Physical Chemistry of Surfaces
Homework2
Evaluation of low temperature N_2 vapour adsorption isotherms by DR model

1. Apply the linear Dubinin-Radushkevich plot if your system is microporous.

From the linear fit conclude the p/p_0 range where the fit can be used. Get the best fit, conclude the slope, the intercept and the regression (R or R^2) From the intercept calculate the micropore volume (conversion is similar as in Homework 1.

2. Supposing that all the molecules filling the micropores have direct contact with the surface estimate the surface area of the micropores.

3. Summarize your results in a table.

4. Compare BET and DR surface areas. Are you puzzled? Any hint for explanation?

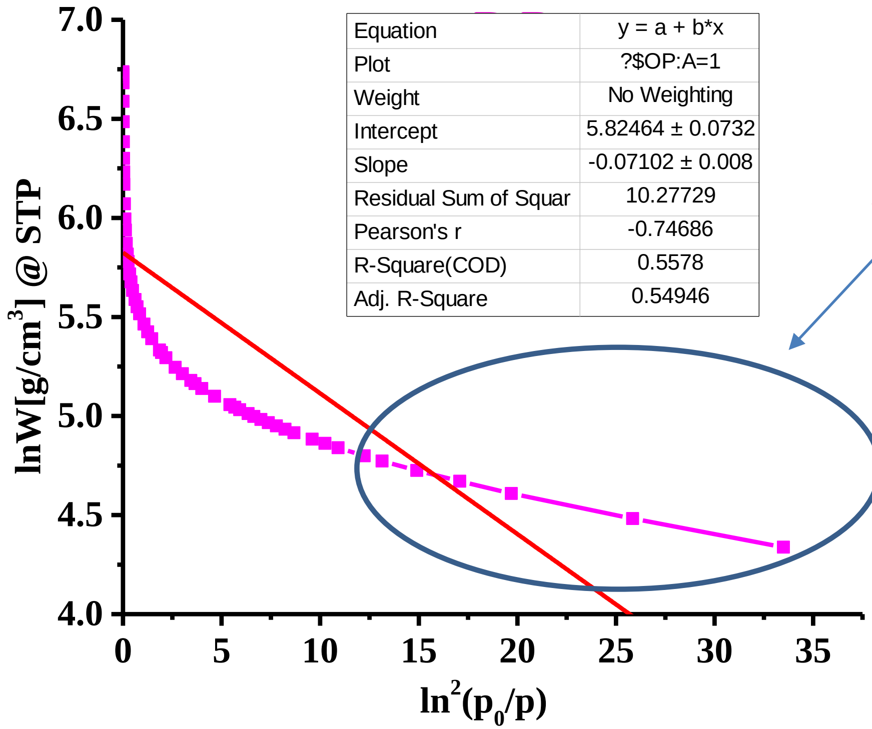
Plot the linearized form of DR model for the adsorption branch in separate graphs.

Table 2. linearized DR model.

Model	Linearized form	Plot
DR	$\ln W = lnW_0 - (\frac{RT}{E})^2 ln^2 \frac{p_0}{p}$	ln W vs $ln^2 \frac{p_0}{p}$

1. Apply the linear Dubinin-Radushkevich plot if your system is microporous.

Pls. recognise, that the horizontal axis contains p_0/p,
i.e., the isotherm „reads" from the right to left!!!

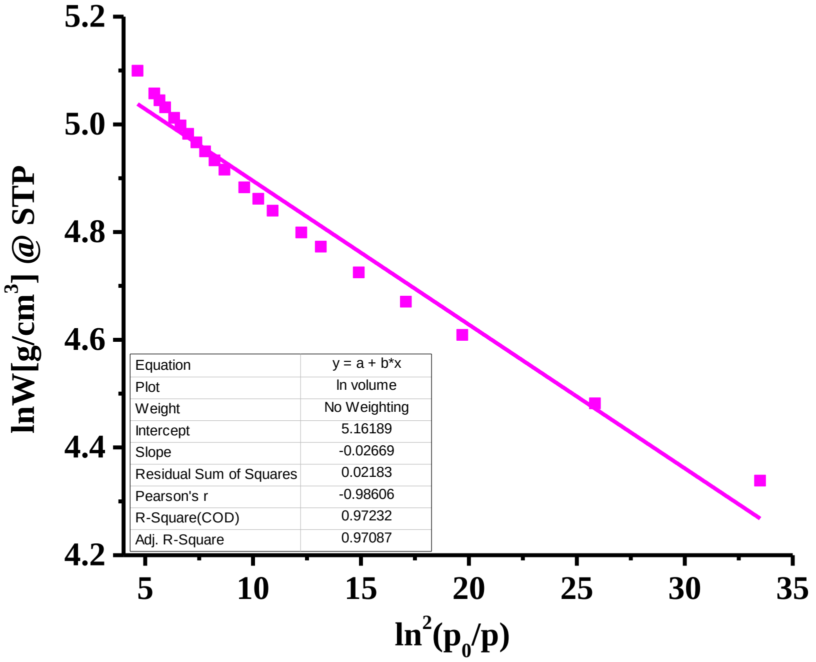


Low pressure range, where micropores are filled.

It cannot be fitted with a straight line in the whole range.

Try to apply the least square linear fit for the model and find the lower and upper limits of the range where the quality of fitting is good (R^2).

Trial 1:

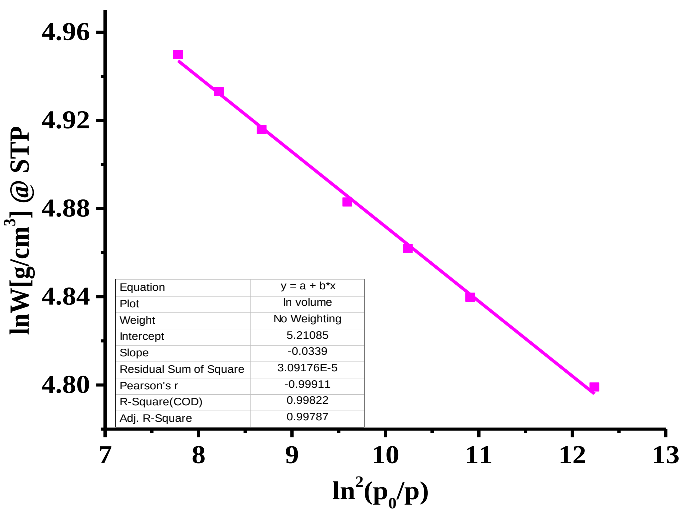


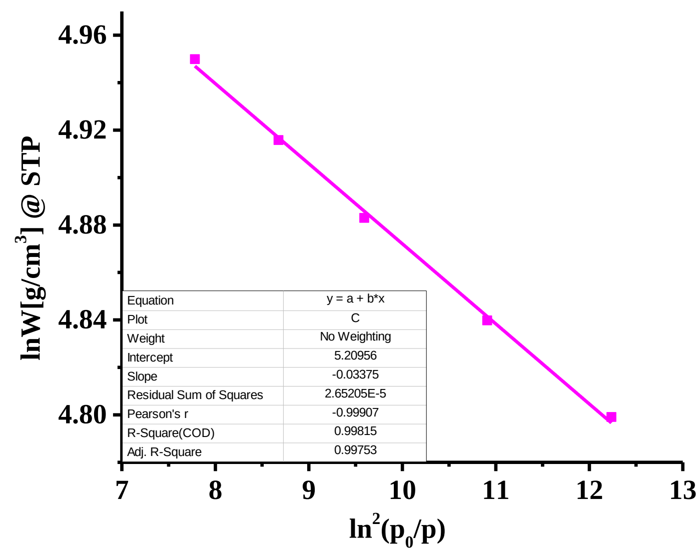
Although R or R^2 might be acceptable, by naked eye it is visible, that this fit is not correct.

Get the best fit, conclude the slope, the intercept and the regression (R or R^2)
From the linear fit conclude the p/p_0 range where the fit can be used.

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.

<u>Trial 2</u>





p/p_0 range 0.03-0.06 in this example

Based on the data obtained calculate the parameters of the models: W_0 and energy; E.

Intercept	**5.20956**
Slope	**-0.03375**

$\ln \frac{W}{W_0} = -(\frac{RT}{E})^2 ln^2 \frac{p_0}{p}$

$\ln W = lnW_0 - (\frac{RT}{E})^2 \, ln^2 \frac{p_0}{p}$

- $lnW_0 = Intercept = 5.20956$
- $W_0 = e^{5.20956}$ = 183.013~~5145~~ cm^3 /g @(STP) =183.014 cm^3 /g @(STP)
- -$(\frac{RT}{E})^2 = Slope$

-$(\frac{RT}{E})^2 = -0.03375$

$\mathrm{E} = 12.3548 \ \mathrm{kJ/mol}$

Calculate the micropore volume (conversion is similar as in Homework 1.

To convert the gas volume (W_0) to liquid volume:
1. Number of moles of adsorbed N_2 form $pV = nRT$

Table 1 Constant values for calculating micropore vsolume.

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

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

$$V_{liquid\ nitrogen} = V_{micropore} = \frac{101325\ \cancel{N/cm^2}\ 183.014\,cm^3/g \times 28\ g/\cancel{mol}}{10^6 \times 8.314 \frac{\cancel{Ncm}}{\cancel{Kmol}} \times 273\cancel{K} \times 0.808\ \cancel{g/cm^3}} =$$

$$0.283122\cancel{86}\ \frac{cm^3}{g} = 0.283123\ \frac{cm^3}{g}$$

2. Supposing that all the molecules filling the micropores have direct contact with the surface estimate the surface area of the micropores

Avogadro Number (N_A) = 6 × 10²³ , a_s = 0.162 nm

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

$$n_{m,DR} = \frac{101325\ \cancel{N}/\cancel{cm^2}\ 183.014\ \cancel{cm^3}/g}{10^6 \times 8.314 \frac{\cancel{Ncm}}{\cancel{K}mol} \times 273\cancel{K}} = 8.17011\cancel{7} \times 10^{-3}\,\text{mol/g}$$

$$= 8.17012 \times 10^{-3}\,\text{mol/g}$$

$$S_{micro,DR} = 8.17012 \times 10^{-3}\,\cancel{mol}/g \times 6 \times 10^{23}\,\cancel{mol^{-1}} \times 0.162 \times 10^{-18} m^2$$

$$= 794.135\cancel{664}\ \frac{m^2}{g} = 794.136\ \frac{m^2}{g}$$

3. Summarize your results in a table.

Table 2

Sample name: Silica6

Type of the isotherm: IV

Model	DR	Unit
Pressure range where the linear DR fit is applicable (if at all)	0.03-0.06	-
R^2	0.9982	--
Slope	-0.03375	
Intercept	5.20956	--
Micropore volume @ STP	0.283123	cm^3/g
Surface area of micropores	794.136	m^2/g

EITHER YOU INCLUDE THE BET SURFACE IN THE TABLE AS WELL,
(OTHERWISE YOU HAVE TO OPEN THE 1ST HOMEWORK ALL THE TIME)
OR MENTION IT IN THE NEXT PAGE IN THE COMPARISON

4. Compare BET and DR surface areas. Are you puzzled? Any hint for explanation?

The surface area obtained by DR model (794.136 m^2/g) IN THIS EXAMPLE is much higher than that obtained by BET model (699.966 m^2/g). This might be attributed to the assumption made for DR model which is consider that all the molecules filling micropores are in direct contact with the surface, though it is not in reality. If $S_{DR} > S_{BET}$, some of the molecules filling the micropores are not in contact with the wall, but are in between molecules already adsorbed.

If $S_{DR} < S_{BET}$, some of the molecules filling the micropores are in contact with both walls.

If $S_{DR} = S_{BET}$, the assumption of the direct contact of the molecules filling the micropores was correct.

Therefore, assuming that all molecules are in direct contact with the "walls" of micropores MAY lead to over- or underestimation of the surface area. Nevertheless, the comparison helps to judge how the molecules accommodate the micropores.