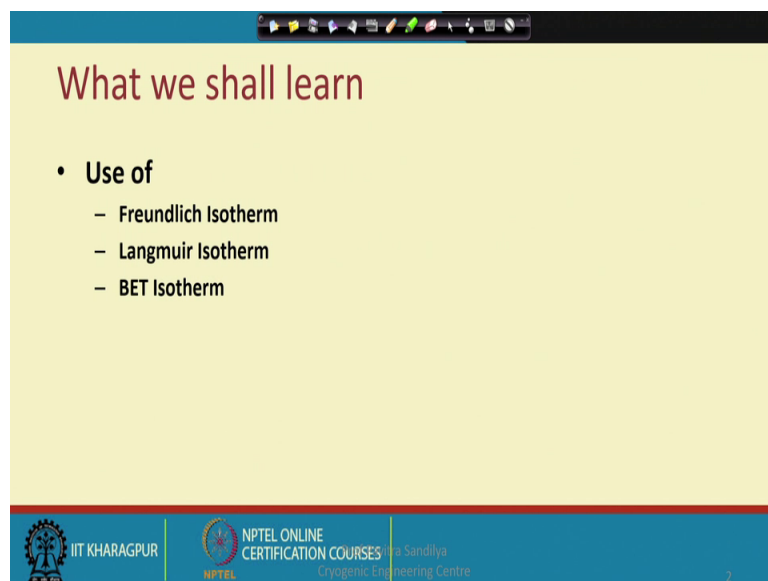


Upstream LNG Technology
Prof. Pavitra Sandilya
Department of Cryogenic Engineering Centre
Indian Institute of Technology, Kharagpur

Lecture – 39
Tutorial on equilibrium gas - solid separation

Welcome, after learning something about the adsorption process. Today we shall be looking into some of the problems; to solve this kind of processes.

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The slide is titled "What we shall learn" and lists the following topics:

- Use of
 - Freundlich Isotherm
 - Langmuir Isotherm
 - BET Isotherm

The slide footer contains the logos of IIT Kharagpur, NPTEL Online Certification Courses, and the Cryogenic Engineering Centre, along with the name Prof. Pavitra Sandilya.

Here we have, if the processes we shall be talking about; we shall be looking into the Freundlich Isotherm, Langmuir Isotherm and the BET Isotherm, how these isotherms; this Freundlich and Langmuir are fitted and how to use these isotherms for finding out the amount of mass adsorbed of the species.

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Problem statement

The following table gives the adsorption characteristics of pure propane on activated carbon at different temperatures and pressures.


T = 311 K		T = 338.7 K		T = 394 K		T = 422 K	
p	q	p	q	p	q	p	q
2.266	1.044	6	1.069	7.067	0.7099	13.07	0.6798
15.6	2.819	27.2	2.469	38.67	1.677	41.73	1.264
31.74	3.48	53.2	3.078	83.21	2.238	71.07	1.611
59.6	3.968	92.67	3.512	98.54	2.37	96.27	1.831
89.74	4.207	99.97	3.635	99.97	2.4	99.97	1.894
99.97	4.342	244.8	4.188	303.4	3.251	313.7	2.785
293	4.94	424	4.475	482.6	3.599	493	3.144

p: pressure of propane (kPa), q: amount of propane adsorbed at equilibrium (millimol/g carbon)

- Draw the adsorption isotherm at the above four temperatures
- Test the applicability of Langmuir and the Freundlich isotherms for the given data



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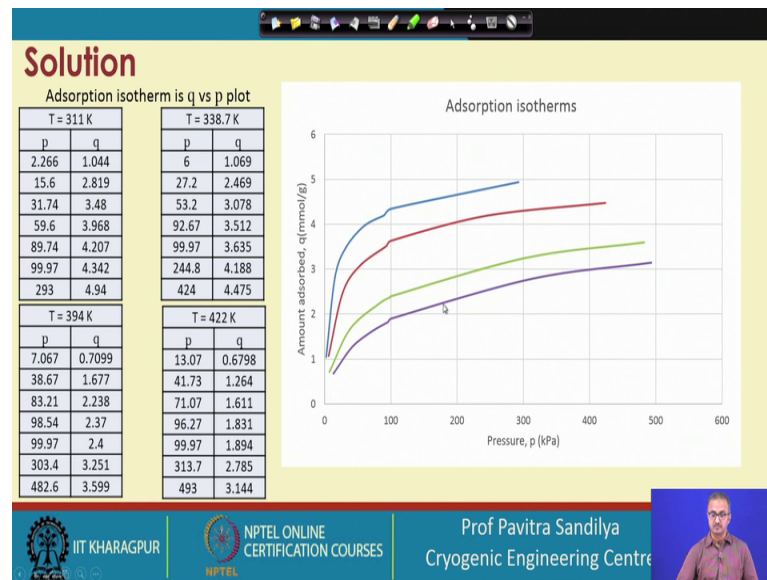


Now, first problem here we have that, there we are given some tables in which we have the partial pressure versus the loading of the adsorbate for different temperatures, for the adsorption of pure propane on the activated carbon.

So, in this case, the p represents the actual pressure of the particular species propane. And these are given here and the pressure is given in terms of the kilopascal and the adsorbate loading is given in terms of millimol per gram of the activated carbon.

And what we find that, for different temperatures, we are given this data and what we are needed to do is, first draw the adsorption isotherm at the above four temperatures. And then test the applicability of Langmuir and the Freundlich isotherm for the given data. So, in this case, what we will do? First we shall look into the adsorption isotherm by plotting the adsorbate loading versus the pressure.

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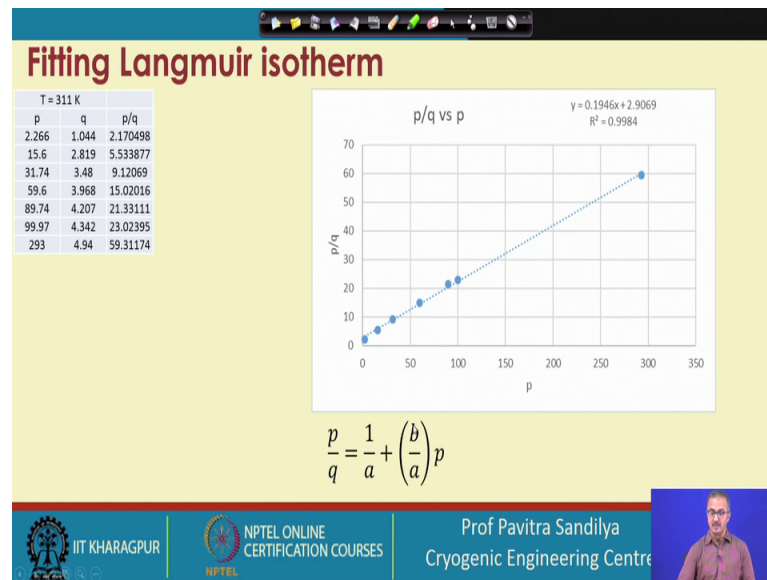
So, first we shall talk about the temperature of 311 K. And here we have the plotting; on the x axis we are plotting the pressure and you have to choose appropriately the skill and on the y axis we are plotting the adsorbate loading in terms of the millimol per gram.

So, this is the kind of plotting we get typical plotting we get. And we find that as we learnt earlier, that initially it increases and then it slowly and slowly goes towards kind of a Plato and by looking at this particular graph, we find that this is representing a favourable isotherm.

Next, we go to the next temperature; next higher temperature and we plot it and we find the this case, we find that the plotting is there 2 things. And we are finding with the increase in the temperature the amount has decreased as we learned that increase of temperature favours desorption and increase of pressure favours adsorption. So, in this case of pressure, temperatures increased. So, we find that the amount adsorbed has also come down.

Next, we go for the next higher temperature of 394 K and again, we find the amount adsorbed has come still further come down. and lastly, we go to the highest temperature. We find that this material then represents the highest temperature. By looking at the 3 these all the isotherms, we can conclude that, this one represents the lowest temperature and this one represents the highest temperature.

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Now, coming to the fitting of the Langmuir isotherms, what we have to do that, you have to remember that this is the equation represents the Langmuir isotherm.

So, in this case, as we learnt earlier that, if we plot the pressure by the loading versus the pressure, we shall be getting a straight line equation with a slope of b by a and a . Intercept of 1 by a and from these slope and the intercept, we can find the value of these 2 things a and b . So, that is what we shall be doing; first, let us consider this temperature 311 K. And for that, we are plotting this p versus q on the y axis. And this p on the x axis of p by q and then, what we do? p by q versus p .

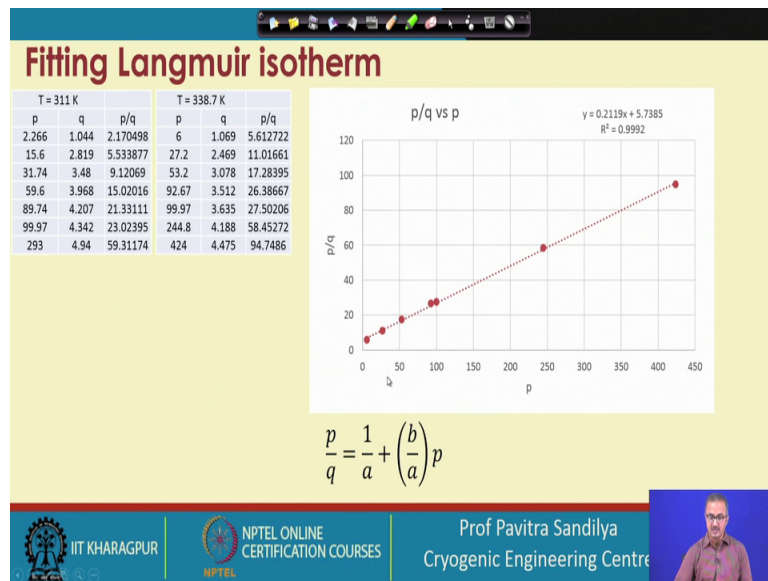
We put these values here as from this particular table, we first plot these points. Then, through these points, we use the regression or the curve fitting to fit a straight line. This, you can do on an excel sheet or other appropriate a processing data processing software like origin j new plot.

So, any of these things you can use and you can find that it will give you the sum equal base fit equation with the value of the correlation coefficient. And if this value goes near the 1 ; that means, we are able to relate it very nicely. So, depending on the value of the correlation coefficient, it will tell us about the goodness of our feet and in this case, we find it is quite good fit.

So, this is the way we are finding that we are getting a straight line. And from this straight line, if we take the slope of the straight line, we shall get the value of b by a and the y intercept. If you look into this y intercept will give us 1 by a.

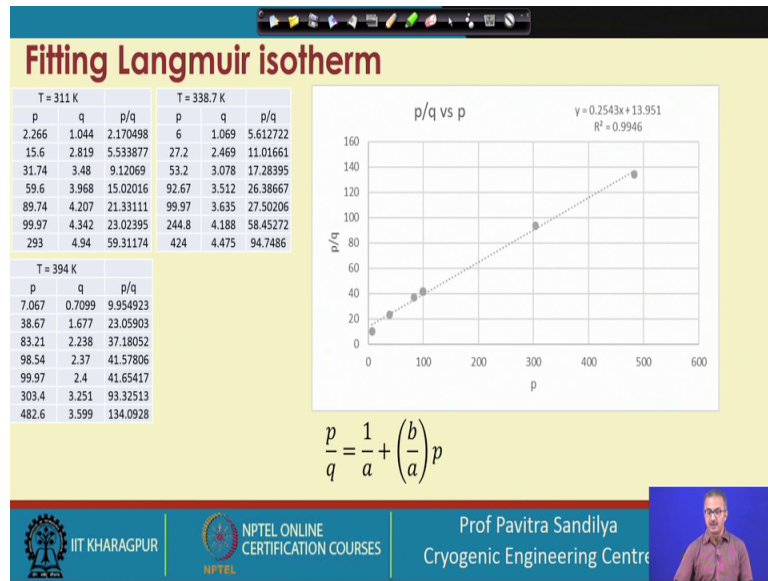
So, the reciprocal of the intercept is the value of a; whereas, if we divide the slope by the intercept, we shall be able to get the value of b. So, that is how we can find the parameter values for the Langmuir isotherm from this kind curve.

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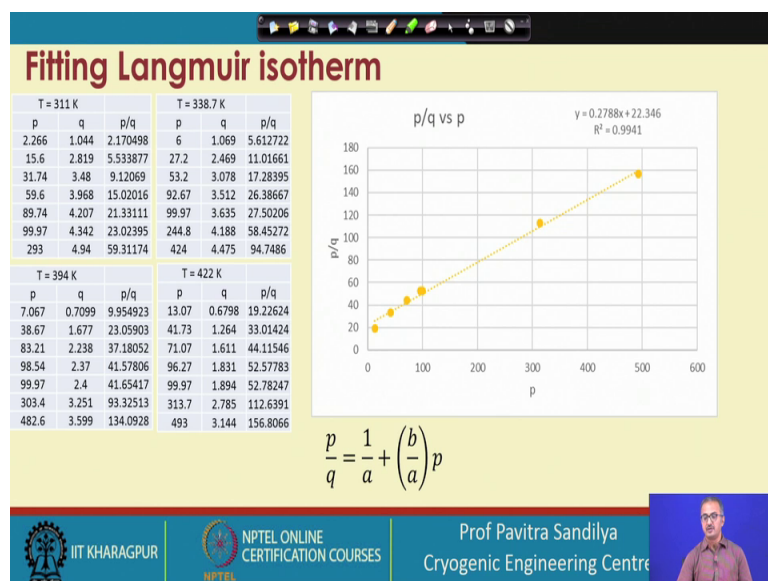


And then, we can do it for the other temperatures also, we find that, for each of them we are getting different values of the a and b.

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So, here we are showing four different temperatures. We are getting these different plots for this p by q versus p and we are getting different values of a and b.

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Fitting Langmuir isotherm

T = 311 K			T = 338.7 K		
p	q	p/q	p	q	p/q
2.266	1.044	2.170498	6	1.069	5.612722
15.6	2.819	5.533877	27.2	2.469	11.01661
31.74	3.48	9.12069	53.2	3.078	17.28395
59.6	3.968	15.02016	92.67	3.512	26.38667
89.74	4.207	21.33111	99.97	3.635	27.50206
99.97	4.342	23.02395	244.8	4.188	58.45272
293	4.94	59.31174	424	4.475	94.7486

T = 394 K			T = 422 K		
p	q	p/q	p	q	p/q
7.067	0.7099	9.954923	13.07	0.6798	19.22624
38.67	1.677	23.05903	41.73	1.264	33.01424
83.21	2.238	37.18052	71.07	1.611	44.11546
98.54	2.37	41.57806	96.27	1.831	52.57783
99.97	2.4	41.65417	99.97	1.894	52.78247
303.4	3.251	93.32513	313.7	2.785	112.6391
482.6	3.599	134.0928	493	3.144	156.8066

$$\frac{p}{q} = \frac{1}{a} + \left(\frac{b}{a}\right)p$$

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Next, we come to the comparing these all these things, we find that, as we found for the other ones that the highest temperature lowest temperature, you can see that these are highest temperature. So, in this case, we find for the highest temperature. We are getting it on a top and our lowest, we are getting at the bottom.

So, this is showing the comparison of the various plots at different temperatures. And from this, we can see that, how this value of a and b would change for the different temperatures.

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Fitting Freundlich isotherm

T = 311 K				T = 338.7 K			
p	q	ln p	ln q	p	q	ln p	ln q
2.266	1.044	0.818016	0.043059	6	1.069	1.791759	0.066724
15.6	2.819	2.747271	1.036382	27.2	2.469	3.303217	0.903813
31.74	3.48	3.457578	1.247032	53.2	3.078	3.974058	1.12428
59.6	3.968	4.087656	1.378262	92.67	3.512	4.529045	1.256186
89.74	4.207	4.496917	1.43675	99.97	3.635	4.60487	1.290609
99.97	4.342	4.60487	1.468335	244.8	4.188	5.500442	1.432223
293	4.94	5.680173	1.597365	424	4.475	6.049733	1.498506

$$\ln q = \ln k + \frac{1}{n} \ln p$$

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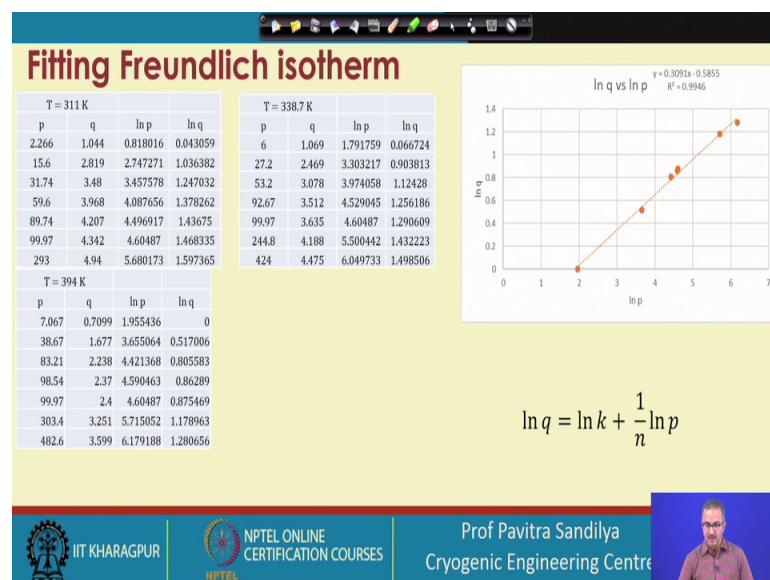
Now, next we come to the fitting of the same data set for the Freundlich isotherm. And this is the Freundlich isotherm in a rearranged fashion. And in this case, as we learnt earlier [vocalized-noise,] that if we plot the logarithm of the adsorbent loading versus logarithm of the pressure, we would get a straight line in which the slope will be $1/n$ and the y intercept will be $\log k$, which are the parameters from the Freundlich isotherm.

So, again we considered all the temperatures and we find that, we are fitting these things. And in please note that, in this case, the value of the R square has come down substantially from about 0.99 which was obtained in the previous case to this value of 0.91.

So, the value of this R square, if we compare the value of the R square for the various isotherms, whenever we find for the for the isotherm for which the R squared is nearly 1, that will be the best fit isotherm for. So, in this case, we find that the Freundlich is not able to predict the adsorption behaviour as it was done previously.

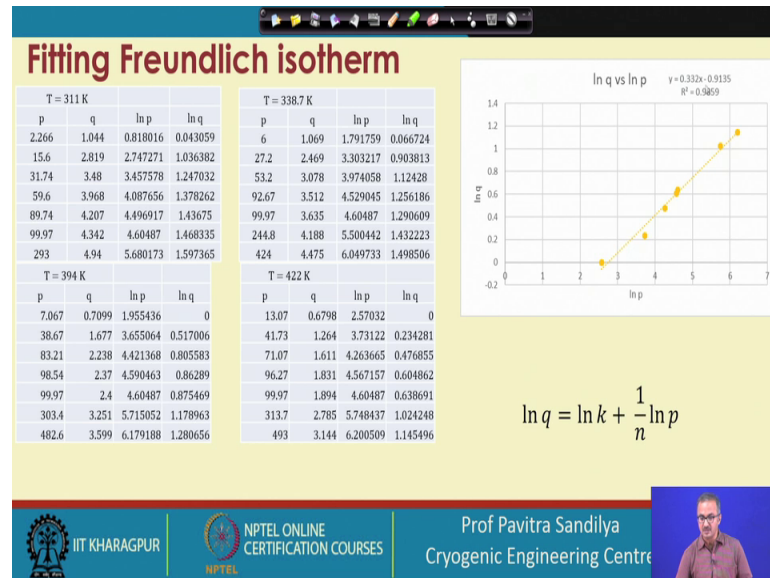
So, now we have this Freundlich and this for the other temperatures also, we find these plots.

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And we find again this value of the R square is coming almost of the same order. And in this case, we find that in the higher temperature, they are matching. Here also, we find for higher temperature, we are getting a very good match of 0.99.

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And if you go to still higher temperature, we are getting a slight decrease, but it is quite good.

So, what we find that, for higher temperature Freundlich is able to give us a better fitting to the given data set than at lower temperature. But, in general, if we compare the two, we find that the Freundlich and the Langmuir, then we find that for Langmuir, the fitted fittings are better than the Freundlich.

So, we conclude that, the Freundlich should be the one sorry, the Langmuir will be the one which should be used for fitting this particular dataset. And that is a how is come conclude that the propane and charcoal activated carbon. This pair for those the Langmuir isotherm better than the Freundlich isothermal.

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Problem statement

Determine the mass of silica gel required to adsorb 10 m^3 of carbon monoxide at 50 kPa and 90.1 K . The saturation pressure for CO at 90.1 K is 241.5 kPa .

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So, this is how we compare the various isotherms by fitting them individually to a given data set. Next we come to the other problem. In this case, we shall be using the BET isotherm to find out the amount of the particular solute adsorbed on a given adsorbent at some particular temperature pressure.

Now, in this particular problem, we have a silica gel at the adsorbent and we have carbon monoxide and we have been given that, we have to adsorb about 10 cubic meter of the carbon monoxide at this particular pressure of 50 kilo Pascal and a temperature of 90.1 Kelvin. And you can say it is a cryogenic temperature very much much lower than the 0 degree centigrade; the cryogenic temperature.

And the saturation pressure for carbon monoxide at this particular temperature is given as 241.5 kilo Pascal. So, with these data, we have to figure out what would be the amount that is a mass of the carbon monoxide that can be absorbed on this particular silica gel adsorbent.

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Solution

Given:

Pressure, $p = 50 \text{ kPa}$
 Saturation pressure, $p_{\text{sat}} = 241.5 \text{ kPa}$
 Temperature = $T = 90.1 \text{ K}$
 $V = 10 \text{ m}^3$

To Find:

Mass of CO adsorbed (m_a)

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Now, first let us see what are the things given to us. The pressure, the saturation pressure, the temperature and the volume to be adsorbed and we have to find out the carbon monoxide that can get adsorbed.

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Solution | Parameters for CO adsorption on silica gel at 90.1 K

Given:	Adsorbent	Adsorbed gas	Temperature (K)	v_m (m ³ /kg)	ϵ_a (kJ/kg)	ϵ_1 (kJ/kg)	$(\epsilon_a - \epsilon_1)$ (kJ/kg)
Pressure	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
Saturation	Silica gel	A	90.1	0.122	424.030	361.693	62.337
	Silica gel	O ₂	90.1	0.132	289.324	212.596	76.728
Temperature	Silica gel	CO	90.1	0.132	345.876	200.269	145.607
	Silica gel	CO	195	0.102	700.126	573.126	127.000
$V = 10$	Charcoal	H ₂ O	282.8	0.185	2326.011	2477.190	-151.179
	Charcoal	H ₂ O	257.8	0.185	2581.860	2581.860	0.0
To Find:	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
Mass of	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 ₂ O ₃ gel	N ₂	90.1	0.0505	291.680	181.428	110.252

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Now, here are the parameters. First, which we have to have for this isotherm? We are going to use a BET isotherm and the parameters are listed here. And we shall be choosing the silica gel versus carbon monoxide at 90.1 K and we see the various

parameter values are listed in this particular table. So, we shall pick up these values appropriately.

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Solution

Given:

Pressure, $p = 50$ kPa
 Saturation pressure, $p_{\text{sat}} = 241.5$ kPa
 Temperature = $T = 90.1$ K
 $V = 10$ m³

To Find:
 Mass of CO adsorbed (m_a)

Parameters for CO adsorption on silica gel at 90.1 K
 $v_m = 132.0$ dm³/kg $\theta_a = 490.6$ K
 $z = \exp(\theta_a/T) = \exp(490.6/90.1) = 231.6$
 $p/p_{\text{sat}} = 50/241.5 = 0.207$

$$\frac{V}{m_a} = \frac{v_m z (p/p_{\text{sat}})}{(1 - p/p_{\text{sat}})[1 + (z - 1)(p/p_{\text{sat}})]}$$

$$\frac{V}{m_a} = \frac{(132.0)(10^{-3})(231.6)(0.207)}{(1 - 0.207)[1 + (231.6 - 1)(0.207)]} = 0.1637 \text{ m}^3/\text{kg}$$

$$m_a = 10/0.1637 = \mathbf{61.07 \text{ kg}}$$

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And now, we shall be using these from this v_m and θ_a , if we find the value of z which is needed for the BET isotherm. And when this is the BET isotherm here, and here we find the ratio of p by p_{sat} as 0.27 and then we keep on plugging in the values of the various parameters in this equation.

And in this case, V is the 10 cubic meter and then, we find this is the value we get. And here, ultimately by knowing the V by m_a value, then the m_a is this V divided by this particular value. And we get this 61.07, that is the; that means, this much is the amount of the carbon monoxide that can get adsorbed on the silica gel for that given particular pressure and the given temperature.

Please understand that, if the temperature or the pressure or both of them get changed, then this amount will also get changed. And you can of course, we have to for this to compare these values, we have to use the data appropriately.

Maybe we have to take some data from the literature and which are not listed in the given table.

So, in the we in this particular lecture, we have learned about, how to use the Freundlich isotherm, the Langmuir isotherm and the BET isotherm to analyse the adsorption separation in some natural gas system.

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Problem statement (breakthrough curve)

An adsorption bed has to be designed to remove water from natural gas. Two adsorbents A and B are being evaluated for using in this adsorption column. Permissible exit H_2O concentration is 5% of the inlet H_2O concentration. The breakthrough curves for these adsorbents are given in the following figure. Which adsorbent would you suggest for H_2O separation? Justify your suggestion.

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Next, we come to a breakthrough. Now, we learned about breakthrough. Their breakthrough indicates that, when a particular adsorption bed will be taken has to be taken for regeneration.

Now, now, the problem is here that, we have an adsorption bed to be designed to remove water from natural gas and we have 2 adsorbents A and B to be evaluated that which one we should take.

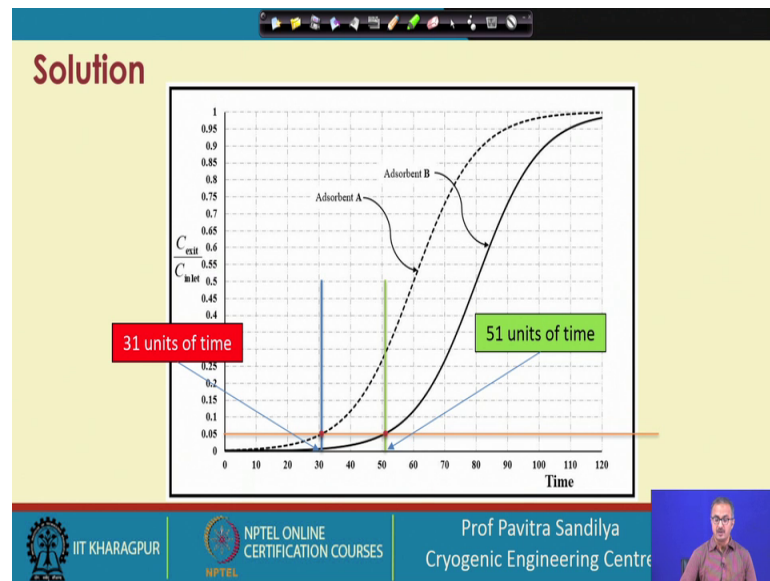
So, for that, we conduct to evaluate the efficacy of any adsorbent to separate a given species. What we do? We take the breakthrough other than the (Refer Time: 13:20) also. Then we look at a breakthrough and we find that, the we have been that permissible H_2O concentration is 5 percent of the unit H_2 concentration and the breakthrough curves are given by the following figures and we have to suggest that which of these 2 may be used for separating out the water.

So, here we have the breakthrough curve that what is one is for the adsorbent A, one is for the adsorbent B. And on the y axis, we have plotted this ratio of c_{exit} by c_{inlet} and

in and this C_{exit} by C_{inlet} is the normalized concentration and on the x axis, we have plotted the time.

And now, we see that the nature of this to breakthrough curves seems to be almost same similar, that is; sigmoidal nature. But, we find that, there are there differences in their nature that, this for adsorbent A the breakthrough takes gets away from 0 optima of the this normalized concentration at earlier time then for adsorbent B.

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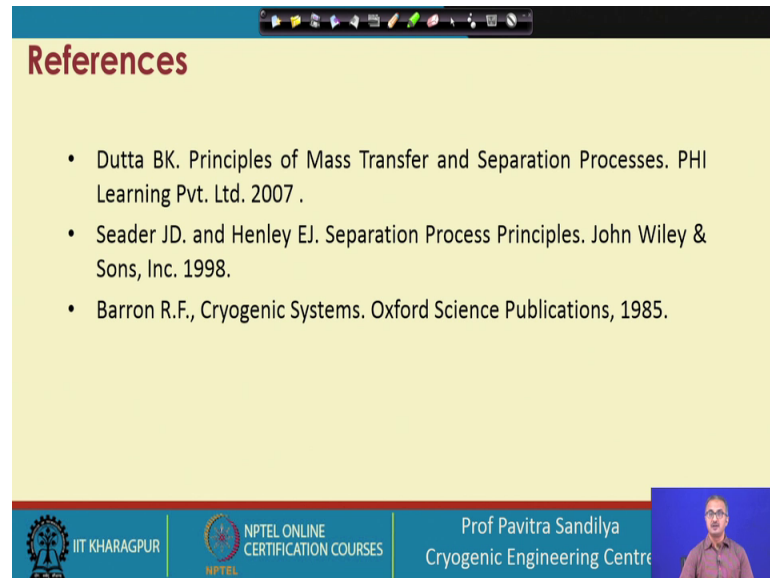
Now, to solve this problem, what we shall do? We will consider this particular plots and then we shall be locating the given permissible exit concentration, that is, 0.05. And we draw a horizontal straight horizontal line and from this, we can see these intersection points represents the breakthrough time.

Now, looking at the breakthrough time, we find that, this for this adsorbent A, this is about 31 units of time and for adsorbent B, it is about 51 units of time. Now, because the breakthrough times are different, it means that whenever the breakthrough is higher; that means, that particular bed is able to retain the solute or the separated the particular solute more effectively than the other bed.

So, by looking at the breakthrough time, because for adsorbent, we are finding the breakthrough time is were higher than that for adsorbent A. So, we conclude that

adsorbent B should be used for this particular system. So, that is how we make use of the breakthrough curve.

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And you can refer to these books for further detail.

Thank you.