Upstream LNG Technology

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Lecture – 33
Equilibrium fluid solid separation

Welcome. Today we shall be looking into the fluid solid separation, which is used for adsorption of liquids or gases on some adsorbents. So, today's lecture is on Equilibrium fluid solid separation.

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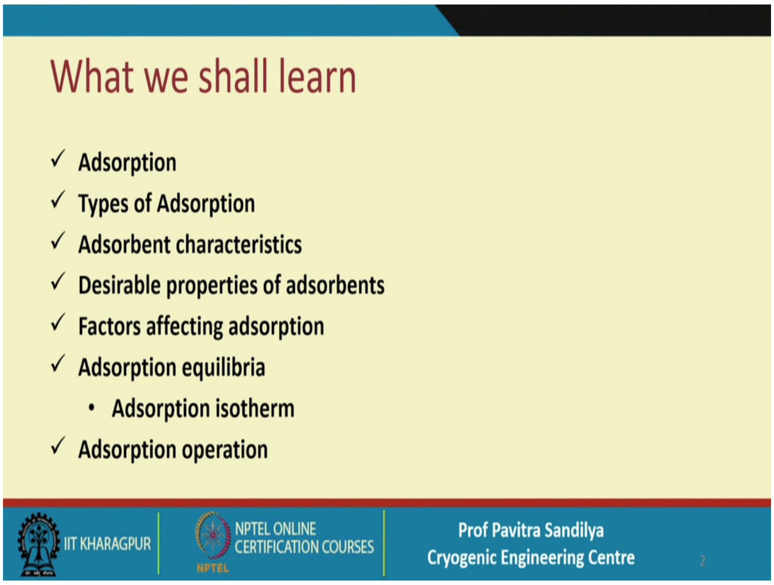

Now, in this particular lecture what we shall be learning? We shall be learning about adsorption, various types of adsorption, the characteristics of adsorption, the various desirable properties of adsorbents, then the factors which affects the adsorption separation, then adsorption equilibria, their representations through isotherms and lastly we shall look into some brief about the adsorption operation.

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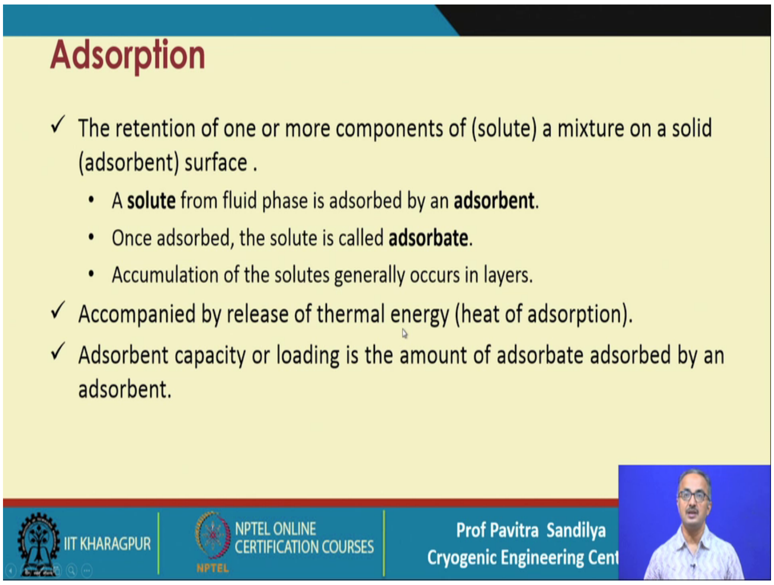

Now, first let us see what is adsorption. Adsorption is the attachment of a solute on a solid. Now the solute will can be from some liquid or it can be from some gas. The solute when it gets adsorbed its adds it is called adsorbate and the solid on which it gets adsorbed is called adsorbent. So, the accumulation of those solutes on the adsorbent happens generally in one or more than one layers.

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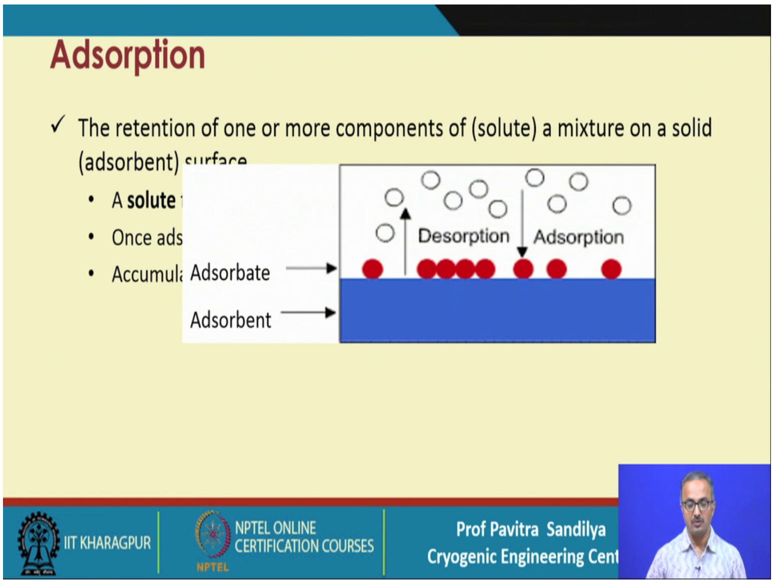

So, here is a pictorial representation of the adsorption, here we see there is a solid substrate this blue and this then we have the adsorbates given by the red balls and these white balls are the solutes. So, these solutes are coming and sitting on the adsorbent and called adsorbate and some of these adsorbates can again go back to the fluid phase and that we call desorption.

Now, generally adsorption is accompanied by release of thermal energy; that means, there will be some kind of heating when adsorption goes on, and such kind of processes are called exothermic processes. So, adsorption is an exothermic process and we have some adsorbent capacity or what we call loading, this is the amount of adsorbate that gets adsorbed by unit mass of the adsorbent.

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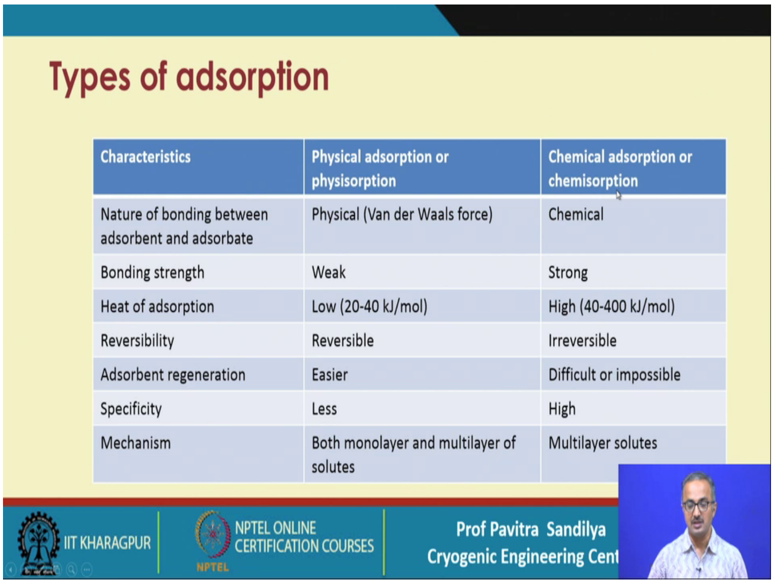

Here we show the two types of adsorption; one is the physical adsorption and another is the chemical adsorption. The physical adsorption in short is called physisorption while chemical adsorption in short is called chemisorption.

Now, here are the differences between these two types of adsorption; first based on the nature of bonding between the adsorbent and the adsorbate. In physisorption we have physical forces like Van Der Waal force which is a short range force; that means, only when the solute is very near to the adsorbent only then the adsorption is possible and in case of chemical adsorption, we have the chemical bonding that is there could be some kind of reaction between the solutes and the adsorbent.

In terms of bonding strength, the physisorption has weaker bonding because it is physical force whereas; in case of chemisorption due to the chemical force it is a much stronger bonding. In case for a heat of adsorption it is very low, that is about 20 to 40 kilo joules per kilo mole whereas, in case of chemisorption the heat of adsorption is higher this also means that we need more energy for desorption in case of chemical adsorption than in case of physical adsorption, and this is important when we think of regeneration of the adsorbents.

In terms of reversibility the physisorption is generally reversible, but chemisorption is generally irreversible; that means, the adsorbent can be used only once in case of chemisorption whereas, in case of physisorption the adsorbent may be reused a few times. Then the regeneration of the adsorbent is easier in case of physisorption than in case of chemisorptions. Then specificity means this is the this determines that how selective the adsorbent will be to a given solute.

So, we find that the physisorption is less specific whereas, the chemisorption is more specific and the mechanism of adsorption in case of physisorption is either monolayer or multilayer and in case of chemisorption it is generally multilayer.

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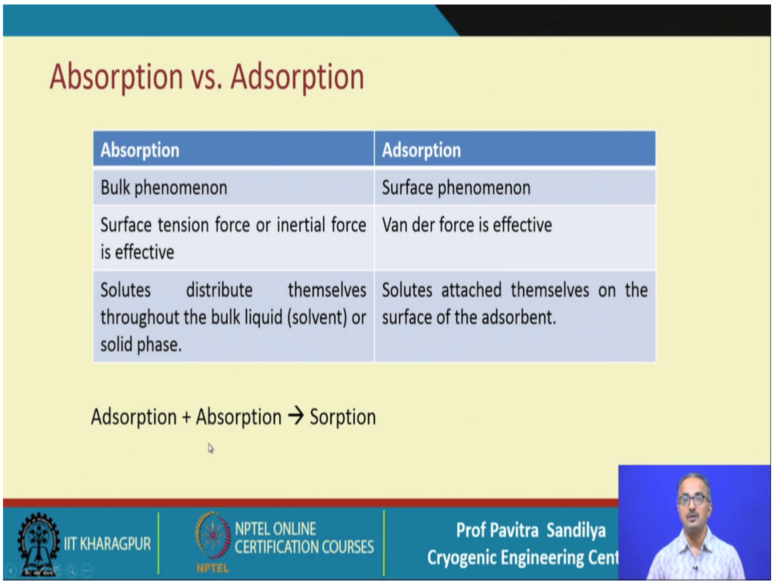

Now, we know that we have some absorption and there is some adsorption, sometimes we confuse between these two.

So, here is are some points based on which we can differentiate between adsorption and absorption. Now absorption is basically bulk phenomena; that means, the solute will go inside another liquid or solid phase and will be spread over in the whole phase.

Whereas in adsorption this surface phenomenon; that means, the solute will sit only when there is some surface available. The absorption is generally dictated by the surface tension force or inertial force whereas, in case of adsorption it is Van Der Waals force. Then the solute distribute themselves throughout the bulk liquid which we call solvent or a solid phase whereas, in case of adsorption, the solute attach themselves to the surface of the adsorbent.

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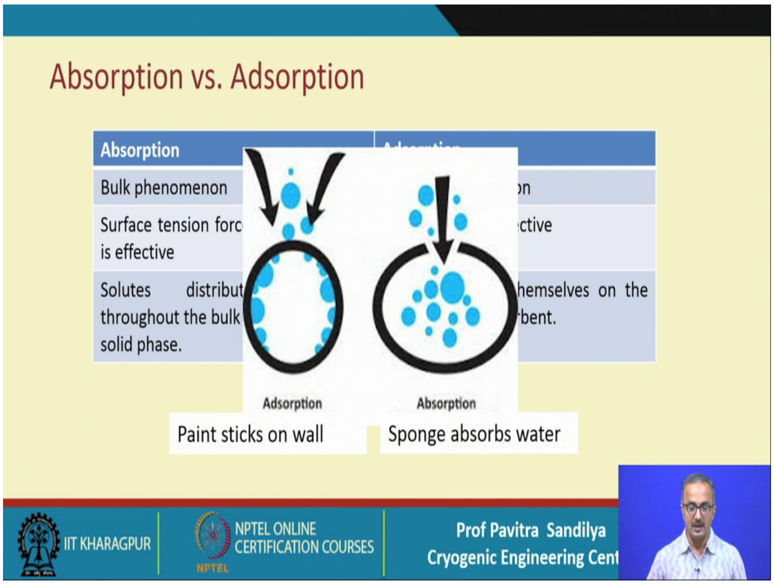

Here is it the pictorial representation that in case of absorption we find these blue colored balls are the solutes, which gets spread over the whole solvent or the solid phase whereas, in case of adsorption they sit on the surface of the adsorb adsorbent. So, this is the mechanism you can see in our day today life a sponge absorbs water, and this we find then when we are painting the wall, the paint is this paint is sitting on the wall that is by adsorption.

Now when in some cases we cannot say that, specifically whether adsorption or absorption is there so, both this phenomena may occur together and then we call them absorption.

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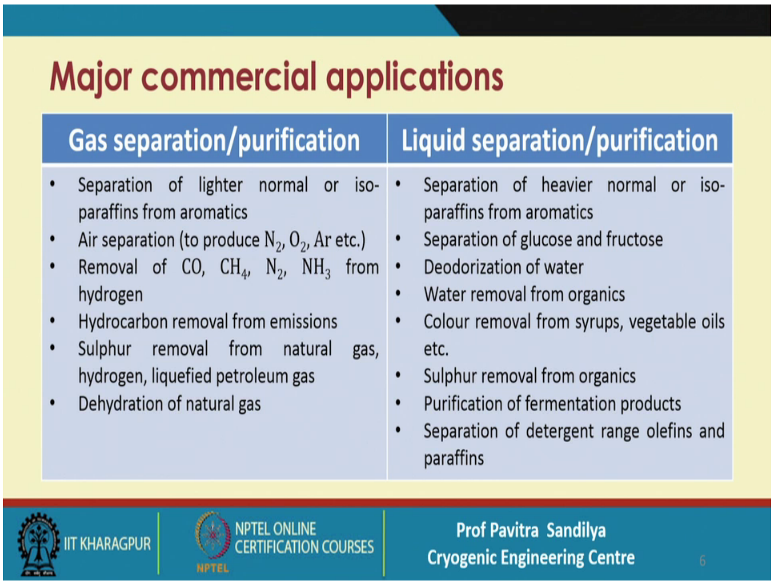

Now, here are some commercial applications of this adsorption. So, this adsorption is used both for gas separation or purification and a liquid separation or purification.

Here we find there are a most of applications, these are just some representative applications there are many more applications for adsorption, we find that the broad ones are like air separation to obtain nitrogen, oxygen, argon etcetera then for removal of carbon monoxide, methane, nitrogen ammonia from hydrogen. The hydrocarbon removal from emission gases, sulphur removals from natural gas, liquefied petroleum gas dehydration of natural gas and similarly we have many applications of liquid separation and purification by adsorption.

Here are some like deodorization of water, then from organic chemicals to remove water, then sulphur removal from organics purification of fermentation products etcetera.

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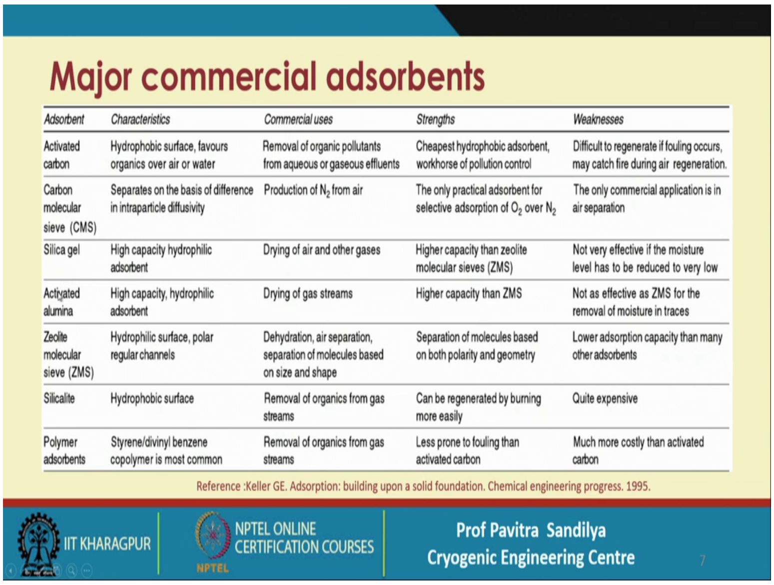

And in this table we find the various types of commercially available adsorbents, there are many adsorbents available and many are being developed here are some few representative ones, here we see activated carbon, carbon molecular sieves, silica gel, activated alumina, zeolite, molecular sieves, salicylate and polymer adsorbents.

This silica gel we may find in our day to day life very much like for example, when you go to purchase these water bottles at the shop, you will find that there is a small pouch kept inside the water bottle or in some case in sometimes you also find in some briefcases or boxes they have put some pouches these are nothing, but silica gel which are kept there to adsorb any kind of water present to avoid any kind of formation of any other microbes inside the vessel.

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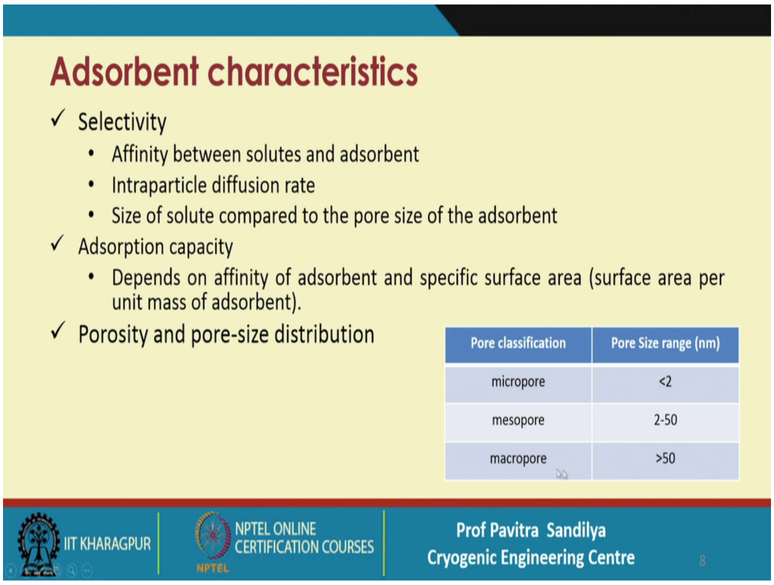

Now some of the characteristics which and therefore, adsorbents are selectivity. The selectivity means it will be attracted towards some particular solute and this is necessary for adsorption, if there is no affinity it will not be absorbed. Then there will be intra particle diffusion; that means, the there are various particles are there among the particles how one particle is diffusing through the other particles, and that will determine that how selectively that particle would be adsorbed by the adsorbent.

And then we have the size of the solute compared to the pore size, because if the pore size is smaller than the solute size the solute cannot enter inside the pores. So, it will be only on the surface of the adsorbent and these determine the selectivity of a particular solute on a given adsorbent. Then you have adsorption capacity, it means that how much loading we can have and this depends on the affinity as well as the specific surface area that is how much surface area is offered per unit mass of the adsorbent.

Then we have porosity and pore size distribution, it means that how porous the adsorbent is because if the adsorbent is non porous, then the inside of the adsorbent will not be available for adsorption. So, we need some porosity to increase the specific surface area, and pore size distribution means how uniform the pore sizes are if their pore sizes may be big and small. So, we want uniform pore sizes so, that we can be very specific about some particular type of solute.

And here depending on the pore sizes, we differentiate where the pores like we have micropores which means their sizes are less than 2 nanometer, mesopore their sizes are between 2 and 50 nanometer and macropore they are more than 50 nanometer.

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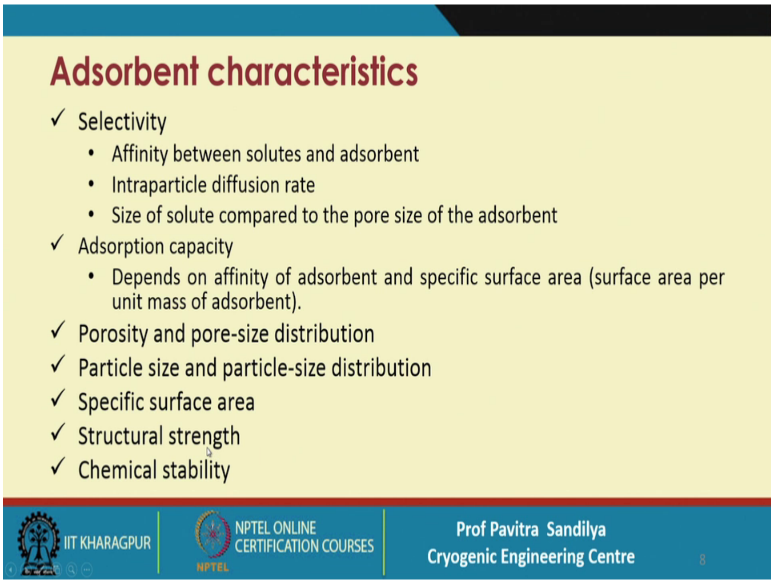

Other characteristics are the particle size and particle, size distribution if the bigger the particle the lesser the specific surface area the smaller the particle the more the specific surface area on the other hand if the particles are too small, then they will be packing too densely in a column and that will increase the pressure drop of the fluid passing through the adsorption bed.

So, we have to see that what kind of particle sizes we should be having in the adsorption bed. Then we have the specific surface area as I told you the surface area offered per unit mass of the adsorbent, the structural strength we want that the adsorbents must be enough mechanical stable so that they do not break up and get into powders, otherwise we shall be losing both their particle size as well as their porosity with which they were designed the adsorption was designed.

So, we want enough structural strength of the adsorbent particles so, that they do not get broken by the attrition during the actual operation. Then lastly we have chemical stability; that means, the adsorbent should not react with the process fluids otherwise it will lose its adsorption capacity.

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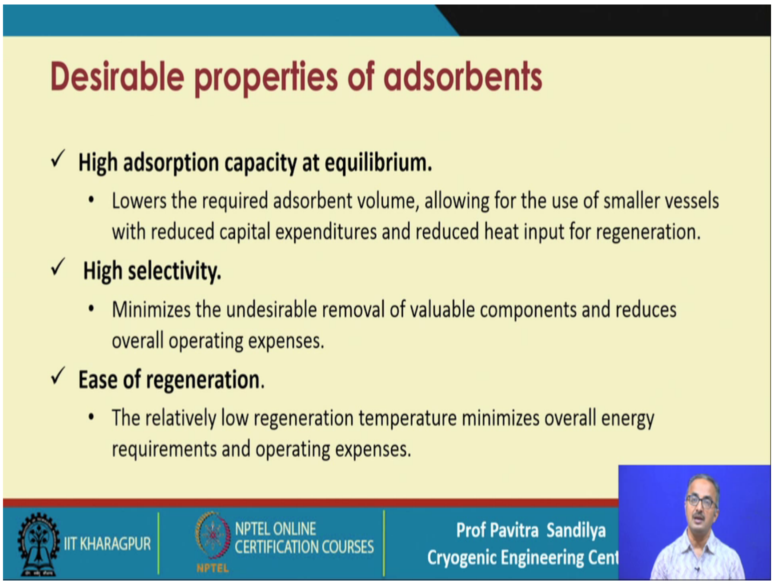

So, desirable properties of adsorbents are that it should have a high capacity to adsorb at equilibrium, and if we have high capacity what will happen that we can lower the adsorbent volume and that will mean, that we need a smaller vessel and smaller vessel means, it will be having less capital cost.

And if and also the heat needed for regeneration will also get reduced so that we shall be saving on the energy requirement. Then we have a high selectivity that if it is highly selectable then selective then what will happen that we shall be avoiding the impurities to be going with the actual products and that will also reduce the overall expense. And ease of regeneration; that means, we want that if that the after the adsorbent has been used for some time, it gets saturated and we should be able to reuse it and for reuse we want that the solutes which were earlier adsorbed should get removed easily so, that we spend less amount of energy for regeneration the adsorbent.

So, we want that regeneration should be easy and that will reduce both the operating cost as well as the energy cost.

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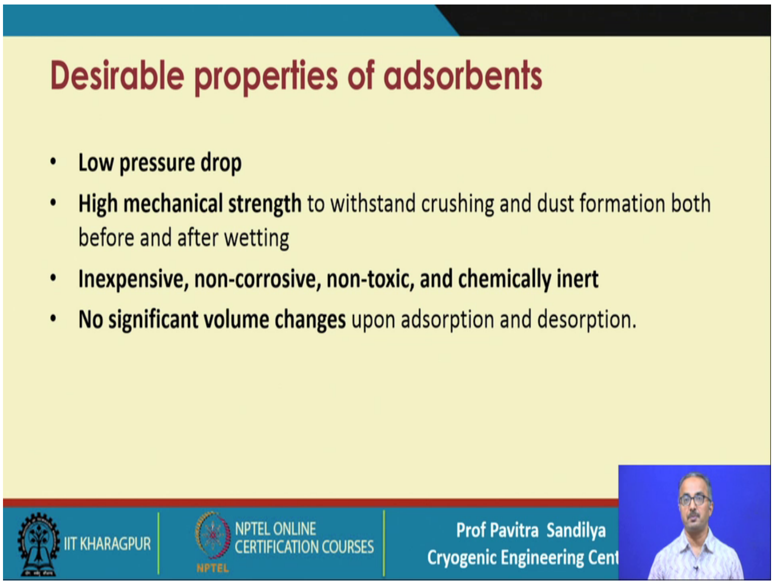

Then there should be low pressure drop, pressure drop means it translates into the pumping power or the compression power. So, we should have low pressure drop to the bed, then a high mechanical strength as I explained that they should not lead to any kind of dust formation by crushing and these should be inexpensive, non corrosive nontoxic and chemically inert.

And during their adsorption and desorption, there should not be any significant change in the volume otherwise we shall find that all the other properties like the specific surface area etcetera every the porosity, everything will get changed. So, we do not want any kind of volume change during this adsorption and desorption.

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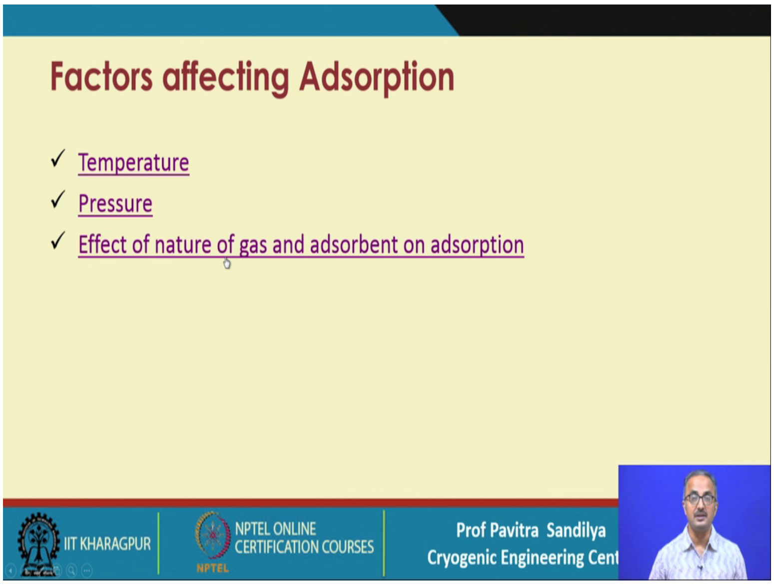

Now, what are the various factors which affect the adsorption? So, first factor is a temperature let us see how temperature affects.

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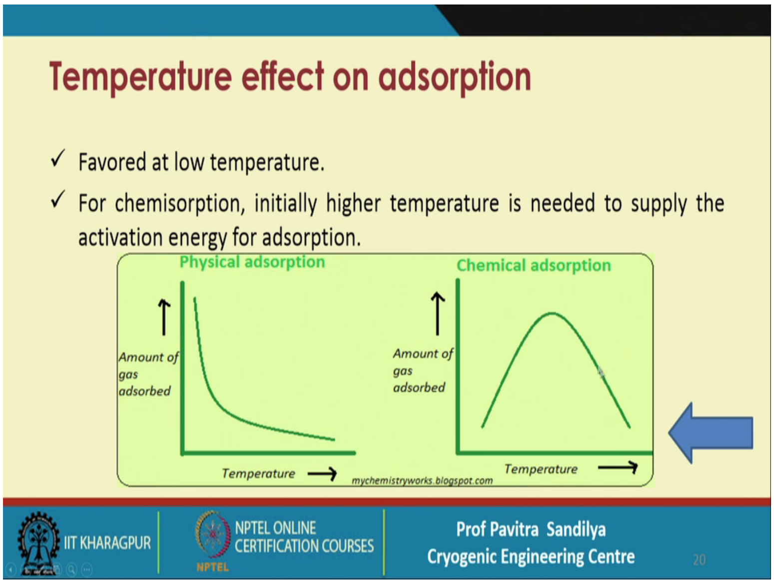

Here are the temperature effects; we find that adsorption is favored at low temperature and this chemisorption and physisorption, so, different characteristics and dependency on the temperature. We find for physisorption we find that as we increase the temperature, we find the amount of gas adsorbed starts decreasing.

So, there is a continuous decrease in the amount of adsorption with increase in the temperature. Whereas, in case of chemical adsorption we find that initially the rate of adsorption increases and then after reaching some maximum, it starts decreasing. Now this behavior is because that initially we need some amount of activation energy for the chemical reaction to take place and that can happen only at higher temperature.

So, by when we initially the by raising the temperature, we are able to achieve the activation energy for chemical reaction chemical bond formation and once it has been done, then we find after further increase in temperature there is no more of adsorption and their adsorption start decreasing.

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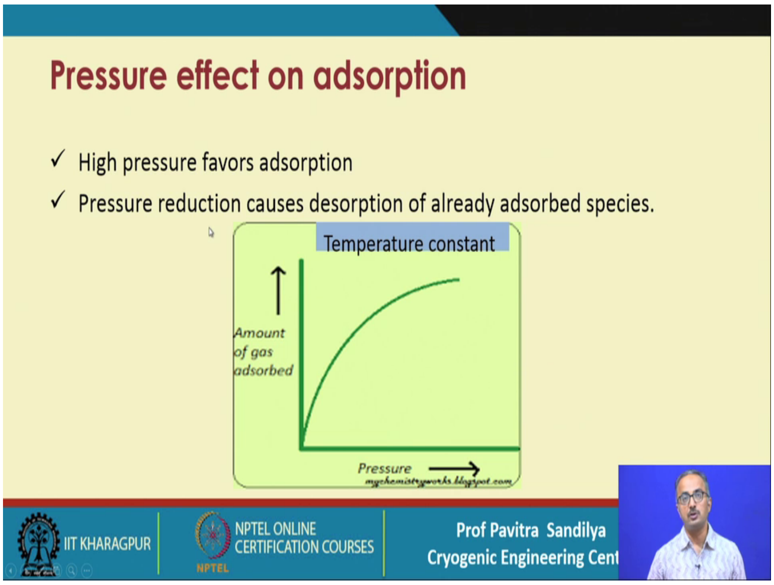

Next factor is the pressure the increase of pressure we find that the adsorption is favored at high pressure.

So, in case of both physisorption and chemisorptions, as we increase the pressure we find that the amount of the solute adsorb also start increasing and in this case we are keeping the temperature constant. Next is the effect of the nature of the gas and the adsorbent.

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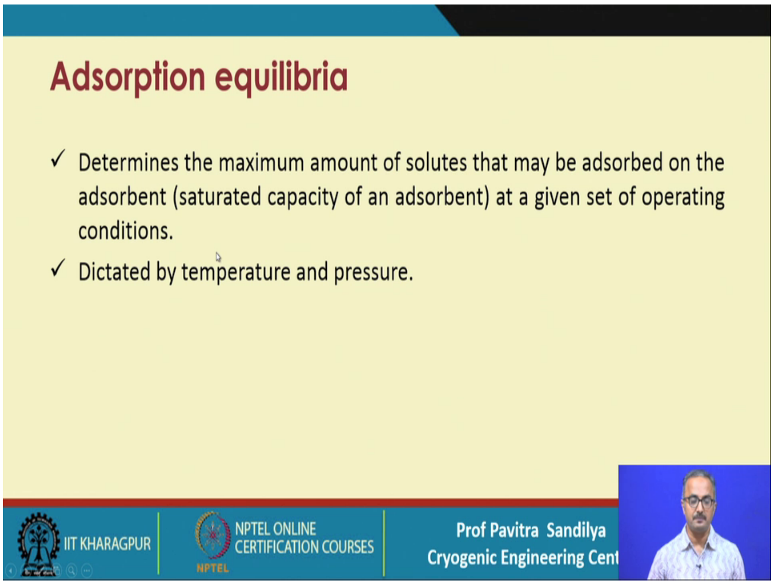

In this case we find that the nature of the gas impacts in a way that it affects.

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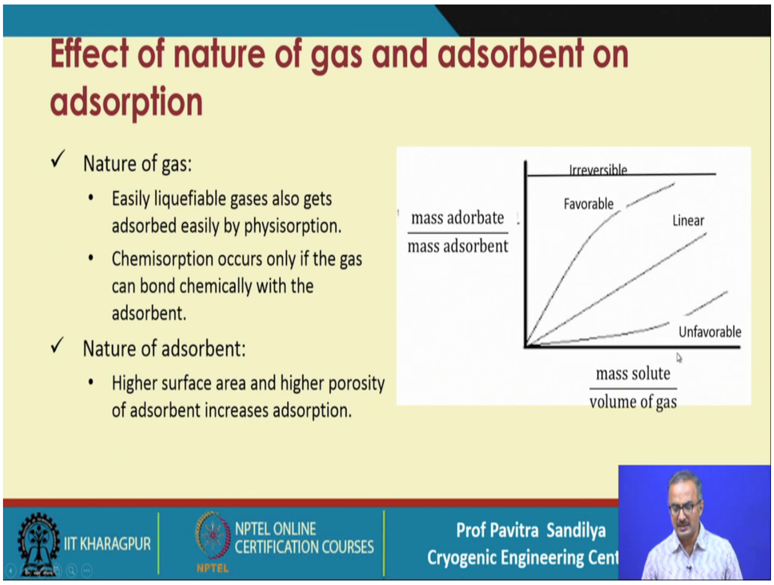

The adsorption a way that those gases which can get liquefied easily have been found also could to get adsorbed easily because liquefaction is one way of deposition of the solutes on some surface.

So, any gas which is which can be liquefied easily can also get adsorbed easily, and chemisorption occurs only if the gas can bond chemically with the adsorbent and nature of adsorbent means the adsorbent should have high surface area and high porosity for higher adsorption. And here we see in this particular graph that on the x axis we are having the solute concentration, on the y axis we have the adsorbent loading, and we find that depending on the type of the solute and the particular adsorbent, we have having different types of adsorption characteristics about which we shall be learning later.

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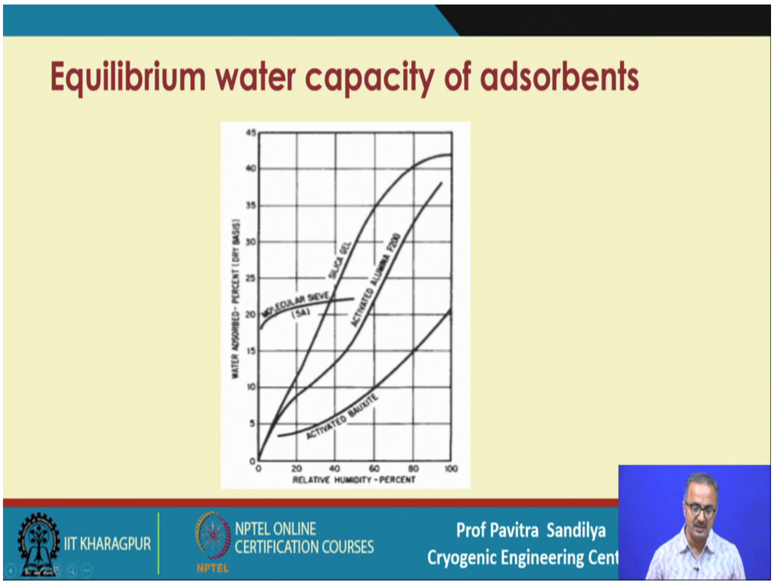

And here in this particular graph we show that how that all water gets adsorbed on different types of adsorbents. Here we have different adsorbents which are represented by different curves; first we have activated bauxite, then activated alumina, silica gel and molecular sieve. So, water can be adsorbed in any of these adsorbents and we find that all of them are showing different characteristics; in this case we find that for a higher concentration of water, silica gel shows the best performance.

Whereas in case of the lower concentration of water, we find molecular sieve is showing very good performance. So, these are the curves which are generated experimentally to select a given adsorbent for adsorbing some particular solute. After learning the factors now we come to the adsorption equilibria. Now water at the equilibria? They determine the maximum amount of solutes that may be adsorb under some given operating conditions decided by the temperature and the pressure.

So, what is the maximum amount that can be adsorbed that is given by the adsorption equilibria.

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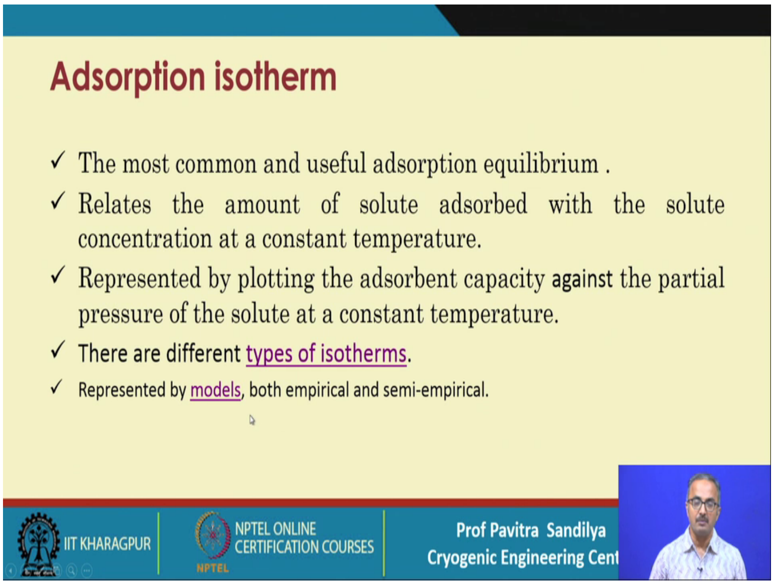

And the there are various ways of representing the equilibria, one of the most common ways is the adsorption isotherm. As a name signifies that it is related to the constant temperature isotherm that is constant temperature and at constant temperature we try to relate the amount of solute adsorbed with the solute concentration in the fluid.

And we shall see how we can get these things and these adsorption isotherms are obtained by plotting the adsorbent capacity against the partial pressure of the solute this partial pressure is nothing, but a way to denote the concentration of a solute in a fluid. So, we when we plot the adsorbent loading with the partial pressure at a constant temperature, we get the adsorption isotherm.

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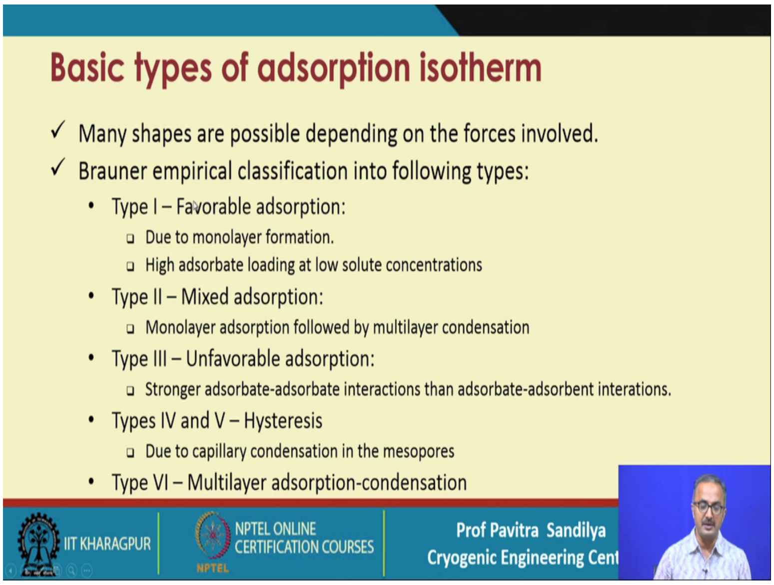

There are various types of actions possible and we show a few basic types of isotherms and these isotherms can have different types of shapes, a browner proposed some of this isotherms we classified this isotherms into few groups.

We shall be checking those groups, and they have been grouped in different types Type I, Type II, Type 111, Type IV, Type V and Type VI, these are named as favorable adsorption, mixed adsorption, unfavorable adsorption hysteresis and multilayer and these are characterized by the number of layers formed on the adsorbent and the type of loading characteristics they show by virtue of this number of layers formed.

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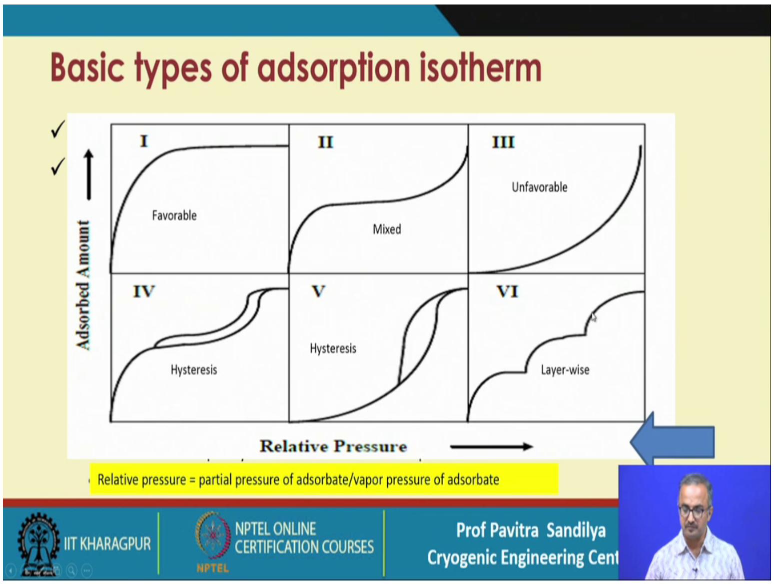

So, here we were see that how they are represented pictorially. So, we find this is a favorable unfavorable isotherm by favorable, because we find that the amount adsorbed becomes very high for a small change in the solute concentration and this is mixed because, here we find initially it is favorable and then it goes to unfavorable, and this is totally unfavorable and here we have hysteresis; hysteresis comes because during the adsorption some solid particles may enter which we call capillary condensation.

So, due to this capillary condensation the solute particles enters the adsorbent adsorbents and while we are trying to regenerate it, they may not be able to come out of the adsorbent body, due to not enough force to take to dissolve themselves from the solid that network, inside the adsorbent particles. So, that is why we obtain hysteresis in case of this adsorption and regeneration.

And next we have layer wise type six layer wise, in this time we say that the adsorption goes on in layers after layers. So, each of these are representing the formation of different layers. Next all these isotherms can be modeled by various manners and some of these models are either empirical or they are semi empirical and these are some of the models.

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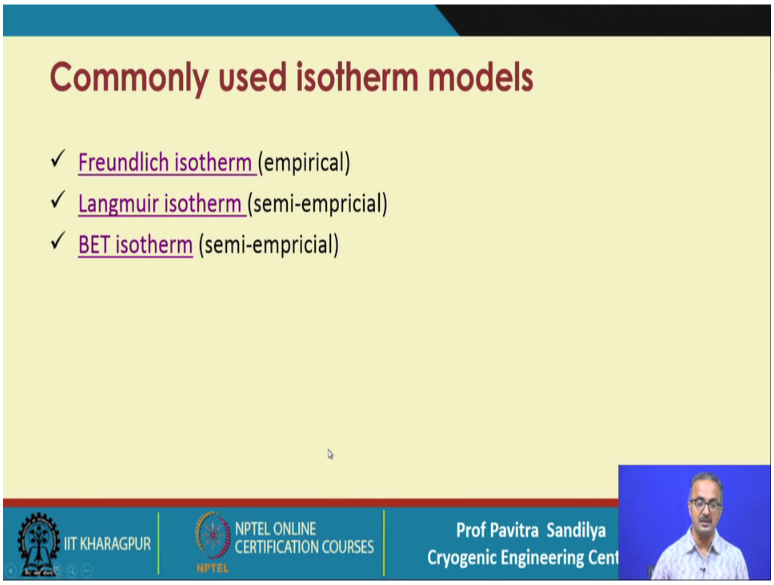

So, these are some of the models which are very common otherwise in literature you will find there are many other isotherms proposed by different workers.

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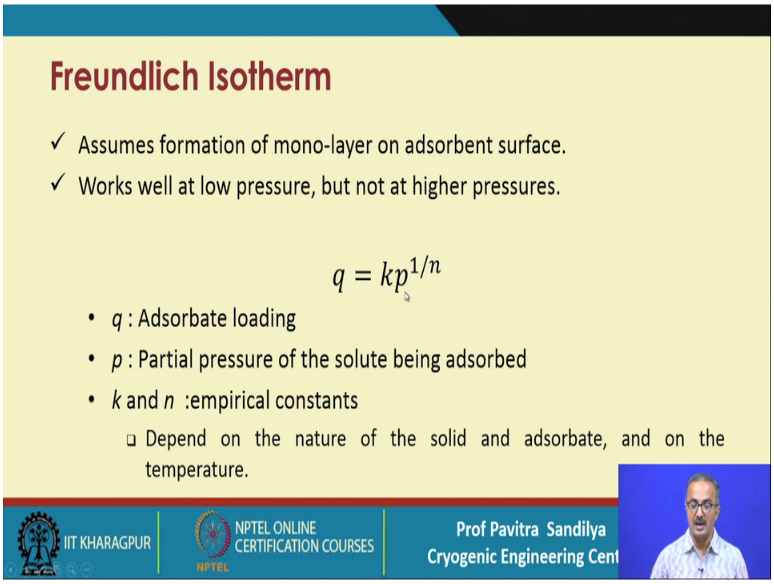

So, one is Freundlich Isotherm, which is given by this particular expression q is the adsorbate loading and p is the partial pressure, k and n are some kind of parameters and this assumes that there is mono layer formation on the adsorbent surface. So, our intention is to figure out the value of this k and n from the adsorbent data.

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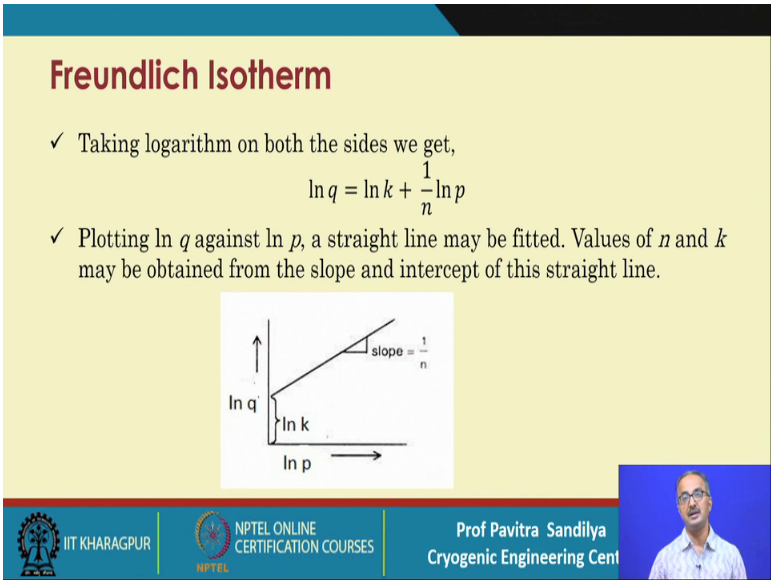

So, what we do to get the value of k and n we take the log on both sides, and now we find that log q becomes a linear function of log p; that means, if we plot log q versus log p and put make a regression analysis on the experimental data, to plot a straight line then we will find the slope of the straight line is 1 by n whereas the intercept is log k.

So, this way we can find out the value of the k and n and then we using the k and n we can predict the adsorbate loading for different solute concentrations, for that particular adsorbent solute pair under different conditions. Similarly we go to the another type of isotherm this also be popular Langmuir isotherm.

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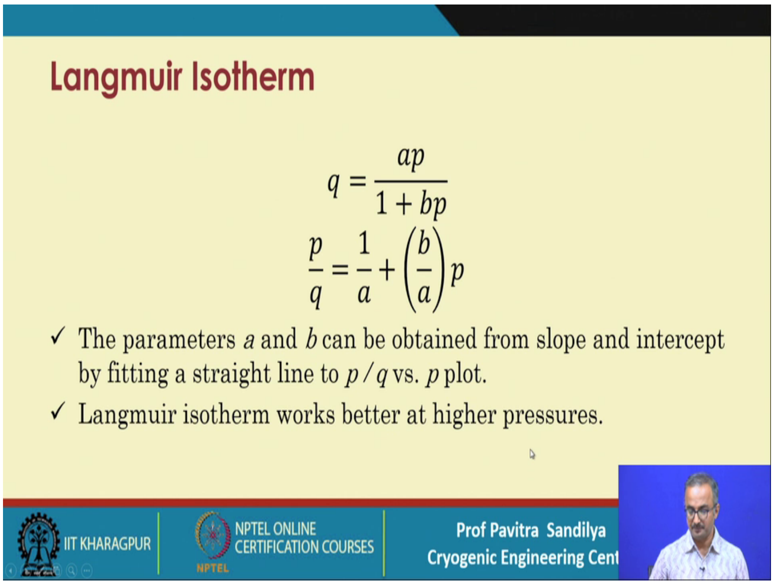

Which is semi empirical and this isotherm is given by this particular equation this can be derived also theoretically to some extent with some assumptions without going into derivation; we see this is the nature of isotherm and we if we rearrange this isotherm in this fashion, we again find that p by q becomes a linear function of p.

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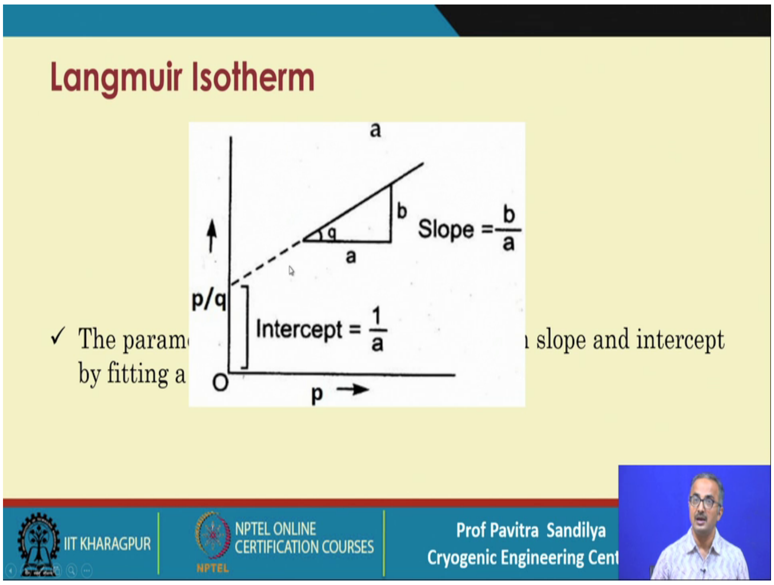

So, if we plot p by q versus p like this we again we can do regression to fit a linear um curve through these experimental points, we find that this slope of this line will be b by a and the intercept will be 1 by a from this we can figure out the value of a and b for the

Langmuir isotherm and Langmuir isotherm; has been found to work better at higher pressures.

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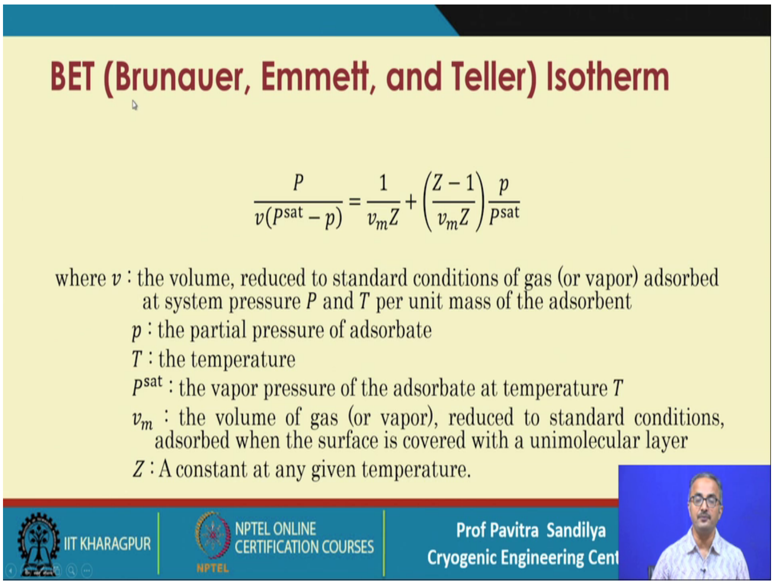

Next we come to another isotherm that is BET isotherm, this is also semi empirical the name it is derived from the name of names of three scientists Brunauer Emmett and Teller and this is the particular type of isotherm equation they are proposed in this equation we have p as the pressure, p sat as the saturation pressure of vapor pressure and v is the volume reduced to a standard conditions for per unit mass of the adsorbent; that means, volume of the solute adsorbed per unit mass of the adsorbent that is the adsorbent loading.

But loading we defined in terms of mass of solute in this case we are define in terms of volume of solute, and then we have the v m as the volume of gas reduced to a standard conditions when the surface is covered with a unimolecular layer, and Z is the is the constant given at any given temperature.

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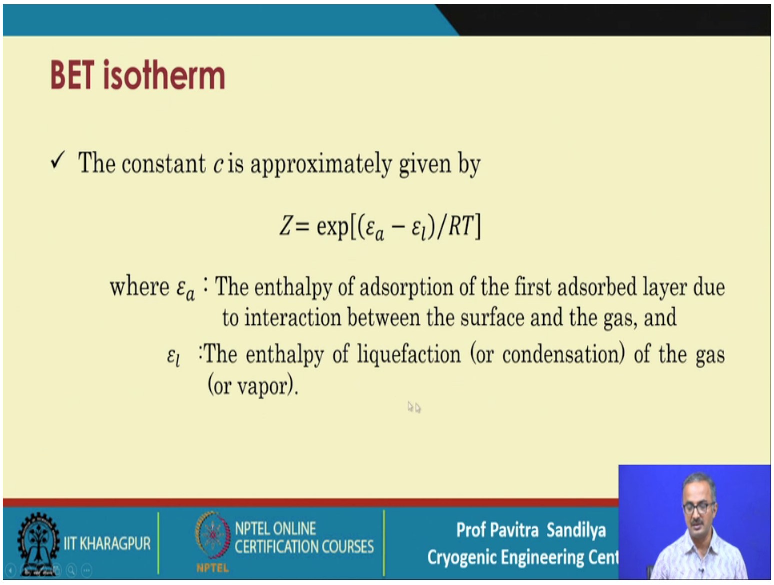

So, many of these parameters have to be found experimentally and Z is given in terms of some enthalpy of adsorption and enthalpy of liquefaction or condensation.

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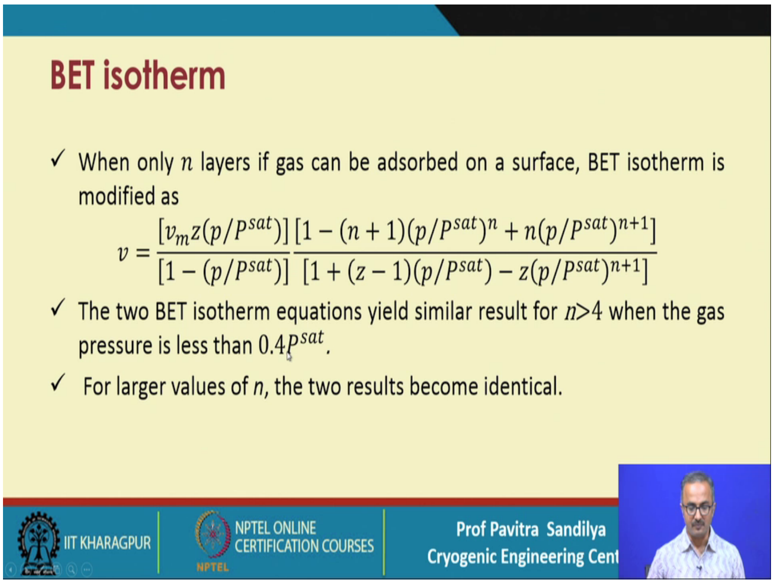

So, these are the parameters which we need to estimate the loading, and this is another expression for the bet isotherm itself, but this assumes n layers of the solids getting formed on the adsorbent. So, this is also very popular and the previous one was for monolayer this is for n number of layers and these two bet isotherm equations yield similar result for n more than 4, when the gas pressure is less than 0.4r into p sat that is 40 percent of the saturation pressure.

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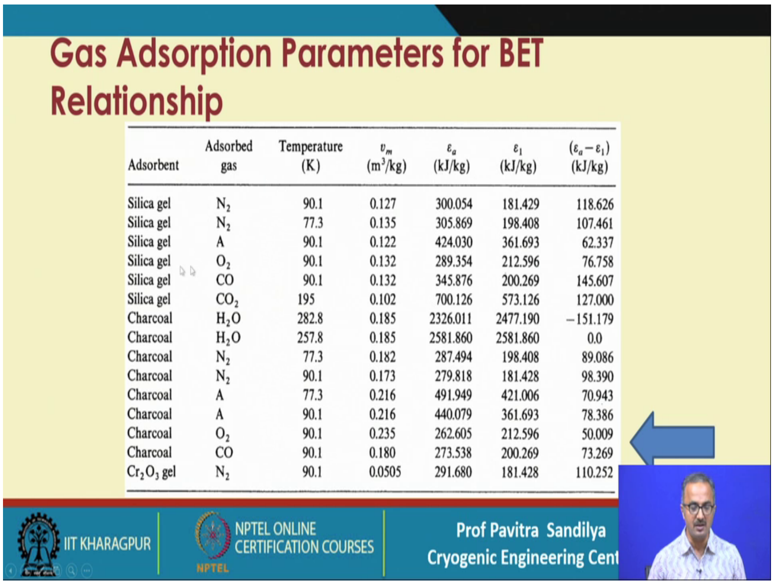

Adsorbent	Adsorbed gas	Temperature (K)	v_m (m^3/kg)	ε_a (kJ/kg)	ε_1 (kJ/kg)	$(\varepsilon_a - \varepsilon_1)$ (kJ/kg)
Silica gel	N_2	90.1	0.127	300.054	181.429	118.626
Silica gel	N_2	77.3	0.135	305.869	198.408	107.461
Silica gel	A	90.1	0.122	424.030	361.693	62.337
Silica gel	O_2	90.1	0.132	289.354	212.596	76.758
Silica gel	CO	90.1	0.132	345.876	200.269	145.607
Silica gel	CO_2	195	0.102	700.126	573.126	127.000
Charcoal	H_2O	282.8	0.185	2326.011	2477.190	−151.179
Charcoal	H_2O	257.8	0.185	2581.860	2581.860	0.0
Charcoal	N_2	77.3	0.182	287.494	198.408	89.086
Charcoal	N_2	90.1	0.173	279.818	181.428	98.390
Charcoal	A	77.3	0.216	491.949	421.006	70.943
Charcoal	A	90.1	0.216	440.079	361.693	78.386
Charcoal	O_2	90.1	0.235	262.605	212.596	50.009
Charcoal	CO	90.1	0.180	273.538	200.269	73.269
Cr_2O_3 gel	N_2	90.1	0.0505	291.680	181.428	110.252

Now these are this is the table from which we can get the various parameter values the vm, epsilon, epsilon l etcetera for different types of adsorbent solute combinations like here we have silica gel nitrogen silica gel nitrogen for different temperatures. So, with temperature difference also we find the these values of the parameters also change. So, we have silica gel carbon dioxide, charcoal argon then charcoal carbon monoxide. So, this is the table which can be used as a two estimate the salute loading from the BET isotherm.

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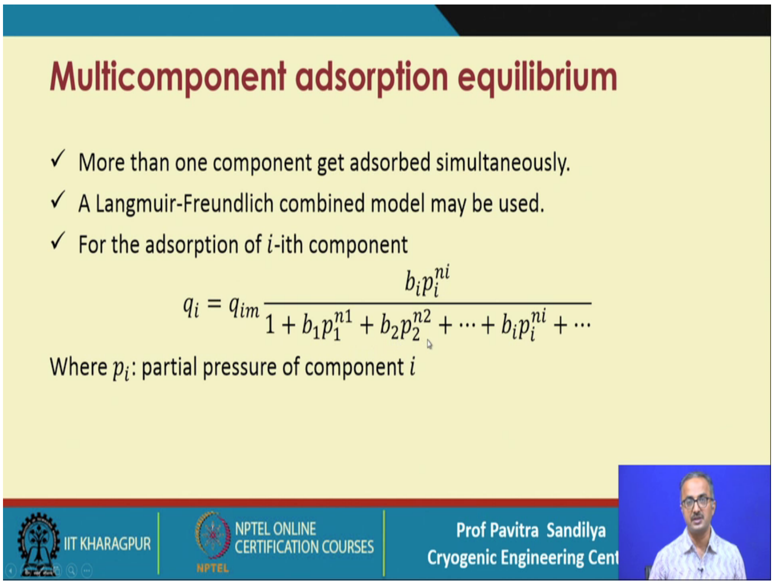

Now, we go to multi component adsorption, in this case we mean that when more than one components are getting adsorbed and in this we just modify the Langmuir Freundlich in this way that, we put this in the loading of the i th component when there are all the components have the tendency to get adsorbed and we put this in terms of this equation. This is we find that the combination of the both Langmuir and Freundlich and this you know this n 1 n 2 etcetera and the b 1 b 2 etcetera may be estimated from some experimental data.

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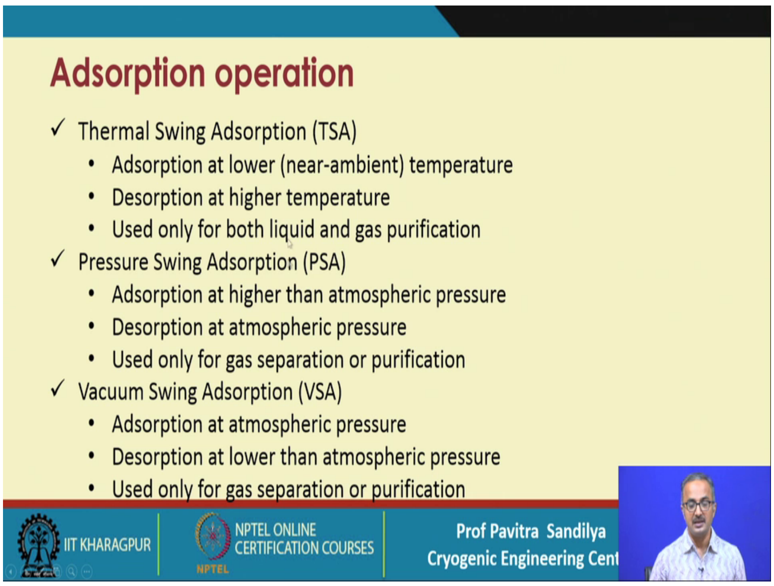

Next we come to the adsorption operation, in this operation we have different ways of operating a carrying out the adsorption, we have thermal swing adsorption, we have pressure swing adsorption and we have vacuum swing adsorption, and these have been differentiated by the way the adsorbents are regenerated. In case of TSA we find that the regeneration is done by increasing or heating the adsorbent. The in case of PSA the regeneration is done by lowering the pressure of the adsorbent, in the VSA also we lower the pressure.

The difference between PSA and TSA are that, in case of PSA adsorption is done at a pressure higher than atmospheric whereas, desorption is done at a pressure at atmospheric pressure whereas, in case of VSA adsorption is done at atmospheric pressure. Whereas, regeneration or desorption is done at a pressure lower than atmospheric that is vacuum pressure. So, that is why the name VSA and then we have a very important parameter breakthrough.

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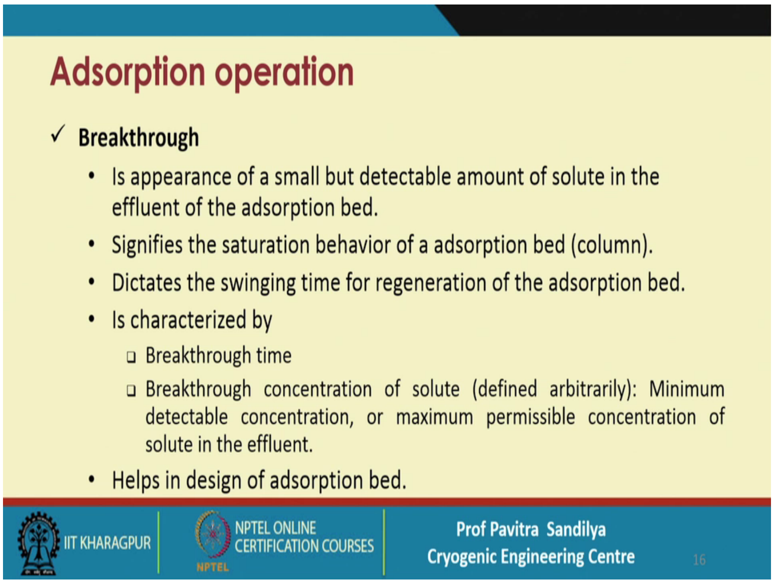

This breakthrough signifies that how long we can carry out the adsorption process when we are when we see that the solute concentration the or the concentration of the impurity in the outlet increases some user specified value then we have to stop the adsorption operation.

So, we keep monitoring the exit concentration of the impurity in the process fluid, and when we find that the impurity level has increased some specified value then we have to stop this operation and take the bed for regeneration.

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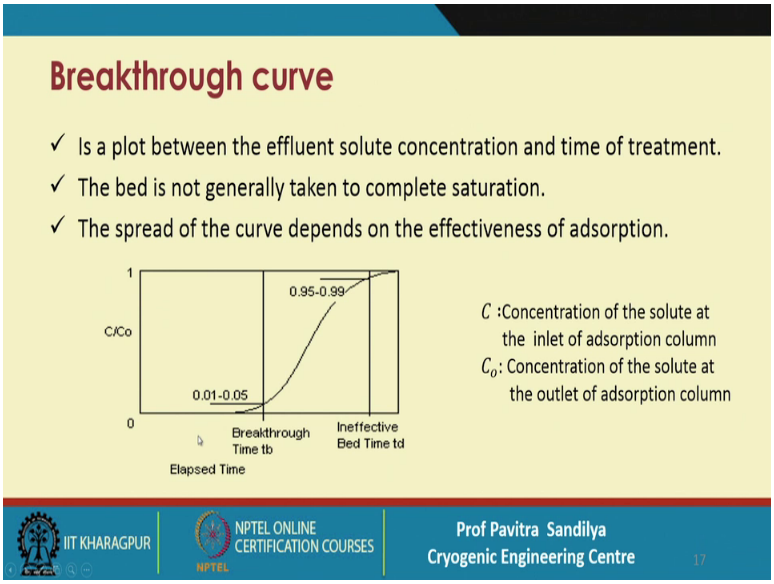

And this is how we plot this breakthrough curves on this we have the time and on this we have the normalized concentration of the impurity. And we find that these kind of thing that initially there is no impurity and slowly the impurity level increases, and we define some breakthrough time, which is taken as the time to have about 1 to 5 percent of the concentration of the impurity in the exit.

So, we want that some the impurities must go out and the desirable solute must be retained inside the bed. So, as soon as we find that the desirable solutes starts coming out of the bed we have to stop adsorption and we have to take the bed for regeneration. So, this way we are able to generate this breakthrough curve.

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For further details you can consult these books.

Thank you.