Powder Metallurgy

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Lecture – 28
Surface Area Analysis - II

Hello and welcome back again to this lecture series on Powder Metallurgy. Right now, we are discussing a very important property of the powder, that is, the Surface Area. And, this is important because the surface area correlates to a range of particle properties which affect various phenomena involving the powder particles including the compaction, and the sintering process in powder metallurgy.

So, when it comes to measuring the surface area, the BET method stands out. And we have seen that the BET method is based on the adsorption of a gas on a solid surface. And with regard to that, we discussed about the Langmuir adsorption theory which basically considers the adsorption process, that is, the binding of the adsorbed molecules on the adsorbent surface as a chemical reaction, where the adsorbent surface is considered as a homogeneous surface in which, this adsorbed molecules attach in specific sites.

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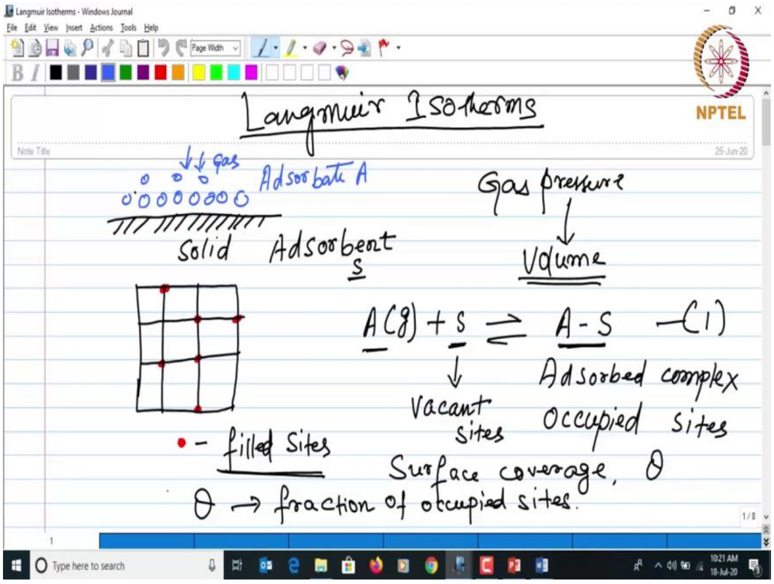

And from that we derived the surface coverage, and from that we have derived an equation or an isotherm which correlates the amount of gas which is adsorbed on the solid surface to the gas pressure. And ultimately, this forms the basis of the BET technique.

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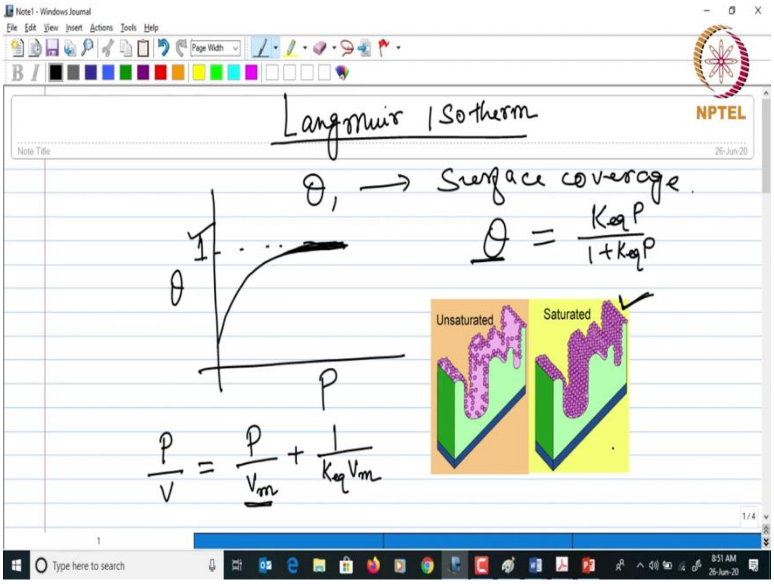

Langmuir Isotherm

θ, → Surface coverage.

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

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

In the last class we learned about the Langmuir isotherm, which basically talks about the formation of a monolayer on a solid surface when the gas is being adsorbed on the surface. The surface coverage was defined by a parameter called θ. And then we derived the isotherm and saw that θ increases with P, and then ultimately, it saturates when θ becomes equal to 1. The corresponding equation for this isotherm is given below:

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

So, when it saturates and θ becomes 1; that means, the entire surface is covered by the gas molecules and a monolayer is formed. And that can be depicted by this picture (slide above). So, in the beginning, the gas molecules are adsorbed on the solid surface at specific sites and that is how we define θ as the surface coverage; which basically talks about the adsorption of these molecules on specific sites on the adsorbent surface.

Now, as the pressure increases more and more of the gas molecules get adsorbed on the surface and then at some point it saturates when θ becomes 1.

And from this we have also derived the equation (above) which correlates the pressure with the volume and that equation is given below

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

So, here V_m is the volume of the gas corresponding to the formation of the monolayer.

The BET surface area is basically an extension of the Langmuir isotherm, wherein instead of a monolayer, the layers beyond, that means, formation of multi-layers is considered and this isotherm equation is modified accordingly, and this modified equation can be used to calculate the specific surface area. But before we come to that let us also have a look at the different types of isotherms.

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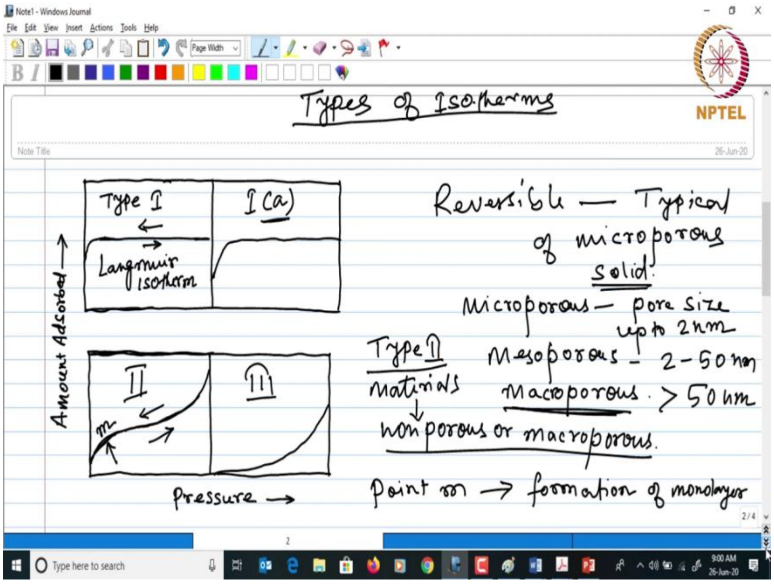

Types of Isotherms

Reversible — Typical of microporous solid.

Microporous — pore size upto 2nm

Mesoporous - 2-50 nm

Macroporous . > 50 nm

Type II materials → nonporous or macroporous.

Point m → formation of monolayer

So, depending on the interactions between the adsorbent and the adsorbate, there could be different types of isotherms. There are basically 6 types of isotherms depending on the interactions (slide above).

Type I is basically the Langmuir isotherm. And this is also reversible type which is typical of micro-porous solid surface. So, this interaction between the adsorbent and the adsorbate will depend on the condition of the surface specially with regard to the porosity. And in terms of the porosity the solids can be categorized into different categories depending on the size of the pores. It is called micro-porous when the pore size is up to 2 nanometers. If the pore size is from 2 to 50 nanometers, that is known as meso-porous. And when the pore size is more than 50 nanometers, that is known as a macro-porous solid. So, this is how the solid surface can be categorized based upon the size of the pores.

Type Ia is describes the materials with wider micro-pores and narrow meso-pores. So, the first type, that means, type I is typical for materials with pore width around 1 nanometer and Ia is for materials where the micro-pores are wider and they also have narrow meso-pores less than about 2.5 nanometers.

Type II is also a reversible type isotherm as shown by the arrows (slide above). And this kind of isotherm corresponds to materials that are non-porous or macro-porous. Here you can see a bend over here at this point (slide above), let us say we call this point m. So, that point m basically corresponds to formation of a monolayer. And when the monolayer coverage is completed the curvature is changed as you could see from here, and it becomes quite steep as opposed to a gradual change over here till the monolayer is formed. So, this indicates the formation of multi-layers, when it goes beyond the monolayer and then the curvature starts to change, this is indicative of the beginning of the multi-layer adsorption process.

Type III isotherm is formed when the interaction between the adsorbent and the adsorbate is weak.

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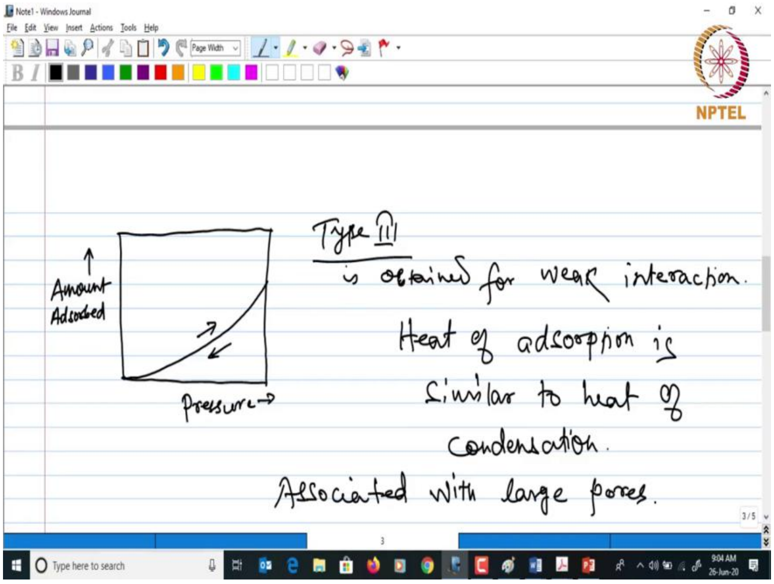

Type III
is obtained for weak interaction.
Heat of adsorption is similar to heat of condensation.
Associated with large pores.

Here the interaction between two adsorbate molecules approaches that between the adsorbate and adsorbent, which also means that the heat of adsorption is similar to the heat of condensation. So, therefore, for this kind of interaction a significantly high partial pressure of the gas is required for the adsorption to happen. And this kind of isotherm is associated with large pores.

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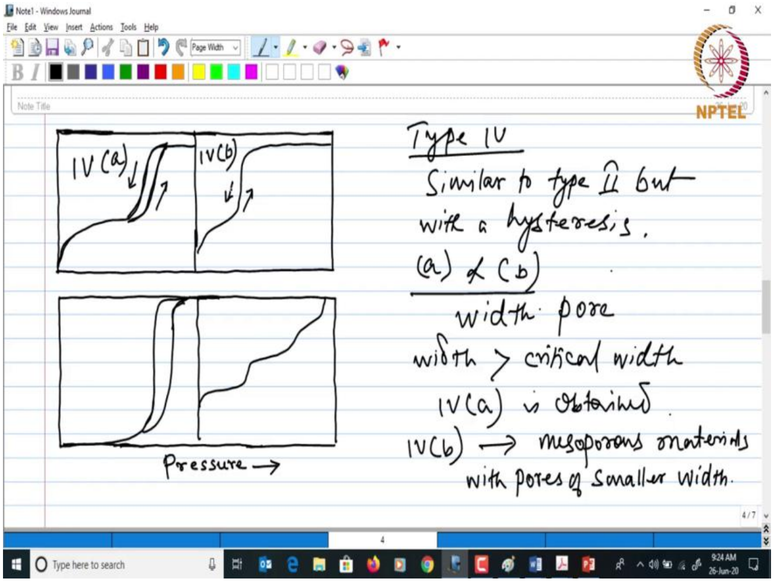

Type IV

Similar to type II but with a hysteresis.

(a) & (b)

width pore

width > critical width

IV(a) is obtained.

IV(b) ⟶ mesoporous materials with pores of smaller width.

Type IV (slide above): It is a variant of type II with hysteresis. And these two types that you have here a and b, are basically related to the width of the pore which is present on the surface of the adsorbent. If the width is higher than a critical width which is related to the materials adsorption characteristics and temperature, IVa type is obtained. And on the other hand, type IVb is observed for materials having meso-pores of smaller widths.

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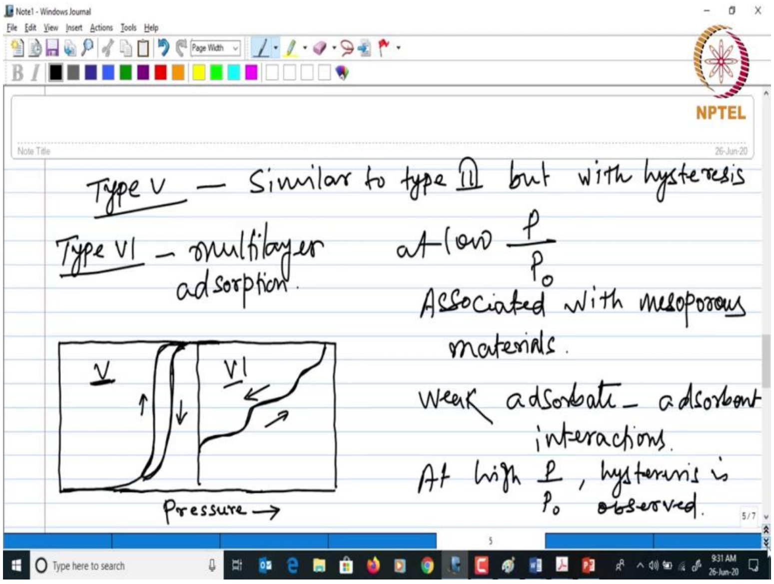

Type V — Similar to type III but with hysteresis

at low $\frac{P}{P_0}$

Associated with mesoporous materials.

Weak adsorbate – adsorbent interactions.

At high $\frac{P}{P_0}$, hysteresis is observed.

Type VI – multilayer adsorption.

Type V is similar to type III with hysteresis. This kind of isotherm is found at low relative pressure and is associated with meso-porous materials. And this shape of the isotherm can be attributed to the weak adsorbent-adsorbate interaction. So, here also the interactions between the adsorbate and the adsorbent are weak. At high relative pressure, the hysteresis can be observed. And here molecular clustering is followed by the filling of pores or the capillary condensation. So, that is associated with this kind of isotherms of type V.

Type VI isotherm is typical for multi-layer adsorption or materials which have highly uniform nonporous surfaces. And the curve that you can see over here (slide above) is like steep shaped curve, and each of these steps corresponds to a monolayer and the nature of the curve will depend on the material the gas and the temperature.

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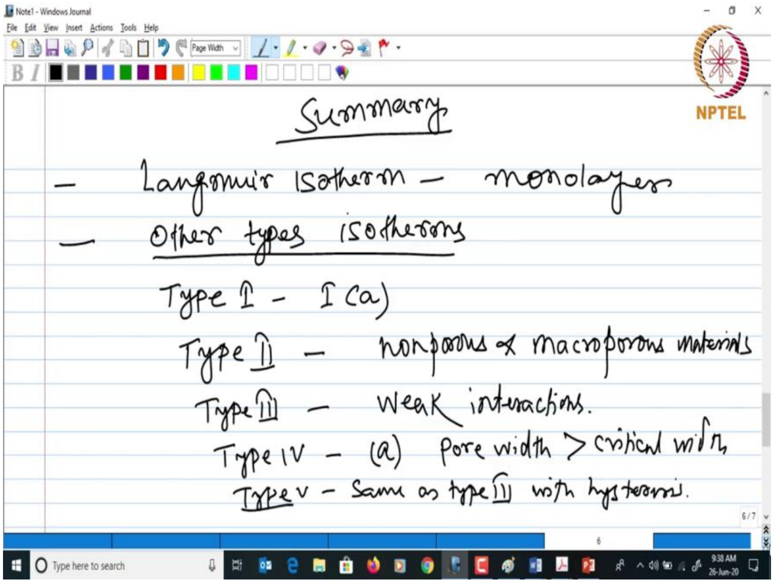

Summary

- Langmuir isotherm – monolayer
- Other types isotherms

Type I – I (a)

Type II – nonporous & macroporous materials

Type III – weak interactions.

Type IV – (a) Pore width > critical width

Type V – Same as type III with hysteresis.

Let us take a moment to summarize this lecture. So, in this lecture apart from the Langmuir isotherm, which represents formation of a monolayer, we have also seen other types of isotherms. Depending on the physicochemical interactions there could be different types of isotherms.

Type I in which you have two types I and Ia. Type I is basically the Langmuir isotherm and corresponds to materials having pores with small width in the range of about 1 nanometer. And the second category of type I, that is, Ia is typical for solids which contain both wider micro-pores and narrow meso-pores in the order of about less than 2.5 nanometers.

Type II isotherm, corresponds to materials which are non-porous or macro-porous and in this case we had seen an inflection point m, which indicates the monolayer coverage and beyond that point, the multi-layer adsorption starts to happen.

Type III isotherm is obtained when the interactions are weak. And in this case, the interaction between two adsorbed molecules; in fact is similar to the interaction between adsorbent and the adsorbate or sometime may be even higher than the interaction between the adsorbate and the adsorbent.

Type IV, we have two categories a and b. When the width of the pore is greater than a critical width type IVa is obtained, and type b is typical of meso-porous materials having pores with smaller widths.

Type V, plays same as type III with hysteresis. And in this case, at higher relative pressure the hysteresis is observed and one typical characteristics of this kind of isotherm is molecular clustering, and pore filling or capillary condensation.

And then finally, we talked about type VI, which has a step like isotherm and here each of the steps represents a monolayer coverage. So, this is typical of multi-layer adsorption.

So, with that we come to the end of this class.

Thank you for your attention.