SPEC902 a – Exercices n°2, year 2024

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.

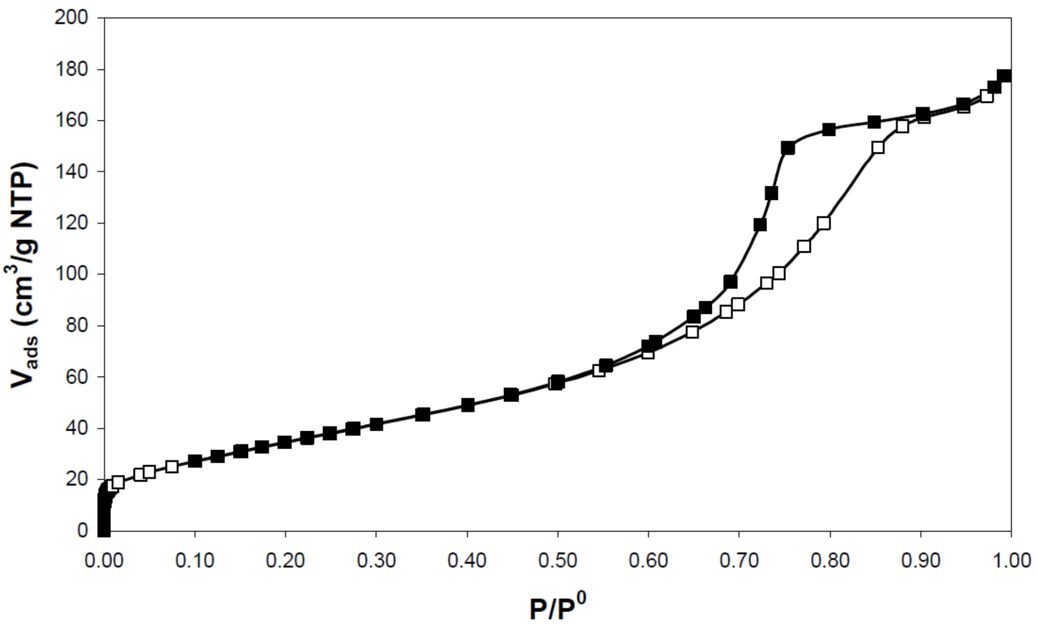

Figure 1 : Isotherm of adsorption-desorption of N_2 at 77 K obtained on a powder of Mn_3O_4

a) Is this physisorption or chemisorption? What type(s) of interactions are involved in physisorption?

b) What type of isotherm is this? What other types exist?

c) What information can be obtained about the material from this isothermal curve?

d) Recall the four main simplifying assumptions used for the BET model.

e) 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 Mn_3O_4 at 77 K

f) Knowing that the transmission electron microscopy data showed that the Mn_3O_4 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 Mn_3O_4: ρ= 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 $cm^3.mol^{-1}$
- Cross-sectional area of the N_2 molecule: $0.162.10^{-18}$ m^2
- Avogadro number: 6.02 10^{23} molecules.mol^{-1}

2) Adsorption of hydrogen (H_2) 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 (H_2) and deuterium (D_2) 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 Vmax (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 :

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

where $-q_a$ is the heat of adsorption.