Physical Chemistry of Surfaces
Homework1
Evaluation of low temperature N_2 vapour adsorption isotherms by Langmuir and BET model

1. Plot your isotherm

2. Compare its shape to the IUPAC isotherms, then conclude your isotherm type and explain why? What information you can get from the type you selected (i.e. the characteristics feature of the isotherm).

3. Read V at $p/p_0 \rightarrow 1$; supposing that V is the volume of N_2 in a condensed form, calculate the total pore volume "V_{tot}" supposing that all the gas adsorbed is in liquid form. The density of the liquid N_2 0.808 g/cm^3 at its boiling point (77 K).

4. Plot the linearized form of Langmuir and BET models for the adsorption branch in separate graphs.

5. Try to apply the least square linear fit for both models and find the lower and upper limits of the range where the quality of fitting is good (R^2). It is possible that only one of them works. Even if both apply, the limits might be different. If only one of the models give a reasonable fit you continue the work with that particular model.

6. Select 5 or 7 points in equal distance within the selected range (see #5) and apply the least square linear fit and estimate the slope, intercept and regression of the fit; R^2.

7. Based on the data obtained in (#6) calculate the parameters of the models: monolayer capacity, K (Langmuir) and/or C (BET).

8. Calculate the surface area from the two models.

9. Supposing that you have cylindrical pores with open ends estimate the average radius of the pores from both models.

10. Take care of the sign, digits and units. Also do not forget to label the axes.

OWELBX_Silica6
Physical Chemistry of Surfaces
Homework1

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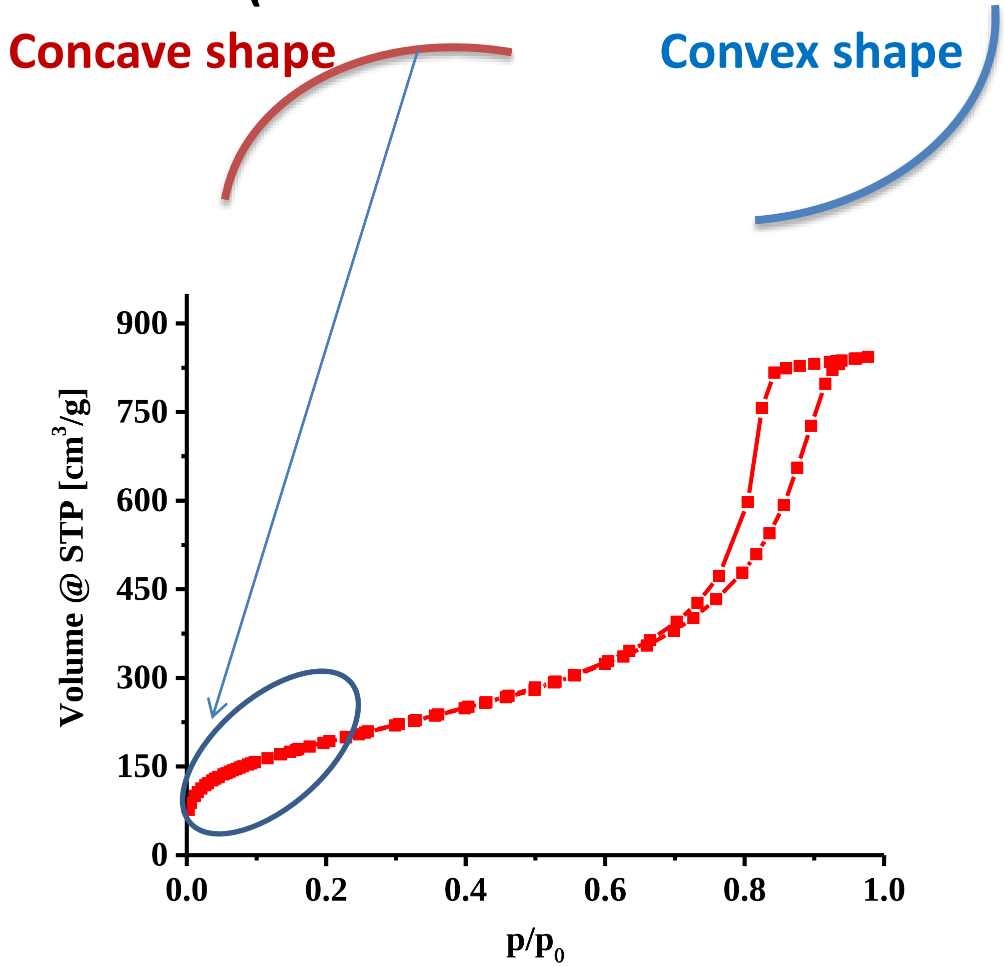
Objective: Evaluation of low temperature N_2 vapour adsorption isotherms by Langmuir and BET model.

1. Plot your isotherm

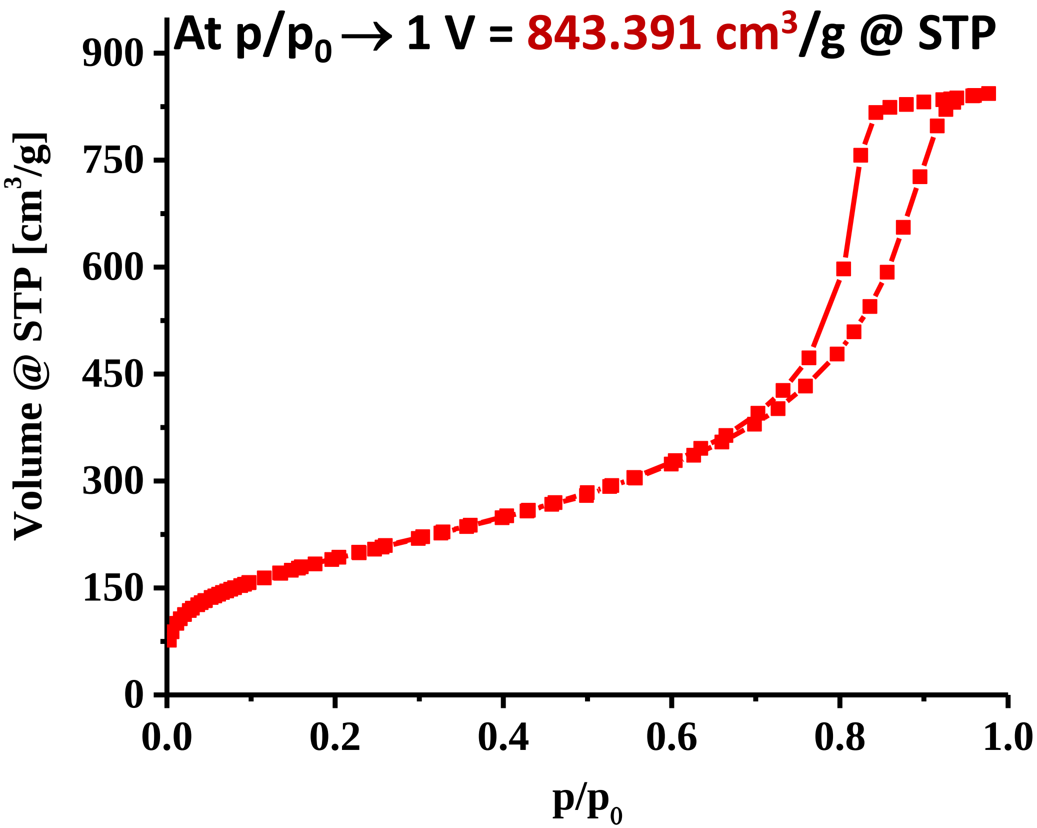
2. Compare its shape to the IUPAC isotherms, then conclude your isotherm type and explain why? What information you can get from the type you selected (i.e. the characteristics feature of the isotherm).



The isotherm has a **<u>concave initial section</u>** with **<u>hysteresis</u>**: According to IUPAC classification it is typically to the isotherm **<u>type IV.</u>** It is typical when mesopores are present, and the adsorption/desorption branches do not overlap (irreversibility).

Volume @(STP): mean that the data has been collected at standard temperature (273 K) and standard pressure (1 atm).

3. Read V at $p/p_0 \rightarrow 1$; supposing that V is the volume of N_2 in a condensed form, calculate the total pore volume "V_{tot}" supposing that all the gas adsorbed is in liquid form. The density of the liquid N_2 0.808 g/cm^3 at its boiling point (77 K).



Convert this gas voulme to V_{tot}:

Condition: all the pores are filled with LIQUID nitrogen, i.e., the gas is condensed.

To convert the gas volume to liquid volume:

1. Number of moles of adsorbed N_2 form $pV = nRT$

Table 1 Constant values for calculating total pore volume.

Constants and given
Gas constant (R) = 8.314 J/K mol = 8.314 Nm/K mol
STP ≡ Standard Temperature (T) = 273 K, and standard pressure (p) = 101325 Pa (N/m^2)
Molecular weight (Mwt) of N_2 = 28 g/mol
Liquid density (ρ) of N_2 = 0.808 g/cm^3

$$n = \frac{pV}{RT} \quad , m_{nitrogen} = n\,[\text{mol}] \times M_{wt}\left[\frac{g}{mol}\right] \quad , V_{liquid\;nitogen} = \frac{m_{nitrogen}}{\rho}$$

$$V_{liquid\ nitrogen} = V_{tot} = \frac{101325\ \cancel{N}/\cancel{cm^2}\, 843.391 cm^3/g \times 28\ \cancel{g}/\cancel{mol}}{10^6 \times 8.314 \frac{\cancel{Ncm}}{\cancel{Kmol}} \times 273 \cancel{K} \times 0.808\ \cancel{g}/\cancel{cm^3}} = 1.30472\cancel{678} \frac{cm3}{g}$$

$$= 1.30473 \frac{cm3}{g}$$

The general rule of thumb "the **calculated result** (e.g. **1.30472678** $\boldsymbol{cm^3/g}$) based on the measured data (e.g. $\mathbf{843.391} \boldsymbol{cm^3/g}$) cannot be more precise than the least precise measurements. Therefore, the reported number (e.g. **1.30473** $\boldsymbol{cm^3/g}$) must contains the same number of significant digits as the least number of significant digits in the measured data.

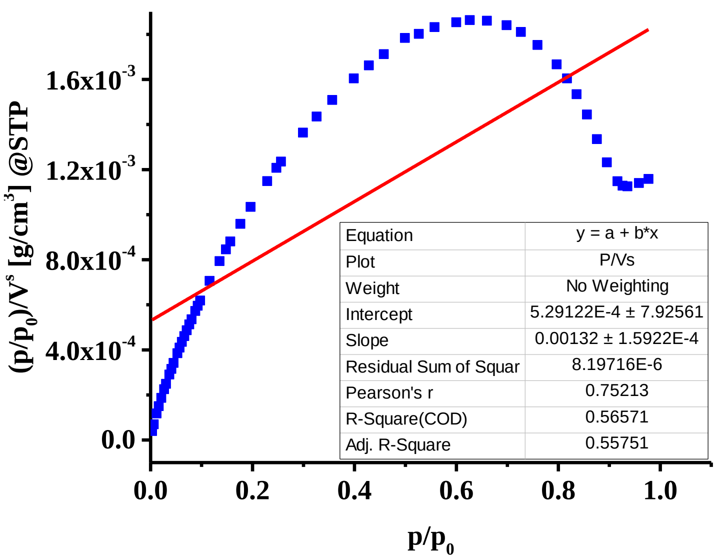
4. Plot the linearized form of Langmuir and BET models for the adsorption branch in separate graphs.

Table 2. linearized Langmuir and BET models.

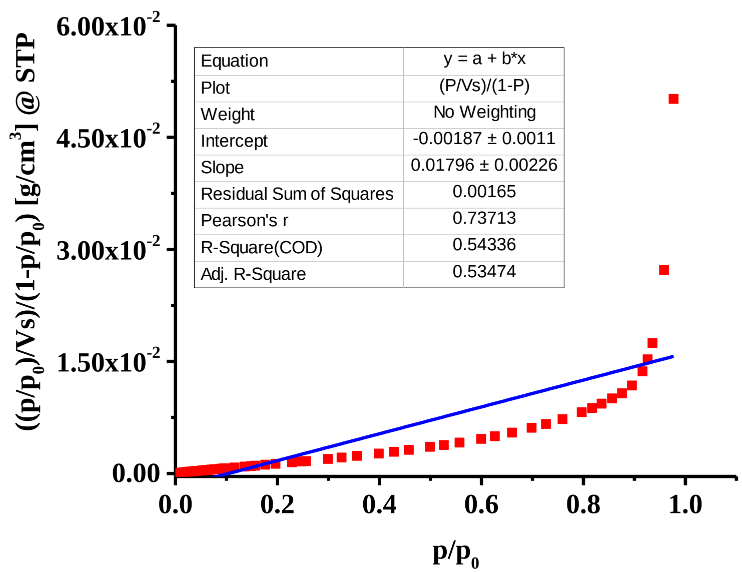
Model	Linearized form	Plot
Langmuir	$\frac{p/p_0}{V^s} = \frac{1}{KV_m} + \frac{p/p_0}{V_m}$	$\frac{p/p_0}{V^s}$ vs p/p_0
BET	$\frac{p/p_0}{V^s(1-p/p_0)} = \frac{1}{CV_m} + \frac{(c-1)p/p_0}{CV_m}$	$\frac{p/p_0}{V^s(1-p/p_0)}$

4. Plot the whole of adsorption branch according to linearized form of Langmuir and BET models.

Langmuir



BET



None of them can be fitted with a straight line in the whole range.

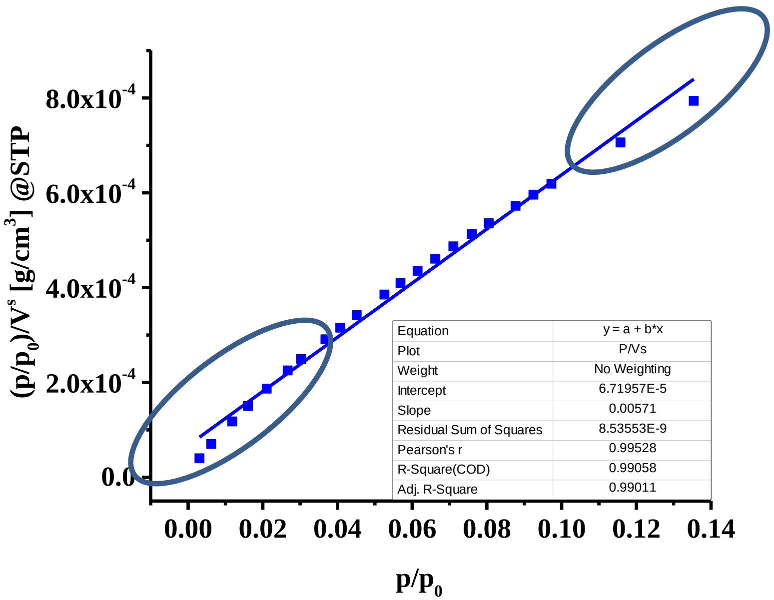
5. Try to apply the least square linear fit for both models and find the lower and upper limits of the range where the quality of fitting is good (R^2). It is possible that only one of them works. Even if both apply, the limits might be different. If only one of the models give a reasonable fit you continue the work with that particular model.

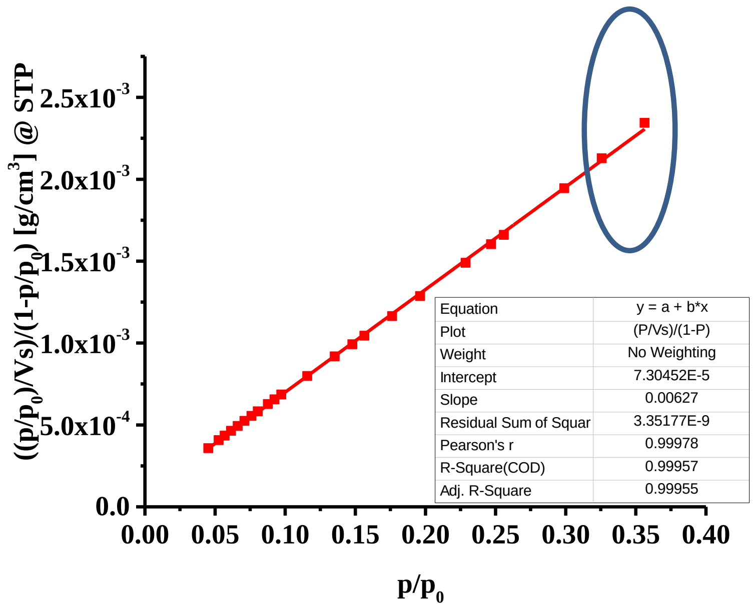
Trial 1: Langmuir

Relative pressure range

0.0 - 0.15 (arbitrarily chosen)

BET is generally applicable in the p/p_0 range of 0.05-0.35



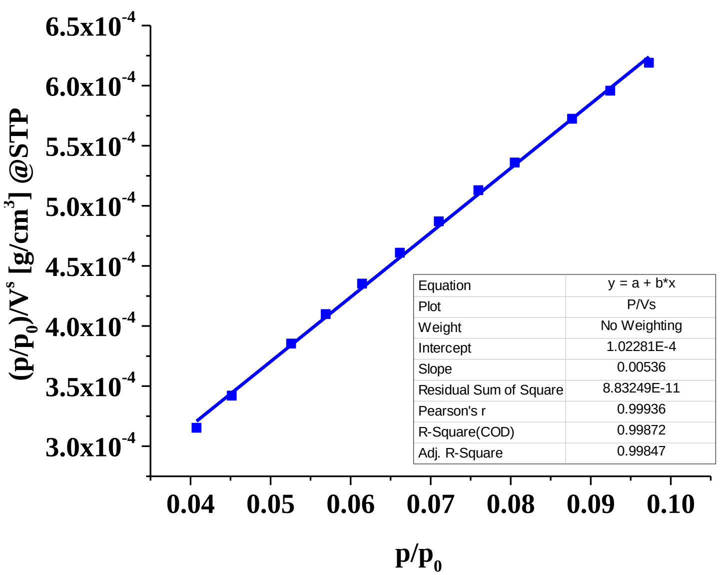


Although R or R^2 might be acceptable, by naked eye it is visible, that these fits are not correct.

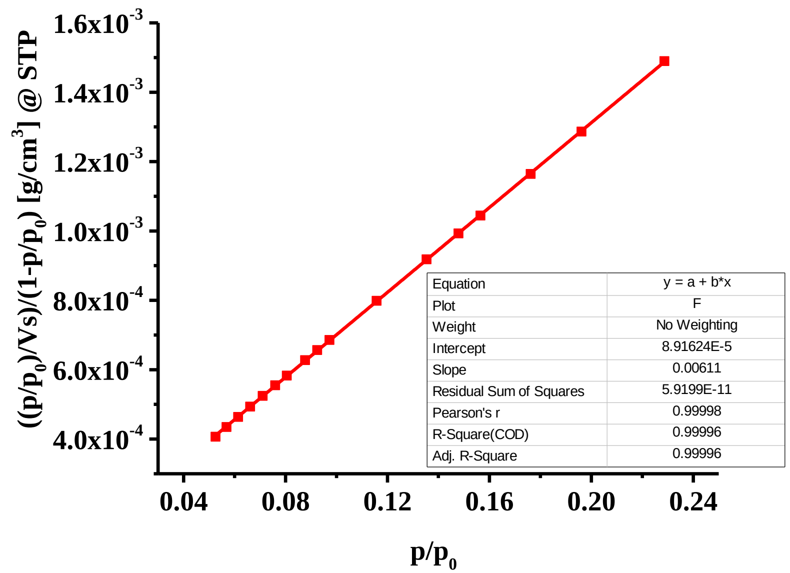
Trial 2:

Based on the plot of trial 1, we changed the limits (narrow the range):

Langmuir: p/p_0 range 0.04-0.10

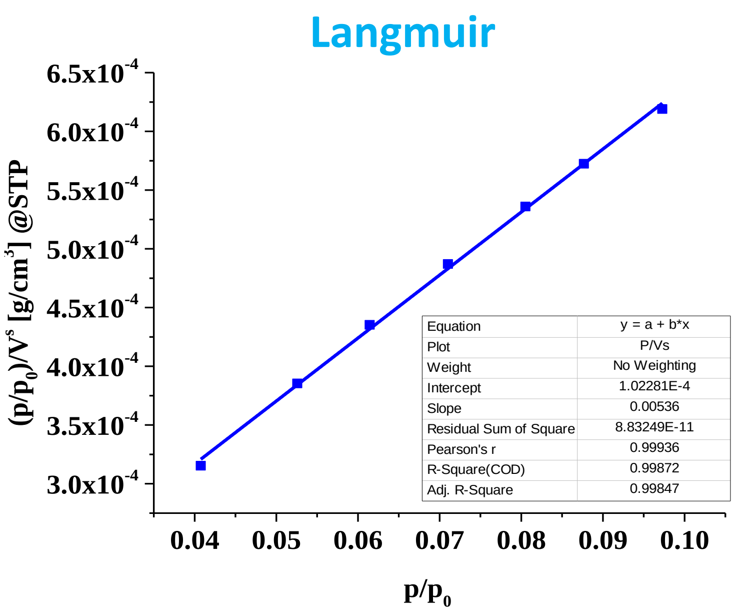


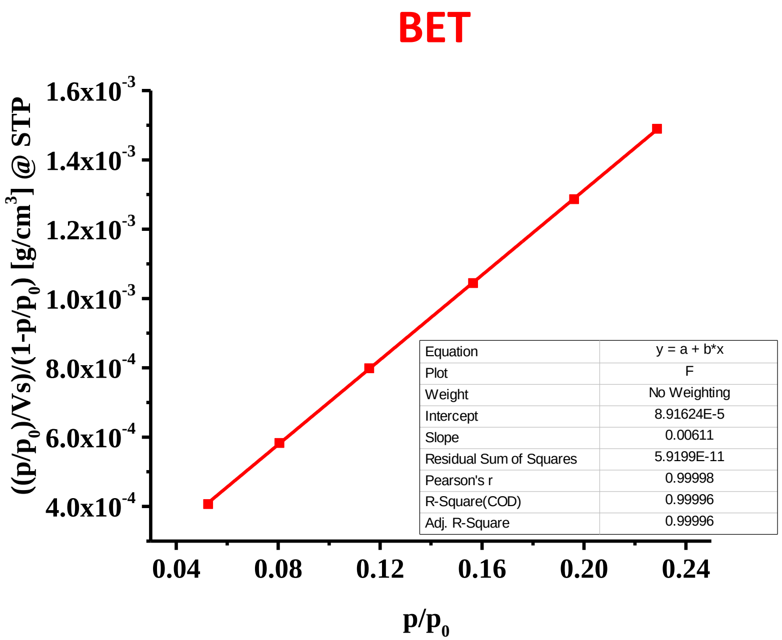
BET: p/p_0 range 0.05-0.20



In this limited range both the visual impression and R or R^2 are acceptable (you have to play with the data as long as you get to this stage: may need several trials).

For statistical reasons we select odd number of points (5 or 7) in equal distance within the selected range (concerning p/p_0) and apply the least square linear fit and estimate the slope, intercept and regression of the fit; R^2.





Based on the data obtained calculate the parameters of the models: V_m (STP) capacity, K (Langmuir) and/or C (BET).

From the slope and intercept show how the V_m and K or C can be obtained and calculate them.

Langmuir

Intercept	1.02281 E-4
Slope	5.36 E-3

$$\frac{p/p_0}{V^s} = \frac{1}{KV_m} + \frac{p/p_0}{V_m}$$

$$\frac{1}{V_m} = Slope$$

- $V_m = \frac{1}{Slope} = \frac{1}{0.00536}$ = 186.567~~164~~ cm^3/g =186.567 cm^3/g @STP
- $\frac{1}{KV_m} = Intercept$

$$K = \frac{1}{V_m Intercept} =$$

$K = \frac{1}{1.0228\times10^{-4}\times186.567}$ = 52.4052~~16~~ = 52.4052

BET

Intercept	8.91624E-5
Slope	6.11 E-3

$$\frac{p/p_0}{V^s(1-p/p_0)} = \frac{1}{CV_m} + \frac{(c-1)p/p_0}{CV_m}$$

$\frac{(C-1)}{CV_m} = \text{Slope}....(2)$

$\frac{1}{CV_m} = \text{Intercept}......(3)$

Divide eq.(2)by (3)

- $C\text{-}1=\frac{\text{Slope}}{\text{Intercept}}$

$C= \frac{0.00611}{8.91624\times10^{-5}} +1= 69.52664 = 69.5266$

- $\text{Intercept} = \frac{1}{CV_m}$, $V_m = \frac{1}{\text{C.Interccept}}$

$V_m= \frac{1}{69.5266\times8.91624\times10^{-5}}$

= 161.312~~12~~ cm^3/g @STP
=161.312 cm^3/g @STP

8. Calculate the surface area from the two models.

Avogadro Number (N_A) = 6 × 10^{23} , a_s = 0.162 nm

$$S_A = n_m N_A a_s \qquad \frac{m^2}{g} \qquad\qquad n = \frac{pV}{RT}$$

Langmuir:

$$n_{m,L} = \frac{101325\cancel{N}/\cancel{cm^2}\,186.567\cancel{cm^3}/g}{10^6 \times 8.314\frac{\cancel{Ncm}}{\cancel{K}mol} \times 273\cancel{K}} = 8.32873\times 10^{-3}\ \text{mol/g}$$

$$S_{A,L} = 8.32873 \times 10^{-3}\cancel{mol}/g \times 6 \times 10^{23}\cancel{mol^{-1}} \times 0.162 \times 10^{-18} m^2 = 809.553\,\frac{m^2}{g}$$

BET:

$$n_{m,B} = \frac{101325\cancel{N}/\cancel{cm^2}\,161.312\cancel{cm^3}/g}{10^6 \times 8.314\frac{\cancel{Ncm}}{\cancel{K}mol} \times 273\cancel{K}} = 7.20130 \times 10^{-3}\ \text{mol/g}$$

$$S_{A,B} = 7.20130 \times 10^{-3}\cancel{mol}/g \times 6 \times 10^{23}\cancel{mol^{-1}} \times 0.162 \times 10^{-18} m^2 = 699.966\,\frac{m^2}{g}$$

Supposing that you have cylindrical pores with open ends estimate the average radius of the pores from both models.

The surface of these pores can be expressed as: $S = 2r\pi \cdot l$, where l is the length of the pore. The volume of the pore: $V = r^2\pi \cdot l$

Substitute: $r = \frac{2V}{S}$

Langmuir:

$$r_L = 2\times \frac{1.30473\times 10^{21} nm^{\cancel{3}}/\cancel{g}}{809.553\times 10^{18} \cancel{nm^2}/\cancel{g}} = \mathbf{3.22334\ nm}$$

BET:

$$r_B = 2\times \frac{1.30473\times 10^{21} nm^{\cancel{3}}/\cancel{g}}{699.966\times 10^{18} \cancel{nm^2}/\cancel{g}} = \mathbf{3.72800\ nm}$$

Table 3
Sample name: Silica6
Type of the isotherm: IV

Model	--	Langmuir	BET	Unit
Total pore volume	1.30473	--	--	cm^3/g
Pressure range where linear fit is applicable (if at all)		0.04-0.10	0.05-0.20	-
R^2		0.99872	0.99996	--
Volume of gas required for monolayer coverage (STP)		186.567	161.312	cm^3/g
K		52.4052	--	--
C		--	69.5266	--
Surface area		809.553	699.966	m^2/g
Average pore radius		3.22334	3.72800	nm