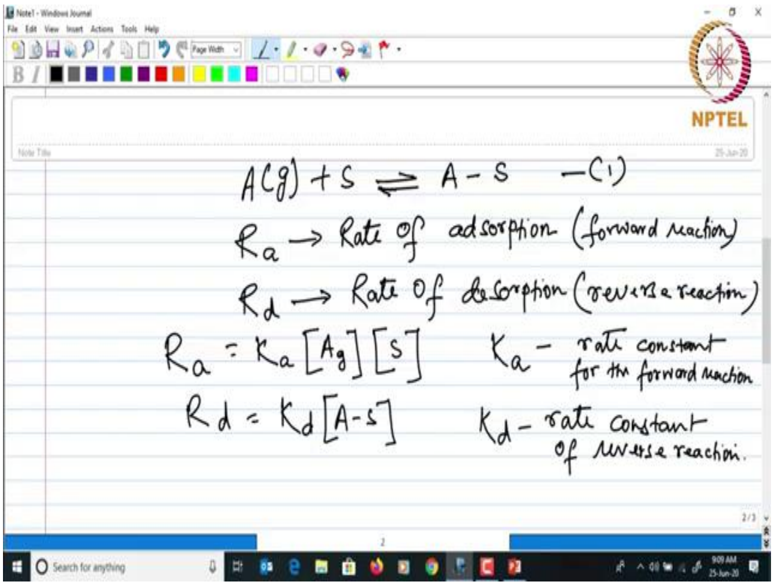

$A(g) + S \rightleftharpoons A-S$ —(1)

$R_a \rightarrow$ Rate of adsorption (forward reaction)

$R_d \rightarrow$ Rate of desorption (reverse reaction)

$R_a = K_a[A_g][S]$ $K_a$ − rate constant for the forward reaction

$R_d = K_d[A-S]$ $K_d$ − rate constant of reverse reaction.

Now, coming back to this adsorption reaction again, the forward reaction is the adsorption process and the reverse reaction is the desorption process. And, each of these reactions will have their own reaction rate. So, let us say the reaction rate for the adsorption process or the forward reaction is $R_a$ and that for the reverse reaction or the desorption process is $R_d$.

And, this rate will be given as below:

$$R_a = K_a[A_g]\,[S] \tag{1}$$

Where $K_a$ is the rate constant for the forward reaction. Similarly, $R_d$ will be given as

$$R_d = K_d[A-S] \tag{2}$$

where $K_d$ is the rate constant of the reverse reaction.

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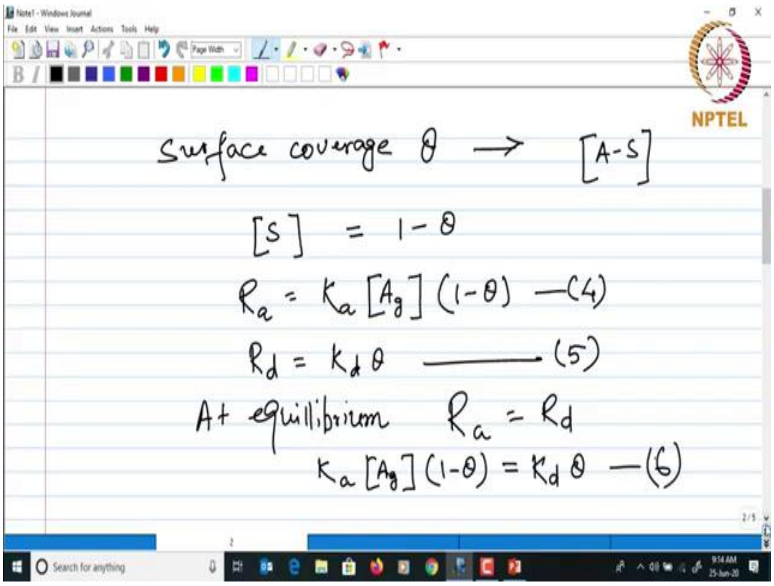

Surface coverage $\theta \rightarrow [A\text{-}S]$

$[S] = 1 - \theta$

$R_a = K_a [A_g] (1-\theta)$ —(4)

$R_d = k_d \theta$ ———— (5)

At equilibrium $R_a = R_d$

$K_a [A_g] (1-\theta) = K_d \theta$ —(6)

The surface coverage, $\theta$, is basically the fraction of occupied sites. So, that can be given by the concentration of the adsorbed complex. And, S represents the vacant sites and therefore, the concentration of S will be given by

$$[S] = 1 - \theta$$

So, therefore, equations 1 and 2 can be written as below

$$R_a = K_a [A_g] \, [1 - \theta]$$

$$R_d = K_d \theta$$

Now, at equilibrium the rate of the forward reaction will be equal to the rate of the reverse reaction and therefore, we can write we can write as below:

$$R_a = R_d$$

$$K_a [A_g] \, [1 - \theta] = K_d \theta$$

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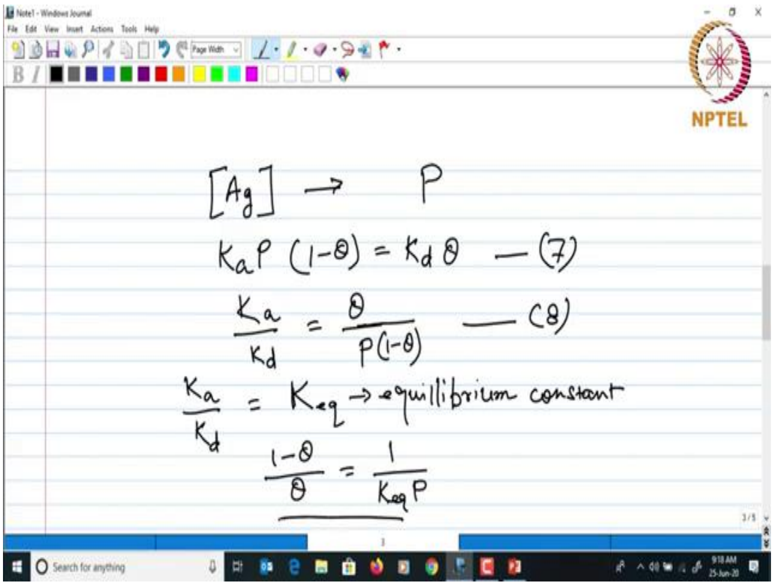

$$[A_g] \rightarrow P$$

$$K_a P\,(1-\theta) = K_d\,\theta \quad \text{— (7)}$$

$$\frac{K_a}{K_d} = \frac{\theta}{P(1-\theta)} \quad \text{— (8)}$$

$$\frac{K_a}{K_d} = K_{eq} \rightarrow \text{equillibrium constant}$$

$$\frac{1-\theta}{\theta} = \frac{1}{K_{eq} P}$$

Now, this concentration of the adsorbate or the gas [$A_g$] is basically the partial pressure or you can say it is proportional to the partial pressure of the gas. And, hence this can be also replaced by the pressure of the gas P and from there we can rewrite the above equation as follows:

$$K_a P\,[1-\theta] = K_d\theta$$

And, if we rearrange this we can write this as follows:

$$\frac{K_a}{K_d} = \frac{\theta}{P(1-\theta)}$$

The term ($K_a$ / $K_d$) is nothing but the equilibrium constant $K_{eq}$. And, therefore, we can write this equation as:

$$\frac{1-\theta}{\theta} = \frac{1}{K_{eq}P}$$

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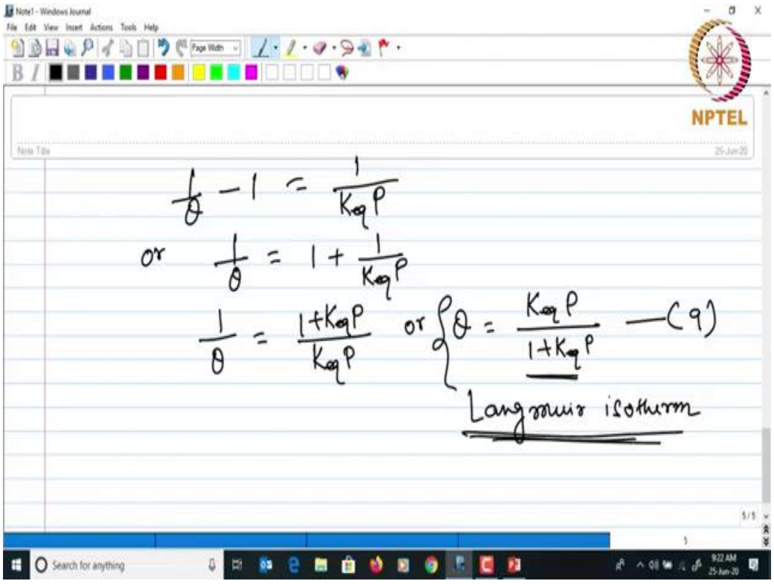

$$\frac{1}{\theta} - 1 = \frac{1}{K_{eq} P}$$

or $$\frac{1}{\theta} = 1 + \frac{1}{K_{eq} P}$$

$$\frac{1}{\theta} = \frac{1 + K_{eq} P}{K_{eq} P} \quad \text{or} \quad \theta = \frac{K_{eq} P}{1 + K_{eq} P} \quad \text{—(9)}$$

Langmuir isotherm

And, we can again rearrange this as this equation below:

$$\frac{1}{\theta} - 1 = \frac{1}{K_{eq} P}$$

So, by all these rearrangement we can get an expression for theta in the form of equation as follows:

$$\theta = \frac{K_{eq} P}{1 + K_{eq} P}$$

And, this is what is known as the Langmuir isotherm.

This equation represents Langmuir isotherm and we can also plot it and you can also see the relationship of θ with the pressure of the gas. So, Langmuir isotherm basically describes the relationship between the volume and the pressure of the gas absorbed on a solid surface.

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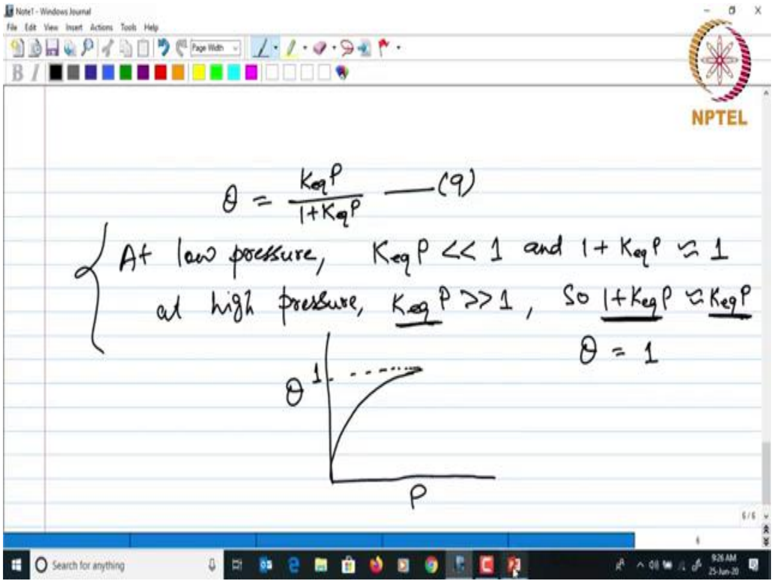

$$\theta = \frac{K_{eq}P}{1+K_{eq}P} \quad \text{—(9)}$$

At low pressure, $K_{eq}P << 1$ and $1 + K_{eq}P \simeq 1$

at high pressure, $\underline{K_{eq}}P >> 1$, So $\underline{1+K_{eq}P} \simeq \underline{K_{eq}P}$

$\theta = 1$

So, we can see that, at low pressure the term, $K_{eq}P$ is much less than 1 and therefore, this can be taken equal to 1. On the other hand at high pressure this is much higher than 1. So, 1 + $K_{eq}P$ becomes approximately equal to $K_{eq}P$, because this is much higher than 1.

So, considering these boundary conditions, if you plot θ as a function of the gas pressure P, it will vary something like this (slide above). So, at high pressure, all the vacant sites are occupied by the adsorbed gas. So, in the beginning, fraction of sites only were occupied, but now as the gas pressure is increased more and more sites will be occupied, and there will be a time at a particular pressure when all the sites will be occupied. So, that is when we say that the surface is saturated and saturated monolayer of the gas has formed on the solid surface.

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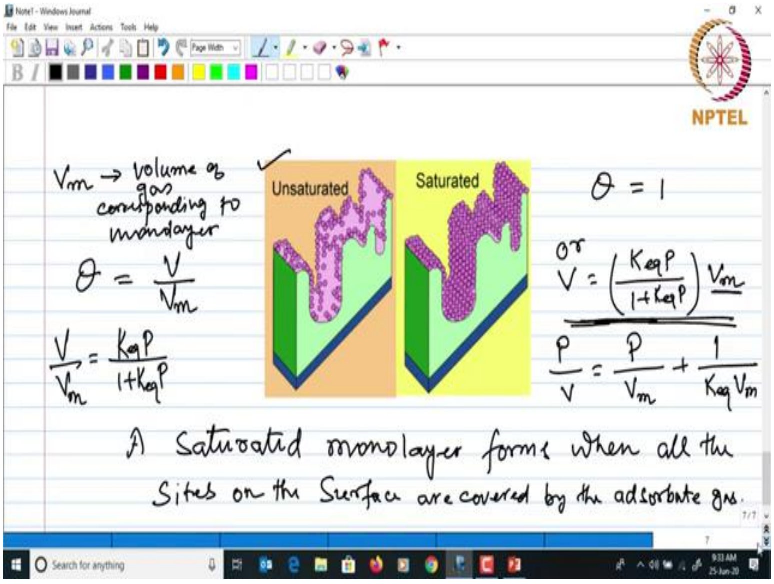

$V_m \rightarrow$ volume of gas corresponding to monolayer

$\theta = \frac{V}{V_m}$

$\frac{V}{V_m} = \frac{K_{eq}P}{1+K_{eq}P}$

$\theta = 1$

or $V = \left(\frac{K_{eq}P}{1+K_{eq}P}\right) V_m$

$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{K_{eq}V_m}$

A saturated monolayer forms when all the sites on the surface are covered by the adsorbate gas.

So, in the beginning only fraction of sites were occupied as we have seen before also. And, now at high pressure all the sites are occupied when θ is 1. And, this is a saturated monolayer formed, which is just one atomic layer thick. And, this is what the Langmuir isotherm basically describes, the formation of a saturated monolayer on an adsorbent surface.

So, we can say that a saturated monolayer forms when all the sites on the adsorbent surface are covered by the adsorbate gas. And, if $V_m$ is the volume corresponding to the formation of the monolayer, then θ can also be written as ($V/V_m$), where V is the volume of the gas and the following equation can be written:

$$\theta = \frac{K_{eq}P}{1 + K_{eq}P}$$

$$\frac{V}{V_m} = \frac{K_{eq}P}{1 + K_{eq}P}$$

$$V = V_m \times \frac{K_{eq}P}{1 + K_{eq}P}$$

This equation relates the volume of the gas to the volume corresponding to formation of a saturated monolayer and from this we can also write it in terms of P upon V.

$$\frac{P}{V} = \frac{P}{V_m} = \frac{1}{K_{eq}V_m}$$

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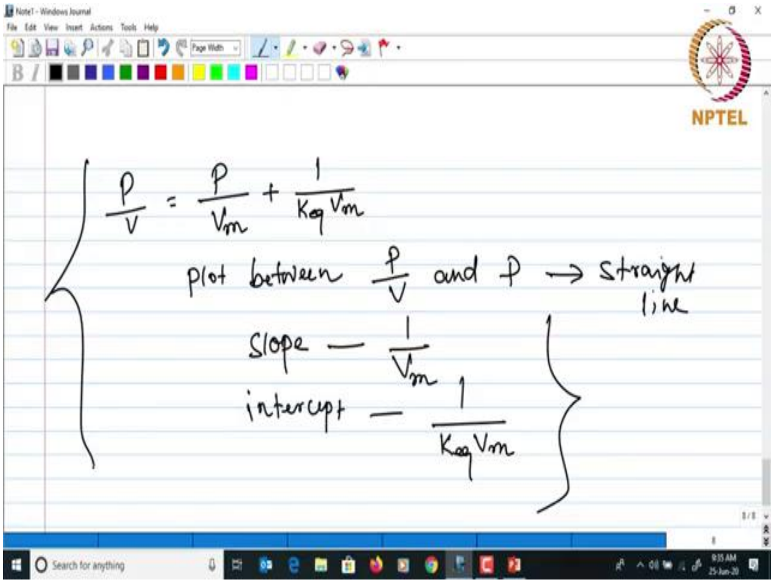

$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{K_{eq}V_m}$$

plot between $\frac{P}{V}$ and P → straight line

slope — $\frac{1}{V_m}$

intercept — $\frac{1}{K_{eq}V_m}$

And therefore, a plot between (P/V) and P will give a straight line, the slope of which is ($1/V_m$) and the intercept is ($1/K_{eq}V_m$). So, this is the Langmuir isotherm which talks about the formation of a monolayer on a solid surface and from that the BET theory can also be explained.

So, in this case we are talking about the monolayer, but this can also be extended to multiple layers, which is actually the case for the BET theory. So, with that we come to the end of this class.

Thank you for your attention.