

## surface third cut

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(0:00 - 0:36)

Now we always talk about experimental isotherms and so on. But now we need to understand what are the mathematical models that are behind these isotherms. And so we have to start in absorption theory, in which we describe experimental isotherms with specific mathematical equations.

(0:42 - 1:17)

We have to say that all the models that we will see, we will face, are semi-empirical equations that consider very simple models for absorption. So for each of these models that were developed, that was developed, a lot of assumptions were made, because without assumptions we cannot obtain the mathematical model. But this is the best that we have at the moment to describe our answer.

(1:18 - 1:39)

We will talk about mainly three models. The simplest one, that is the Harry Isotherm. Then the two main ones, the main models that are the Langmuir model and the LVT model.

(1:41 - 2:02)

Then there are other models that were developed, but in this course we will face just these three models. So let's start from the simplest one, that is called the Harry Isotherm. It is the simplest absorption isotherm.

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And this equation says that the amount of gas absorbed is the surface excess amount changes linearly with the pressure. And this occurs only when we are at small values of pressures. In which  $k_H$  is called, the  $k$ , the energy is constant.

(2:34 - 2:50)

Here is the list of the assumptions that Henry did to develop this equation. I won't show you how to derive the equation. I show just the equation and these are the assumptions, that are very strong assumptions.

(2:50 - 3:02)

The value of very low surface excessive concentration. The absorbent volumes are independent from each other. Homogeneous to have a homogeneous absorbent surface.

(3:02 - 3:24)

This is just an ideal situation. And so on. In some way we can use the Harry equation to describe an isotherm when we are at low values of pressure.

(3:26 - 4:19)

In this sense. Also if we consider a type I isotherm, like this, there will be a region, very low, if we make a zoom of this, in which we can consider that the amount of gas absorbed changes linearly with the pressure. But this model can be applied just when we are in this very low range of pressure.

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Let's consider that this is the amount of gas absorbed as a function of the pressure, that changes linearly with the pressure at low value of pressure. Then if we increase the pressure, what happens is that we have, so the case of Harry is a sort of ideal case, but when we increase the pressure, we can consider the real cases that are the Langmuir isotherm or the Etian isotherm that are not more linear like the Harry's one. So, at low value of pressure, we basically can consider that each isotherm follows this mathematical equation.

(5:19 - 6:08)

And for sure the constant of Harry at low values of pressure will give us an idea of the strength of interaction between the absorbent and the adsorptive. Indeed, the higher the Harry constant for the specific isotherm, the higher would be the interaction strength between the adsorptive and the adsorbent. Then, the following model was developed by Langmuir, and Langmuir developed a model that was able to describe very well the type I isotherm.

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Indeed, the type I isotherm is also called Langmuir type isotherm. We will find type I for Langmuir isotherm. But to develop this equation, Langmuir made a lot of assumptions.

(6:40 - 7:02)

Here are listed the assumptions from the development of the model, again very strong assumptions. Adsorption is localized, means that it is localized on specific sites on the surface. All the adsorption sites are equal on a real surface.

(7:02 - 7:11)

This is not true, for sure. No interaction among adsorbent molecules can occur. So, when the molecules are adsorbed, they don't interact.

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Also, this is a very strong assumption. No change in interaction energy with coverage. So, if you change the coverage, the amount of gas adsorbed, if you increase the amount of gas adsorbed, the interaction strength is always the same.

(7:26 - 7:38)

And, each site adsorbs a single molecule. This is one of the strongest assumptions Langmuir says. For each site, just one molecule.

(7:40 - 8:11)

The last one, and maybe most important, is that Langmuir says that the monolayer formation takes place and that the adsorption stops at the monolayer formation. This is what Langmuir says. The adsorption on a plane surface having only one kind of elementary space and in which each space can hold only one adsorbed molecule.

(8:11 - 8:28)

And, at the end, I take a monolayer. So, it means that, for Langmuir, the multilayer adsorption cannot exist. The adsorption stops when we form a monolayer on the surface.

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But, now we know that it is not true. In any case, the equation that he developed considering this assumption was very useful to describe, mathematically, the type I isotherm. Indeed, the type I isotherm is often used to describe chemisorption phenomena where, indeed, the adsorption stops at the monolayer formation.

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But, the model developed by Langmuir was very important. He was awarded the Nobel Prize for his theory. But, it was very important.

Why? Because, from his model, Brunauer and Macintyre, some years later, were able to develop the new theory on multilayer adsorption, starting from the question of Langmuir. In the following slide, I just will briefly show you how, considering that the Langmuir theory is the most important theory on adsorption, I just briefly show you how Langmuir obtained the equation, the final one. But, at the exam, I will not ask you how to obtain the isotherm, the question.

(10:16 - 10:47)

I can ask you the final equation and you should be able to tell me what type of isotherm describes and which are the assumptions on which his theory is based. But, in any case, let's see. To develop his equation, Langmuir used a kinetic approach in the sense that he says that the adsorbent surface is made of an equivalent array of independent sites, the assumption that

he did, for localized adsorption.

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Localized means that one molecule for one site. And, when we perform adsorption, he says that we reach at a certain moment a dynamic equilibrium, in the sense that when we have a dynamic equilibrium, the rate of molecules striking and adsorbing to each unit area of the surface is equal to the rate at which the adsorbed molecules leave each unit of the surface. This condition was called by Langmuir dynamic equilibrium.

(11:31 - 12:46)

He defined  $\theta_1$  as the fraction of occupied sites on the surface and  $\theta_0$  as the fraction of free sites and the sum of  $\theta_0$  and  $\theta_1$  is always equal to 1. The fraction of occupied sites is given by the number of adsorbed molecules and the ratio between the number of adsorbed molecules and the available surface sites because he considered that for each molecule adsorbed, for each site we have a single molecule adsorbed. And so, saying that the rate of adsorption is equal to the rate of desorption, Langmuir derived the two rates, the rate of adsorption array and the rate of desorption to each unit of area of the surface. And the two rates are given by these two equations in which the different parameters are reported here.

(12:49 - 13:03)

And so, we can read them.  $A_1$  is the condensation coefficient representing the probability of a molecule being adsorbed at one position on the surface.  $\theta_0$  is the fraction of free sites defined here.

(13:04 - 13:25)

$P$  is the pressure.  $K$  is a parameter that contains all these parameters from gas kinetic theory and is the kinetic constant.  $K$  multiplied by  $P$  for the pressure is the number of molecules that hit the surface in the unit of time.

(13:27 - 13:56)

The rate of adsorption instead is given by  $z \cdot \theta_1$  which is the number of sites per unit area.  $z$  multiplied for  $\theta_1$  that is equal to  $z$  is the total number of adsorbed molecules per unit area.  $D_1$  is the number of molecular vibrational frequencies perpendicular to the surface.

(13:56 - 14:07)

$Q$  is the adsorption heat. So, there is something that is related to the heat of adsorption. So, the activation energy for adsorption.

(14:08 - 14:46)

This parameter is the probability of adsorbed molecules possess adequate energy to overcome the attractive potential of the surface to be adsorbed. And all these together,  $\theta_0$  multiplied for this is the number of adsorbed molecules per unit area with an energy equal to that required for the adsorption. But as I told you, it is not important that you know just the final equation.

(14:48 - 15:14)

So, at the equilibrium, at the dynamic equilibrium, we can say the two rates are equal. So, we can say that they are equal. And considering that  $\theta_0$  that is defined here is given by  $\theta_1$  minus  $\theta_1$ , we can obtain by substituting  $\theta_0$  here, this.

(15:15 - 16:14)

And then we can explicit everything as  $\theta_1$  and obtain this. And by considering that this parameter  $B$  is equal to all these, but the assumption implicit in this equation is that as we saw, we said before that the adsorption heat  $Q$  is constant, and so we have an energetically uniform surface, that is one of the assumptions of Langmuir. And considering that  $\theta_1$  can be also explained like this, so  $\theta_1$  that is the fraction of occupied site is given by the ratio between  $V$  and  $V_m$ , in which  $V$  is the volume of adsorbed gas in standard pressure-temperature condition per gram of adsorbent, that is called the coverage.

(16:14 - 17:01)

And  $V_m$ , what is the adsorption, the monolayer capacity that we already defined, the volume of adsorbed gas in STP per gram of adsorbent at the monolayer. And so at the end, if you make all the substitutions, we arrive at the final equation of Langmuir, that is this one, that is  $\theta_1$  equal to  $P$  over  $V_m$ ,  $V$  the volume of adsorbed per gram of adsorbent at the end is the monolayer capacity, that is equal to  $B$  multiplied by  $P$  ratio over  $1$  plus  $B$ , in which  $B$  is this parameter that is an energetic parameter that contains the heat. This is important.

(17:02 - 18:26)

$B$  is called the Langmuir constant, and it is a parameter that is related to the heat of adsorption, so to the strength of interaction, but that we will understand better. And so this equation can be represented in this way, so this is the equation of a type I isotope, I described the type I isotope. And in particular, if the pressure tends to  $0$ , if this becomes  $0$ , you obtain at the end the air is low,  $V$  equal to  $V_m B P$ , that is basically  $V_m$  multiplied by  $P$  is the air rate constant, so at low value of pressure we have a linearity between the amount of gas adsorbed and the pressure, if  $P$  tends to infinity, we reach a plateau that corresponds to the completion of the monolayer  $V_m$ , when  $\theta_1$  is equal to  $1$ . And this is the equation that Langmuir developed.

(18:27 - 19:57)

But if from this equation we write this equation in linear form, I don't show you how you can

change this equation from here to here, but you can do, and then you can find also I think online if you want, but I think during the course that I followed, my professor did everything at the board, filling tens of these boards with calculations, but I think that in this course, in these hours we cannot face this. We can change this equation from this form to this form that is called the linear form of the Langmuir equation, linear in the sense that if I plot  $P$  over  $V$  as a function of the pressure, I obtain a line in which  $1$  over  $V$  multiplied by  $V_m$  is the intercept and in which  $1$  over  $V_m$  is the slope of the line. You can imagine that from the equation in this form, if I know the experimental values of pressure and volume of gas absorbed, we are able to derive what the monolayer capacity  $V_m$  and the constant  $V$ , that are two very important parameters.

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And if I am able to derive the monolayer capacity from this equation, I am able to calculate the specific surface area, if you know, by applying the equation that we saw at the beginning, the specific surface area is given by the monolayer capacity multiplied for the adobo quadro constant, multiplied for the molecular cross-sectional area, but we have to consider also that there is this parameter that is useful because the molecular cross-sectional area is given in Ohmstrom, square Ohmstrom, at the end we want our surface area in square meter, so this is just a number that is useful to the conversion of square Ohmstrom in square meter, and then we have the molar volume because we are considering the amount of gas absorbed in STP and the mass of the sample. And so, from the Langmuir equation we can derive  $V_m$  and we are able to calculate the specific surface area by applying this equation. In general, Langmuir equation describes very well the type I isotherms and often it describes very well isotherms that are collected during the absorption because we have the formation of a single monolayer, they usually have the shape of the type I isotherm, but it fails to generally describe the physical absorption because we know that the physical absorption doesn't stop at the monolayer but it continues in a multilayer way.

(21:58 - 22:48)

Usually, if we calculate the surface area starting from the Langmuir equation, we calculate  $V_m$  starting from the Langmuir equation, we obtain uncertainties because it is difficult to determine the molecular cross-sectional area at the monolayer. And so, the data that you obtain from the Langmuir model are not so reliable. But when we consider physical absorption, type I isotherm is associated with the pore filling of materials with micropores.

(22:50 - 24:14)

In general, in any case, this is an equation that is developed considering a lot of assumptions and was the basis for the development of the following models, that is the BET model that we will see, and from which usually we calculate the monolayer capacity for the evaluation of the specific surface area. During the lab, I will show you how you will try to make the calculation of the specific surface area of a material starting from the experimental isotherm and by deriving

the monolayer capacity applying the BET equation that we will see, not the Langmuir one, but if you want you can do it also starting from the Langmuir equation. What is important, I don't know, it's time to finish, just to briefly to finalize, the parameter B that is present in the Langmuir equation, that is a parameter that contains the heat of absorption Q, is a parameter that is very important because it says how strong is the interaction between the molecule and the surface.

(24:17 - 25:39)

We consider that B increases if the temperature decreases and increases if the absorption interaction strength increases. Look at these isotherms, these isotherms are collected in different conditions and you see that they have a different slope at the beginning, they are all type I, but with a different slope at the beginning of the Q. The B constant of the Langmuir equation increases in this sense, so the higher the B constant, the higher will be the slope of the isotherm and so it will mean that if the slope of this isotherm is higher, it means that the interaction between the absorbent and the surface is higher, the interaction strength in this case is lower. So by looking at different isotherms you can understand, by looking at the slope of the isotherm, of the type I isotherm, you can say ok, in this case the interaction strength is higher than in this.

(25:39 - 26:12)

Why? Because the Langmuir equation contains this parameter B that contains Q, that is the heat of absorption and so on. The parameter B gives us information about the interaction strength of the molecule in the surface. But next time we will come, it starts again from here.

(26:20 - 27:37)

I think that we will do that in two weeks, March, yes? Pay attention that you have to fill in the Langmuir's cell file. We are in 5I plus 4I, at least until we get to Brugliasco it will be a little different, but here is a small place so we have to adapt. Thank you very much.

(28:11 - 28:49)

Thank you. Goodbye.

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