Particle Characterization

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Module No. # 5

Lecture No. # 14

Interfacial Characterization

Welcome to the fourteenth lecture in our particle characterization course. In the previous lecture, we discussed structural characterization of a particle and pointed out that, essentially, the structure of a particle can be divided into three regions - the surface, sub-surface and core. Of the three, the core is the purest representation of the material itself, including its defects and so on. The sub-surface is the region, that shows, a fairly gradual transition between the surface and the interior of the particle. But the surface region is really, is the one, that is most exposed to the exterior environment. The external surface represents the planar, or actually, as we saw, the volumetric interface between the particle and the fluid in which it is immersed. And therefore, from the viewpoint of how a particle interacts with its surroundings, the surface really plays the most crucial role.

And therefore, it is important to understand, certain surface properties of particles. So, in this lecture, we are actually going to look at three of them - surface energy, intermolecular forces of adhesion and adsorption of fluids. These are probably, the three most key characteristics, of how the surface of a particle interacts with its neighbors, as well as the medium in which it is suspended. Now, the first aspect, surface energy. It is something that, it is a term that we hear frequently. Surface energy, surface free energy, or even surface tension; they all mean the same things. Now, surface tension of a fluid is something that you are all quite familiar with, from your lessons in fluid mechanics and so on. But particles, whether solid or liquid droplets, also have a surface energy associated with them.

Now, the surface energy can be defined as the energy that is leftover, when the particle is created. In other words, the higher the surface energy of a particle, the greater is its tendency to react with its environment, because, it is in an energized state. Just like a low surface tension fluid, tends to have very little interaction with surfaces that it comes in contact with, similarly, a low surface energy particle or droplet, will be relatively inert, compared to a high surface energy particle. Now, this has interesting implications for the manufacturing industry; because, sometimes, you want particles that are highly energized, that have high surface energy, and sometimes, you want particles that have relatively low surface energy; it all depends on, whether you want the particle to remain as an isolated particle and not interact heavily with its environment, or, you actually want the particle to behave in a cohesive manner with its nearest neighbors, as well as the fluid molecules that it comes in contact with.

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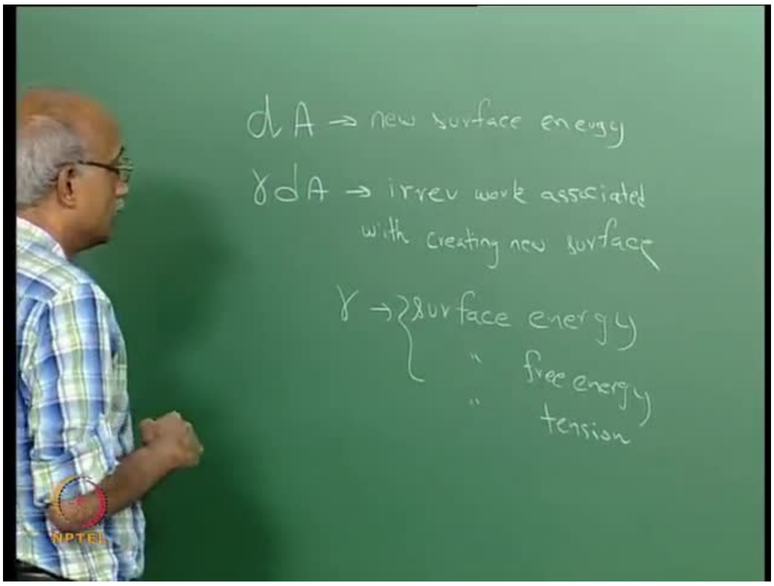

$dA \rightarrow$ new surface energy

$\gamma dA \rightarrow$ irrev work associated with creating new surface

$\gamma \rightarrow$ surface energy
" free energy
" tension

So, the definition of this surface energy parameter is something that we need to be aware of. The surface energy definition goes back to creation of the particle surface; what is the irreversible work involved in creating a surface. This energy, is what is referred to, as a surface energy of the particle. So, if we look at the creation of, let us say, a surface, d A of a particle, a differential surface d A. So, this is the new surface that is created.

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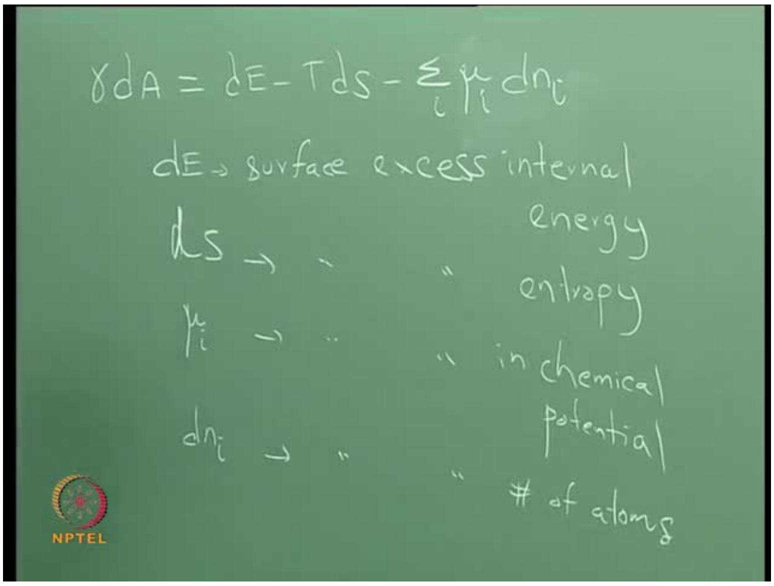

$\gamma dA = dE - Tds - \sum_i \mu_i dn_i$

$dE \rightarrow$ surface excess internal energy

$ds \rightarrow$ " " entropy

$\mu_i \rightarrow$ " " in chemical potential

$dn_i \rightarrow$ " " # of atoms

Then, gamma times d A is the irreversible work associated with creating a new area, or new surface, where this parameter gamma, now, is the surface energy, or surface free energy, or surface tension, associated with the particle. So, what is this gamma d A equal? Thermodynamically speaking, this equals d E, minus T d s, minus summation over i of n i d mu i, mu i d n i, where this parameter d E is termed the surface excess internal energy; d s is the surface excess entropy; mu i is the surface excess in chemical potential and d n i is the surface excess in number of atoms. So, this thermodynamic relationship gives us the context, in which you relate surface energy with parameters such as, internal energy, entropy, chemical potential and also number of atoms that are on the surface.

When you talk about excess, what we mean is, the delta between these values at the surface, compared to their values in the bulk of the material. As we will see when we discuss nano-particles, the reason that nano-particles get their properties, is because, in a nano-particle, the differential can be quite high; a nano-particle tends to have many, many more of its atoms on its surface per unit area, compared to larger particles. And, that is the reason, why nano-particles are so much more reactive, compared to larger sized particles.

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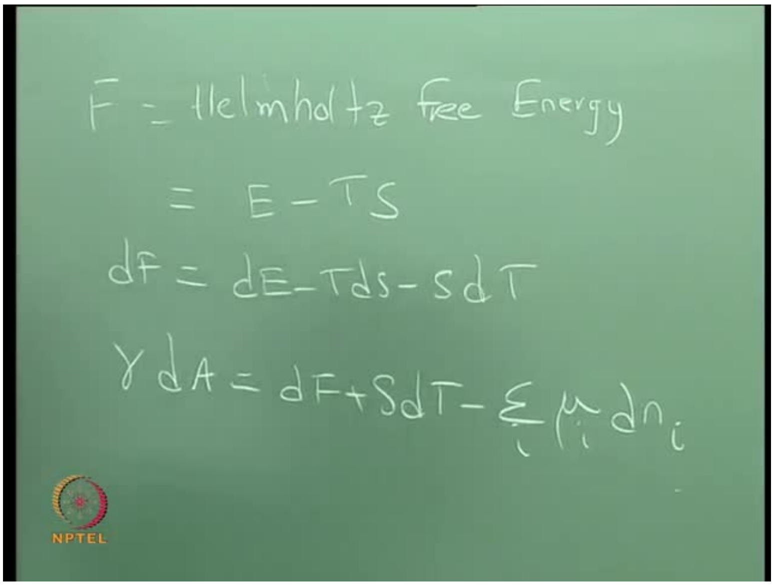

But, it basically goes back to this equation. Now, there is a parameter called the Helmholtz free energy F, which is related to the internal energy by E minus T S, or in other words, we can write, d f equals d E minus T d S minus S d T. So, you can go back to this equation for gamma d A, and substitute, in terms of the, Helmholtz free energy and you will get d E minus T d S equals d F plus S d T minus summation over i mu i d n i; from this, the definition of free energy follows.

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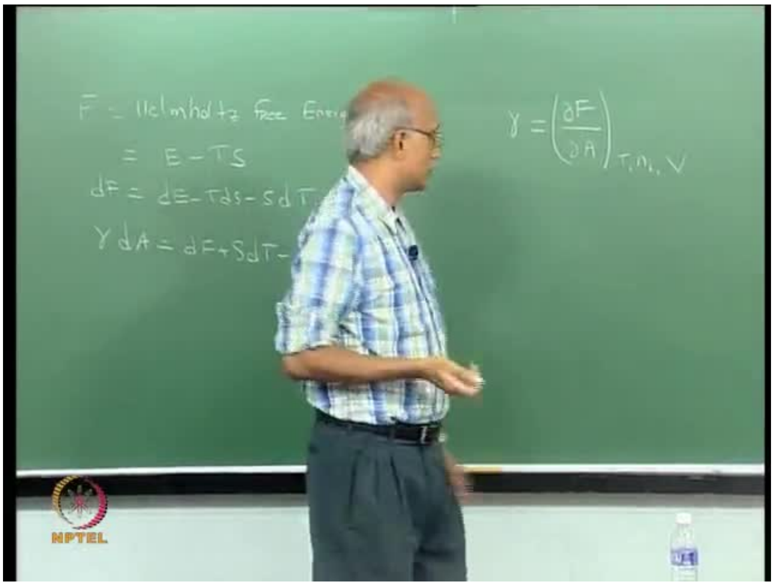

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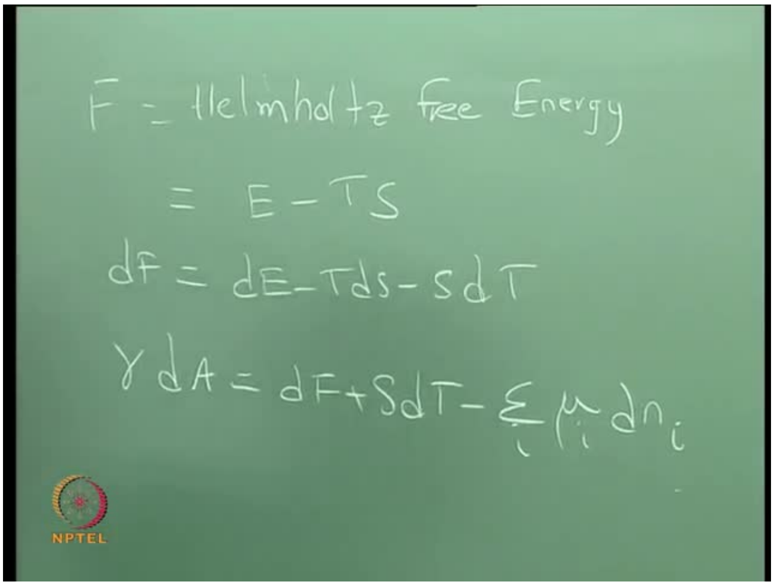

F = Helmholtz free Energy

$$= E - TS$$

$$dF = dE - Tds - sdT$$

$$\gamma dA = dF + SdT - \sum_i \mu_i dn_i$$

So, gamma is defined as del F over del A at constant T, constant n i and constant volume. So, when you keep the temperature constant, this term drops out; the S d T term drops out, and when you keep n i constant, this term drops out. And, the requirement of constant volume basically, refers to the fact that, you are essentially, considering a volume, which comprises of the particle and the fluid, which is in interfacial contact with that particle. So, this is the conventional definition of Hamaker constant.

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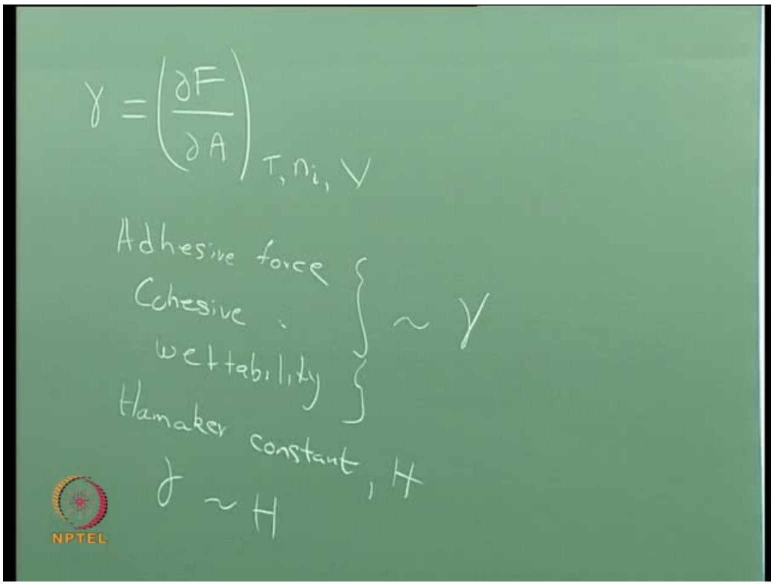

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{T, n_i, V}$$

$$\left.\begin{array}{l}\text{Adhesive force}\\ \text{Cohesive}\\ \text{wettability}\end{array}\right\} \sim \gamma$$

Hamaker constant, H

$$\gamma \sim H$$

And, this is used in a theoretical sense, to calculate gamma, if you know the free energy, the Helmholtz free energy associated with the formation of the particle. Now, in an experimental sense, this is not how you determine surface energy of a particle. The surface energy of, of a particle, just like the surface tension of a liquid, is really determined by looking at how it interacts with the fluids and other particles in its, in its vicinity. So, for example, if you have a high gamma particle, and you bring a surface in contact with it, the sticking coefficient or the adhesion force, is going to be very high. Similarly, if you take a high gamma particle, and you bring another similar particle close to it, again, the inter-particle cohesive force, is going to be very high.

So, forces such as adhesive force, cohesive force, actually, scale as gamma; as gamma values increase, these forces of inter-particle interaction, as well as particle to surface interaction, will increase. And, of course, correspondingly, the wettability of the surface of the particle, when it is interacting with the fluid, will also increase. So, the, the higher the surface energy of the particle, the more likely it is that, you will get good wetting of that particle by a surrounding fluid. Again, the, the counterpart to that, if you think in terms of liquids, if you have a high surface tension liquid, then, it is likely to have good contact with the surface that it is spread on; whereas, a low surface tension liquid will tend to bead up. So, surface energy for a particle plays the same role, as surface tension for a liquid, in, in many ways.

There is a parameter called the Hamaker constant, which we will look at, in more detail, later on. The Hamaker constant is one, that is used to describe intermolecular or inter-particular forces, under conditions, where only the molecular level interactions are present. In other words, there is no surface tension forces; there are no capillary forces. In that case, in the so called, dry state, it is only the Van der Waal's' forces that are in effect, and they can be represented by this Hamaker constant H. And, we will see later on that, there is also, a one on one relationship between surface energy and the Hamaker constant. As the surface energy increases, the Hamaker constant tends to increase, and as the Hamaker constant increases, there is a corresponding increase in the inter-particle forces of adhesion, in a dry state. So, when we are looking at various materials, and ranking them, with respect to their adhesion potential, the Hamaker constant is usually taken as a reference value, because, it has a, such a close relationship to the surface energy parameter gamma.

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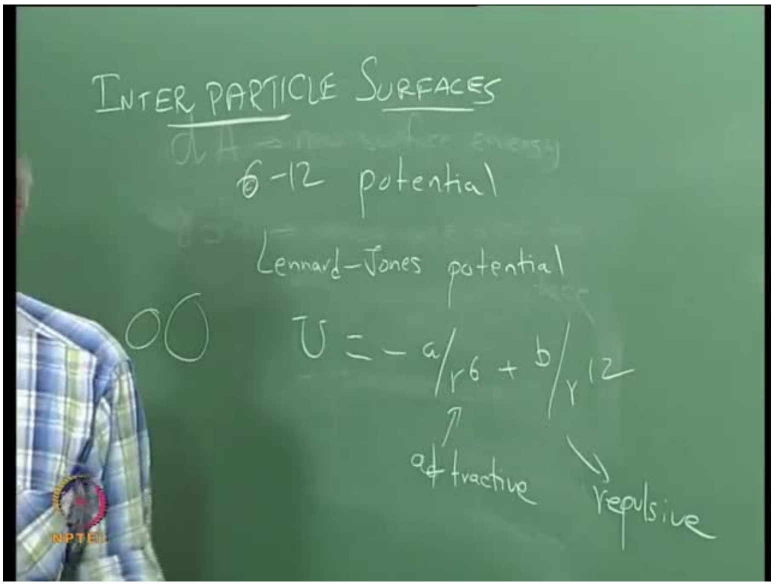

That leads into our discussion, of what we mean by the intermolecular forces. In our context, let us call them inter-particle forces. Again, the differentiation between molecules and particles is very fuzzy. A particle is basically, an aggregate of molecules and it is really up to you to define, when you stop calling something a molecule, and start calling it a particle. But, many of the discussions that we are going to have, apply equally well, to molecular interactions and to particular interactions. Now, when you have two solid objects, whether they are molecules, or particles, or even two liquid objects that are discrete entities, when you bring them close together, they experience two kinds of forces, adhesive force and repulsive force, right.

Now, so, what happens is, the, the two particles, as they approach each other, are experiencing these two opposing forces. So, eventually, they will reach a state of equilibrium, that represents minimum overall force or potential on these particles. That is considered the equilibrium position, and the two, the two droplets or particles, will then essentially, sit at these positions and kind of oscillate, right. Or, if you have a surface that a particle is approaching, the surface will remain stationary; the particle will establish an equilibrium position above the surface, and then, will essentially, vibrate around that position. So, this equilibrium position, at which you have a minimum in the intermolecular energy potential, is a key parameter, that dictates how close the surface can approach each other, and this has huge implications in, again, in many manufacturing industries, that rely on maintaining a certain space between two virtually contacting surfaces.

The inter-particular interaction in the dry state is also called the 9, 6 12 potential. It is also known as the Lennard-Jones potential and it basically says that, if you have two particles that are next to each other, the potential that they develop between them, can be written as minus a by r to the power 6 plus b by r to the power 12, where this is the attractive component and this is the repulsive component. Because, the reason they are called the 6 12 potential because, is, because of the exponents of r in this equation. The adhesive force, or the attractive force, will fall off as the sixth power of the distance between the surfaces; whereas, the repulsive force will fall off as the twelfth power. So, what that means is, as the two surfaces move farther apart, the attractive force becomes more predominant; whereas, as they move closer together, the repulsive force becomes more dominant.

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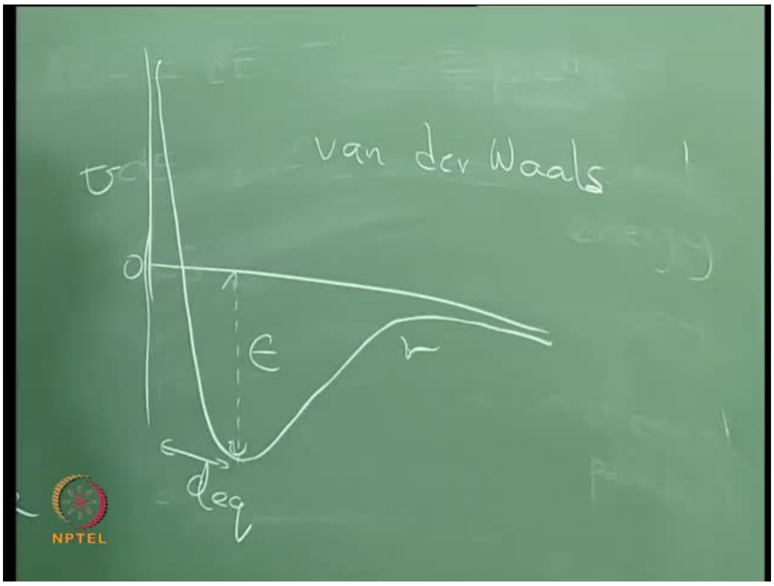

And, that is the reason that, I mean, it is basically, as you move away, the surface pulls you; as you move closer, it pushes you, right. So, obviously, there must be a, an equilibrium position, where the two, perfectly balance each other. And, in fact, if you plot u, as a function of r, according to this 6 12 relationship, the kind of curve that you get, will look like this. And, this distance…So, this is your zero point; this distance of separation, at this minimum energy point, or minimum potential point, is your equilibrium distance of separation between the two surfaces, because, that results in a minimum in the potential energy between the two surfaces. So, the surfaces will have a natural tendency to settle down, at this distance of separation.

And, the depth of this energy well, which is written as epsilon, is also an important parameter. This represents, essentially, the potential energy barrier that must be overcome, in order to get these two particles to attach to each other, or to peel them off from each other; because again, the equilibrium position is the most stable position. So, if you want to disturb a particle pair from its equilibrium position, either way, if you want to push them together, or you want to pull them apart, you have to do work, right. And so, this potential is what determines how much work you have to do, to pull them apart or push them together.

So, the greater the depth of the potential well, essentially, the more work is involved in disturbing the particles from their equilibrium position of, of separation. So, these are also known as Van der Waals' forces of interaction. Although the Van der Waal's' is a term that is more commonly associated with atoms and molecules, but, it applies equally well, to particles pairs as well. And, the surface energy is again involved, in how this forces actually operate; I mean, basically, if you bring two high surface energy particles together, their attractive forces are going to be greater than their repulsive forces, relatively speaking; whereas, if you have two low surface energy surfaces coming together, they are going to want to, naturally, repel each other, right.

So, the, the quantities a and b are very much a function of the surface energies of the particles involved, and thereby, the Hamaker constant also. So, that is why, the surface energy of the particle enters this equation; however, the r to the power 6 and r to the power 12 dependencies in the denominator, apply, no matter what the particles are; whether it is high and high surface energy, or, or low surface energy. The qualitative feature of this curve does not change. What changes is, again, as the surface energy is increased, the point of closest approach, will become smaller and smaller. So, the equilibrium position will be one, that essentially involves, the two particles virtually in contact; whereas, as if, as the surface energies decreased, the equilibrium becomes longer and longer. So, the equilibrium position for the particle pair is to be farther apart when you have a low surface energy particles, compared to, when you have high surface energy particles.

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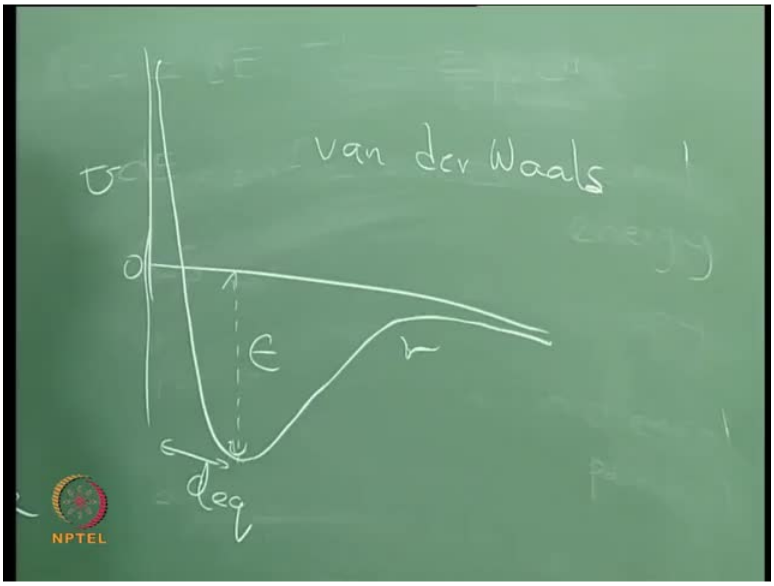

So, these are links that you have to be clear about in your mind. You know, when people talk about surface energies of particles, and they talk about the Lennard-Jones potential, there is a link between the two, which is very, very basic, very fundamental, to how particles and molecules behave, when they approach each other. And, as you can see, these are very much characteristics of the surface. The core, or even the sub-surface of the particle, really does not enter, either that equation, we know that, that, where we calculated the surface energy of the particle, or, these equations, where we are looking at the potential between a pair of particles; it is all based on surface characteristics of the particles.

Now, the third aspect that we are going to discuss, is the…The third aspect that we will discuss, is the adsorption of fluids by particles. Now, this is another important aspect of particle to medium interaction, because, what we have talked about so far, is primarily interaction between two solid surfaces or two liquid surfaces, that are entrained in a continuous medium. But, even before they interact with each other, first, they have to interact with a medium that they are suspended in. So, let us look at some of the equations, that govern the interaction between the particle and the fluid medium that it is suspended in. Now, there are, obviously, four cases of possible interactions; you have a liquid droplet interacting with a gaseous environment; you have a liquid droplet interacting with a liquid environment; or, you have a solid particle reacting or interacting with a, with a liquid environment and you have a solid particle interacting with a gaseous environment. Now, different principles of transfer apply in each case. For example, when you have a liquid droplet that is exposed to a gaseous atmosphere, the primary mode of exchange between them would be absorption of the gas by the liquid, and evaporation of the liquid to contribute vapour molecules, which then get mixed in with the gas. When you have a liquid droplet that is suspended in a liquid medium, now, obviously, that, that only makes sense, when you have immiscible liquids. So, if you have an immiscible liquid droplet, that is suspended in a, in a continuum of another liquid, we call these emulsions.

And here also, the primary characteristic is that, the, the droplet that is suspended, has surface tension characteristics, which prevent the macroscopic liquid medium from wetting it; so that, essentially, there is a repulsive interaction that is set up, between the emulsion droplets and the liquid in which these droplets are contained. Now, the third case of a solid particle that is suspended in the liquid medium, again, it involves two transfer processes; one is absorption of the liquid by the solid and dissolution of the solid, into the liquid. The dissolution part and the evaporation part, we will study later in this course. Now, when we look at liquid take-up by the particle through an absorption process, that is essentially, a surface tension driven phenomenon. And here, actually, the sub-surface can come into play, because, how much liquid can be absorbed by the particle, very much depends on the capillary volume that is available in the sub-surface region.

As we sketched in the last lecture, when you have capillaries, whether they are blind capillaries or interconnected capillaries, they provide a path for liquid to get transferred into the surface, using surface tension as the mechanism. And therefore, essentially, the more porous the particle, the, the more capillaries that are present in the, in the sub-surface, the higher will be the amount of liquid that can be taken up by the particle.

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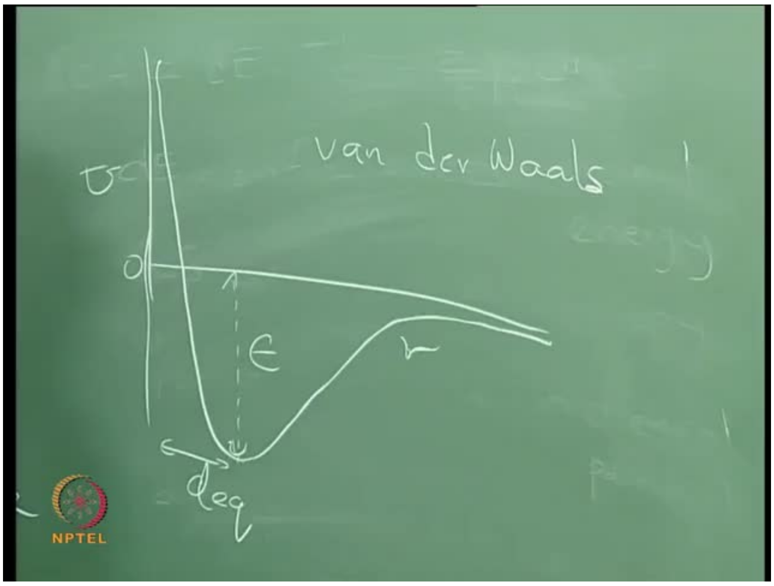

The fourth case is, actually, the most interesting, in the, in the sense of adsorption of gases by a particle. There are many, many industrial applications that involve, for example, catalysis and heterogeneous surface reactions, where it is necessary for a surface to actually, adsorb a gas molecule, in order to promote a reaction that takes place on the surface. So, there has been tremendous interest, in looking at the various phenomena, governing the uptake of gas molecules by surfaces, as a function of pressure, especially. And, one of the names associated with adsorption of gaseous molecules on surfaces, is Langmuir. I am sure everyone has heard of the Langmuir isotherm. Now, the Langmuir principle states, essentially that, only one monolayer of gas molecules can be adsorbed on the surface.

That is really what distinguishes the Langmuir model, from the various other adsorption models, well, such as the B E T model, for example. So, in the, in the Langmuir scenario, you can only adsorb a single monolayer of gas molecules on a surface. Langmuir also stated that, as far as the adsorption is concerned, each location on the surface is equivalent to any other location. So, there is no preferential adsorption of the gas molecules on any part of the surface. The probability or efficiency of adsorption is uniform across the entire surface that is adsorbing the gas. The third assumption in the Langmuir model is, there is no interaction between the adsorbed molecules. So, once a molecule has been adsorbed, it does not even know, that its nearest neighbor exists; so that, the subsequent processes all become interaction between the adsorbed gas molecules and the surface on which the gas molecules have been adsorbed.

And, the fourth assumption, of course, is monolayer adsorption. In other words, once a layer of gas molecule exists on the surface, you cannot adsorb a second layer, on top of the first layer. So, with these four assumptions, Langmuir formulated his model, by assuming that, an equilibrium position, or an equilibrium situation will prevail, where the rate of desorption from the surface equals the rate of adsorption on the surface; that is the central principle behind the Langmuir model.

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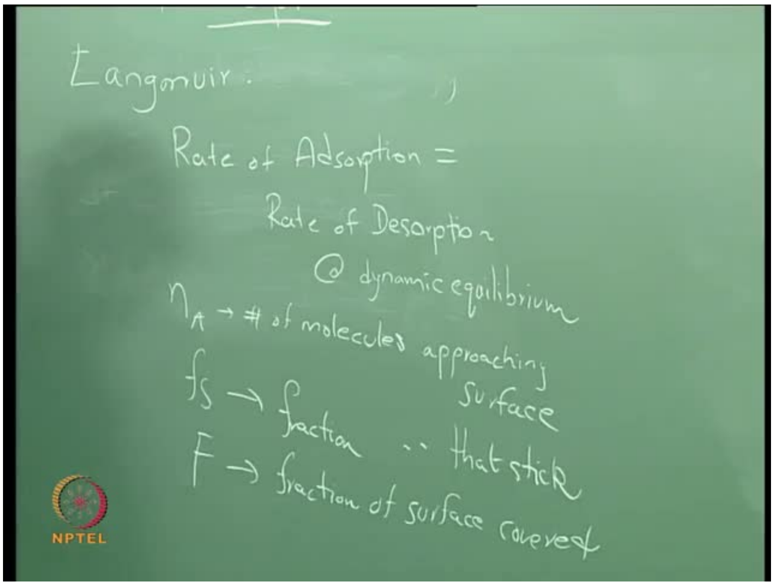

Langmuir:

Rate of Adsorption =
Rate of Desorption
@ dynamic equilibrium

n_A → # of molecules approaching surface

f_S → fraction .. that stick

F → fraction of surface covered

Rate of adsorption equals rate of desorption, at dynamic equilibrium. So, let us, let us consider a case, where you have some species A, that is getting adsorbed on the surface. Let us say that, n A is the number of molecules approaching a surface and let us say that, a certain fraction of them stick to the surface; let us call that some f s. So, this is the fraction of the molecules approaching the surface that, actually, stick to the surface.

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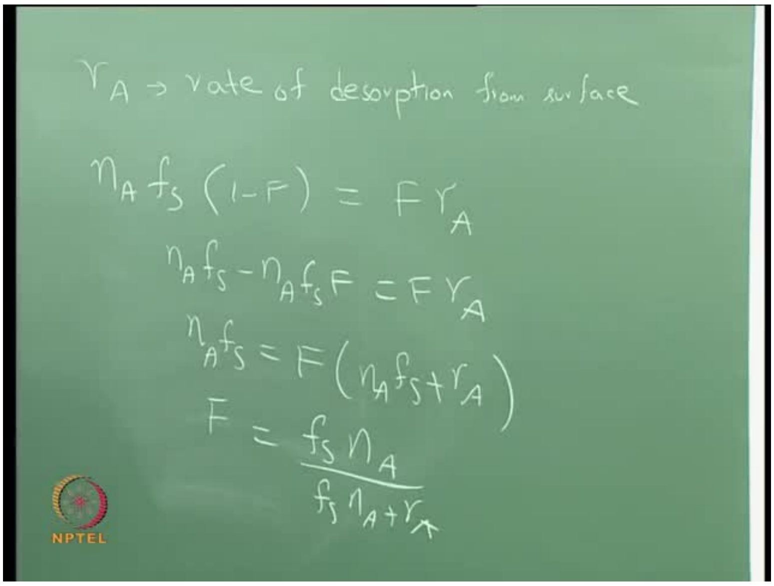

$r_A \rightarrow$ rate of desorption from surface

$$n_A f_S (1-F) = F r_A$$
$$n_A f_S - n_A f_S F = F r_A$$
$$n_A f_S = F(n_A f_S + r_A)$$
$$F = \frac{f_S n_A}{f_S n_A + r_A}$$

And, let us say that, F is the fraction of surface, on which molecules have already adsorbed. So, F is fraction of surface covered by the adsorbed molecules; and finally, let us say that, r A is rate of desorption of species A from the surface. So, given these parameters, now, how do you define the, this equation here? How do you equate the rate of adsorption to rate of desorption? Well, rate of adsorption is going to be equal to n A, multiplied by f s, multiplied by 1 minus F, because, 1 minus F is the fraction of the surface, that is available for further adsorption. And, this has to be equated to F times r A.

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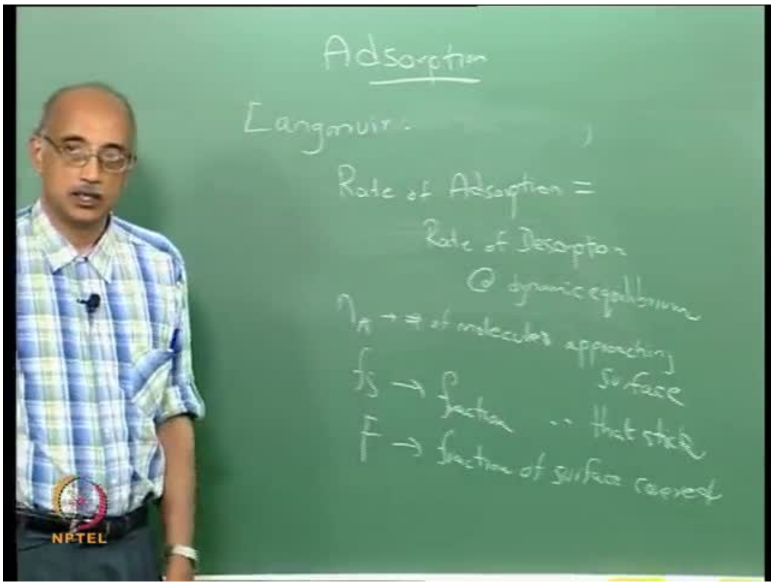

Adsorption

Langmuir:

Rate of Adsorption =
Rate of Desorption
@ dynamic equilibrium

$n_A \rightarrow$ # of molecules approaching surface
$f_S \rightarrow$ fraction .. that stick
$F \rightarrow$ fraction of surface covered

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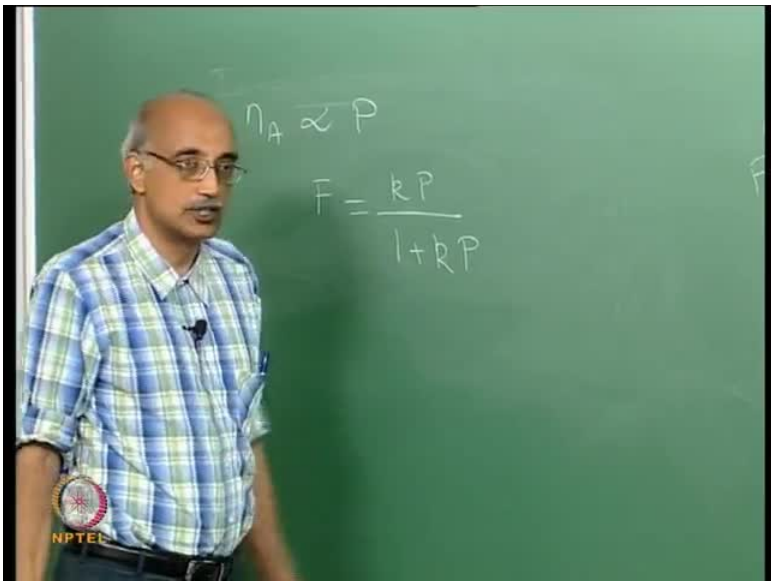

So, if you group the terms…So, this basically means, n A times f s minus n A f s times F, equals F times r A; or, n A times f s equals F times n A f s plus r A. Or, in other words, F is equal to f s times n A divided by f s times n A plus r A. Now, if you look at this parameter n A, which is the number of molecules approaching the surface, for a given temperature, this parameter is primarily dependent on pressure; the greater the pressure that you exert, the more will be the number of molecules approaching the surface. So, since n A is proportional to P, you can actually rewrite that equation as, F equals some k P divided by 1 plus k P. So, this relates the fractional coverage of the surface, to the pressure that is prevailing in the system.

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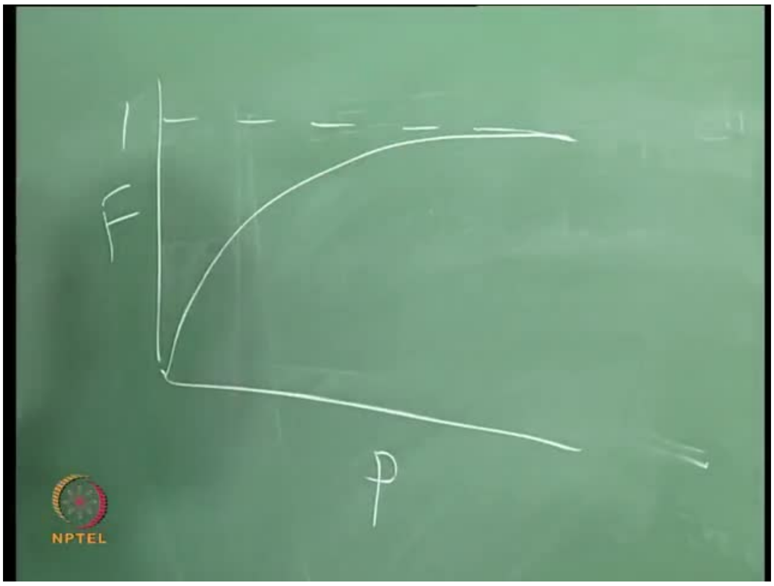

Obviously, the, the constant k will incorporate the f s and r A terms in it, as well as the actual multiplier, that converts pressure into n A. But, regardless, in terms of the qualitative relationship, F equals k P by 1 plus k P is the classic Langmuir isotherm, or Langmuir adsorption isotherm, as it is known. If you plot P versus F, how it is, how is it going to look? For very high pressures, k P will be much greater than 1; F will tend towards 1, right. So, let us say that, this is 1. So, it should approach 1. At very low pressures, it is virtually 0; I mean, if there is no pressure, that means, there is going to be nothing pushing the molecules towards the surface. So, the curve basically looks like this. So, you may all be aware of the shape of, this isotherm; but, it is very important for you to realize, how this was obtained. It is a simple dynamic equilibrium balance, you know, mass balance.

Rate of particle, rate of molecules arriving, equals rate of molecules leaving. So, it is important that, you should be able to derive the Langmuir isotherm from first principles. Now, the other model that has become quite popular, is the B E T model, Brunauer Teller, Brunauer–Emmett–Teller model. The only difference between the B E T model and the Langmuir model is, the B E T model allows for multi-layer adsorption. So, that is the only assumption, out of the four that I had listed earlier, which is relaxed for the B E T case.

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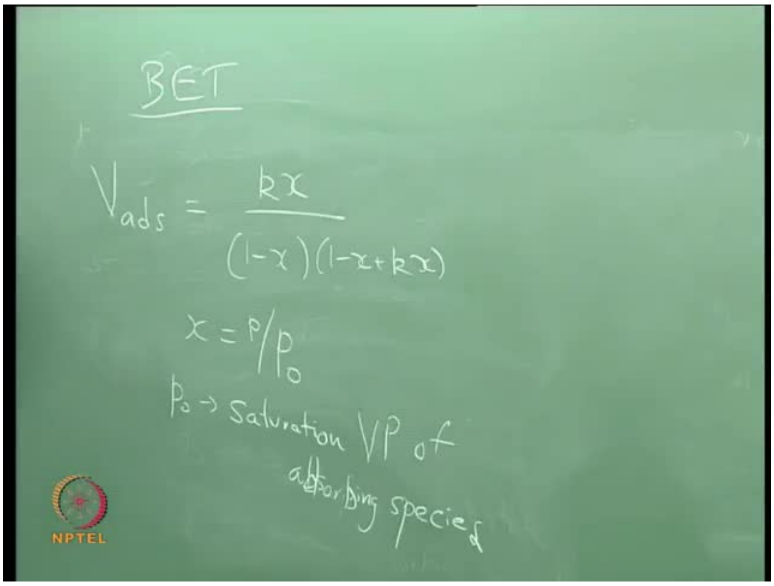

Now, if you look at the adsorption equation in the B E T model, again, the pressure plays a key role; but the adsorption process itself, is related in terms of an adsorbed volume of gases on the surface, instead of fractional coverage of the surface, which does not make sense, when you are considering multi-layer adsorption; we use volume of adsorbate as the metric; and, this is written as k x divided by 1 minus x times 1 minus x plus k x, where x equals P over P 0, where P is a prevailing pressure, and P 0 is a saturation vapour pressure of the adsorbing species.

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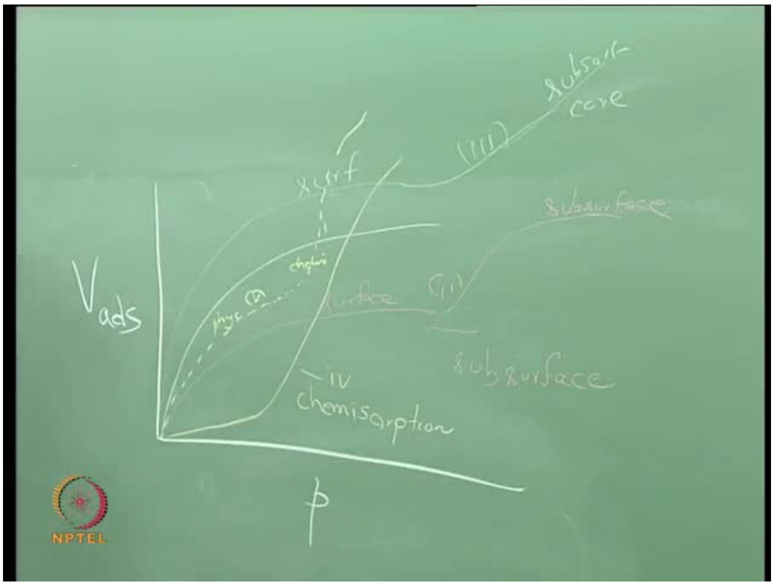

So, in the case of the B E T model, if you plot P versus adsorbed volume, what kind of shape would you expect? It turns out, there are actually five major classes of B E T curves. The first one actually, looks very similar to the Langmuir model. This essentially, is the simplest case, where multi-layer adsorption proceeds in a manner, that is very analogous to single layer adsorption. So, this is one. Now, another model, is a case, where you essentially do this, but then, you again rise the amount of adsorbed material and you establish a new plateau. Now, when can something like that happen?

What is the physical implication of a curve like this? This is a case, where sub-surface adsorption begins, after the top surface is saturated. So, this subsequent increase in the adsorption amount, is related to sub-surface coming into play; and the fact that, it reaches another plateau implies that, there are two adsorption plateaus here; one corresponding to the surface, and one corresponding to the sub-surface. So, this is the second model of B E T adsorption. So, which particle will follow which model, depends on the nature, now, not only of the surface, but also, of the sub-surface region of the particle.

The third model is one, where you again go through an initial plateauing effect, and then, further adsorption proceeds without necessarily, showing a plateauing behavior. Now, when would this happen? Here, not only is the surface involved, but also, the sub-surface, and the core of the particle also gets involved in the adsorption process. So, essentially, the adsorption continues, until the entire particle, is basically transformed, right. So, this is the case, where the sub-surface is such that, there is almost a direct path from the surface to the core, or interior of the particle. So, the extent of adsorption is much greater in this case, compared to the first two. Now, all of these are, what we call, physisorption processes; the process by which the gas molecule is getting adsorbed, is purely physical in nature.

But as we know, when you have possible chemical reactivity between the two surfaces, or between the surface and the gas molecule, then, chemisorption will come into play, also. Chemisorption is not even addressed in the Langmuir model; however, the B E T model, does address chemisorptions specifically; and the B E T scenario suggests that, when you have chemisorption going on, you will see a behavior, that is very, very different, from any of these. What type of behavior would you expect in the case, where chemisorption is happening? The curves cannot flip around. In the case, where chemisorption is going on, initially, the adsorption is very, very poor. But then, there is a sharp knee that happens, a sharp bend in the curve; once chemisorption begins, the increase in the chemisorption rate, is just tremendous. And, it essentially goes to completion. In other words, the entire particle gets saturated with chemisorbed material very rapidly, because, chemisorptions, being a chemical process, the core will actually react even more than the surface and the sub-surface, because, it is a purest representation of the material.

So, this curve four, primarily reflects chemisorption as a significant phenomenon. And, finally, the fifth variation on the B E T is a case, where you essentially have, a combination of chemisorption and physisorption, so that, initially, you follow a physisorption kind of a route, followed by where chemisorption takes over. Now, this would happen in cases, where the surface itself is relatively inert, with respect to the adsorbed molecule. But the sub-surface, and especially the core regions, are much more reactive to the adsorbed gas molecule. This can happen, for example, when the surface is poisoned with impurities, which greatly inhibit the reactivity of the particle material, through the surrounding gas stream.

But once you go below the layer, where the impurities are concentrated, the chemical reactivity is, is greatly enhanced. So, again, these five potential behaviors of B E T adsorption isotherms are very, very important to understand; and you should be able to discuss them in a physical sense; you know, understand the mechanisms involved; understand, what is going on and be able to talk to them in, in reasonable detail. Now, we have not really talked about the effect of temperature. So, what would happen if you have a surface that is adsorbing gas molecules, and you increase the temperature, what is going to happen?

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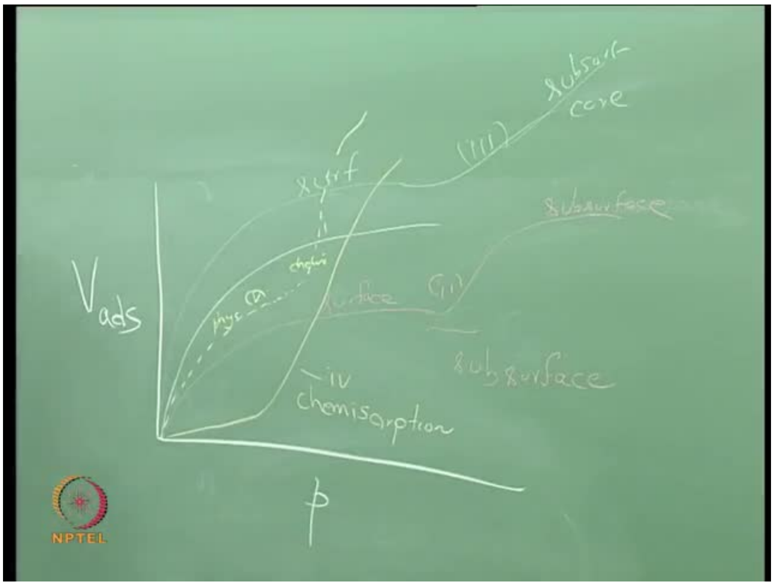

There will be more desorption, right, in general; and therefore, the amount of adsorption typically, will decrease in the case of physisorption; in the case of chemisorption, it may actually increase exponentially, because, if the chemical reaction becomes the dominant a phenomenon, in, in, in dictating the adsorption, then, you will see an exact reverse behavior. In fact, a test that scientists use to assess whether physisorption is dominant or chemisorption is dominant, is simply to measure adsorption at various temperatures. If there is a chemisorption dominance, you will see increased adsorption at higher temperature; if there is a physisorption dominance, you will see a reduced dependence at, at higher temperatures.

So, what we have discussed so far, are three very, very basic phenomena, that represent how a particle interacts with its environment. In the next lecture, we will discuss some of these aspects, in a little more detail. The particle to surface adhesion is a very, very critical phenomenon, which plays a huge role in many manufacturing industries. Similarly, particle to particle cohesion plays a huge role in determining properties, like the flowability of the suspension, stability of suspensions, and so on. So, in the next two or three lectures, we will focus on particle adhesion to surfaces and particle cohesive behavior to each other.