

SPEC902 a – Exercices n°2

1) Characterisation of a nanometric manganese oxide powder by nitrogen adsorption at 77 K

The nitrogen adsorption-desorption isotherm at 77 K obtained for a nanometric manganese oxide powder Mn_3O_4 prepared chemically (polyol process) is given below.

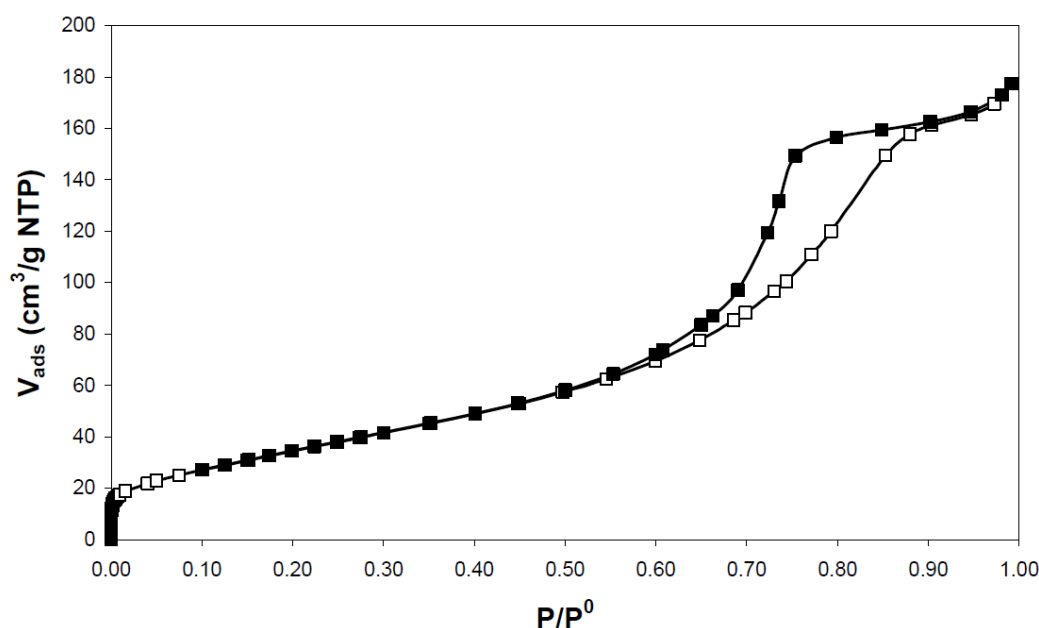


Figure 1 : Isotherm of adsorption-desorption of N_2 at 77 K obtained on a powder of Mn_3O_4

- Is this physisorption or chemisorption? What type(s) of interactions are involved in physisorption?
- What type of isotherm is this? What other types exist?
- What information can be obtained about the material from this isothermal curve?
- Recall the four main simplifying assumptions used for the BET model.
- Determine the specific surface area of the sample using the BET method using the data below (Table 1).

P/P ₀	0.0503	0.0752	0.1005	0.1515	0.2498	0.3006
V _{adsorbed} (cm ³ STP /g)	22.88	25.06	27.14	30.94	38.01	41.62

Table 1 : Isotherm of adsorption du nitrogen on a powder of Mn₃O₄ at 77 K

f) Knowing that the transmission electron microscopy data showed that the Mn₃O₄ particles are spherical in shape and have an average radius of 4.85 ± 0.3 nm,

- calculate the average volume of a particle,
- calculate the average mass of a particle (density of Mn₃O₄: $\rho = 4.80$ g cm⁻³),
- deduce the value of the theoretical specific surface area,
- What can we deduce about the porosity of the sample?

g) How can the observed hysteresis be explained?

Data:

- Molar volume under STP (Standard Temperature and Pressure) conditions = 22414 cm³.mol⁻¹
- Cross-sectional area of the N₂ molecule: $0.162 \cdot 10^{-18}$ m²
- Avogadro number: $6.02 \cdot 10^{23}$ molecules.mol⁻¹

2) Adsorption of hydrogen (H₂) gas onto germanium (Ge): Isotherm of Langmuir

The adsorption of hydrogen onto a germanium film is measured at different temperatures (Tables 2). We also know that a mixture of dihydrogen (H₂) and deuterium (D₂) in contact with germanium leads to the molecule HD.

T=551 K

P (mmHg)	0.084	0.219	0.356	0.815	1
VH ₂ (cm ³)	0.0226	0.0353	0.0439	0.0629	0.0685

T=611 K

P (mmHg)	0.189	0,250	0,527	1.000	2.250
VH ₂ (cm ³)	0.0131	0.0150	0.0214	0.0288	0.0418

T=621 K

P (mmHg)	0.250	0.599	1.000	1.346	2.250
VH ₂ (cm ³)	0.0214	0.0322	0.0407	0.0465	0.0581

Tables 2 : Isotherms of adsorption of hydrogen on germanium at different temperatures

- a/ By linearising Langmuir's relationship, calculate the maximum adsorbed volume V_{max} (saturation) at different temperatures.
- b/ Discuss the Langmuir model representations. Conclude on the nature of the adsorption phenomenon.
- c/ Calculate the heat of adsorption.

Données : Langmuir equation :

$$V_{\text{(adsorbed)}}/V_{\text{max}} = KP/(1+KP) \text{ avec } K=K_0 \exp (-q_a/RT)$$

where q_a is the heat of adsorption.