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EXPERIMENTS ON PHASE TRANSITION OF ADSORBED GASES ON POROUS GLASS - PART II*

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SUMMARY

A fusion point decrease of a gas condensed in pores results in dependence of the pore diameter. Using molecular sieves and porous glass exhibiting mesoporous systems with small ranges of pore diameters the triple point decrease of several gases was investigated observing the hysteresis shape of the adsorption isotherms. Measurements have been carried out using gravimetric apparatus.

INTRODUCTION

Besides calormetric methods, e.g. thermoporometry (ref. 1,2) and NMR, phase transition in adsorbed layers may be detected by volumetric or gravimetric gas adsorption measurements. Steps in the course of an isotherm in the low coverage region (ref. 3), disappearance of the hysteresis loop and slowdown of the adsorption and desorption kinetics as function of decreasing temperature may be the result of a freezing process. The phase of an adsorbed layer can differ from the respective bulk phase as a result of long-range surface forces. In micro- and mesoporous systems the triple point decrease is a pronounced effect.

The aim of the investigation is to examine the effect of triple point decrease in micro- and mesoporous systems and to extend the thermoporometry method for pore size distribution suggested by Eyraud to low temperatures and by means of gravimetry. Supplementing the paper delivered at the Dijon MT Conference (ref. 4) in the present paper relevant pore parameters of porous glasses investigated are presented.

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EXPERIMENTAL

We used a gravimetric apparatus described by Straube at the Dijon MT Conference (ref. 5) comprising of three electromagnetic vacuum microbalances and a magnetic suspension balance. The gas supply was equipped with electrical controlled needle valves, both to the inlet and to the turbo molecular vacuum pumps. Low pressure was measured using heat conductivity instruments and above 1.5 mbar piezoelectric manometers. Samples were thermostatted using liquid nitrogen and oxygen, respectively, in Dewar vessels one meter in length, the level of the liquid being controlled. The calculation routines were developed by Straube.

RESULTS

We measured sorption isotherms of argon, krypton and nitrogen on Vycor glass (Vycor 7930) and controlled pore glass (CPG 120 and CPG 240) at 77 K and 90 K which were investigated earlier. The numerical parameters as obtained from the nitrogen isotherm at 77 K are summarized in Table 1.

TABLE 1

Specific surface area and pore parameters

sample	specific surface area BET 2	BET 3	C-value BET 2	most frequent pore width adsorpt.	desorpt.	Pierce
	$m^2\ g^{-1}$	$m^2\ g^{-1}$		nm	nm	nm
Vycor 7930	201.2 ± 1.5	189.4 ± 1.3	167.42	3.52	4.29	4.34
	201.6 ± 1.4	190.0 ± 1.3	166.97			
CPG 120	119.7 ± 2.1	120.4 ± 0.3	255.66	12.73	15.99	15.44
	121.2 ± 1.7	121.6 ± 0.4	186.68			
CPG 240	92.5 ± 0.3	91.6 ± 0.3	130.76	26.82	29.12	27.37
	92.5 ± 0.4	90.8 ± 0.4	132.01			

The nitrogen isotherms at 77 K, the argon isotherms at 90 K and 77 K and the krypton isotherm at 90 K all correspond to the type H2 of the IUPAC classification. The area of the hysteresis loop increases from nitrogen (77 K) to argon (90 K), and from argon (90 K) to argon (77 K) and from argon (77 K) to krypton (90 K). No change in the shape of isotherms was observed: most probably the adsorbates retained their liquid state as a result of triple point decrease. Only in the adsorption and desorption kinetics the

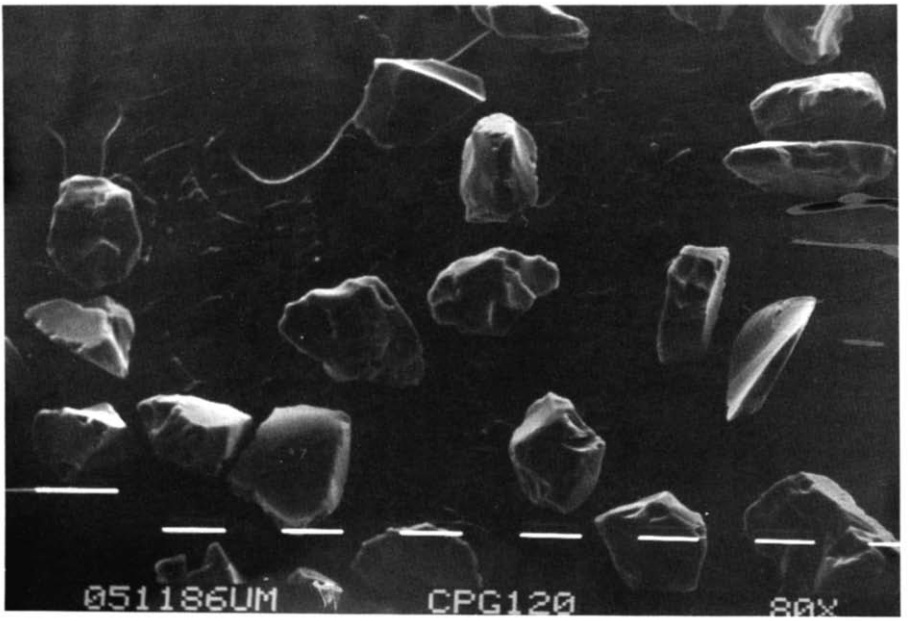

Fig. 1. Controlled pore glass CPG 120. Scale-bar: 100 µm

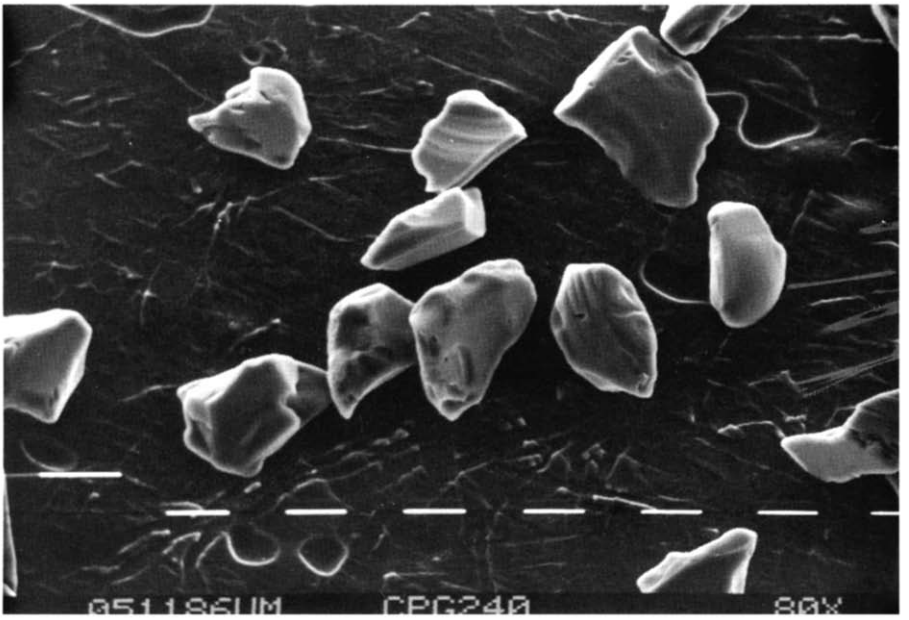

Fig. 2. Controlled pore glass CPG 240. Scale-bar: 100 µm

expected temperature dependent effects were found.

Pore volumes calculated with Gurwitch's rule (Table 2) using the densities of the solid phase for krypton (90 K) and argon (77 K) result in lower values compared with argon (90 K) and nitrogen (77 K) using the densities of the liquid phase, whereas all values agree within a confidence interval of 0.02 ml g^{-1} if the densities of the liquids were applied. Regarding the calculated values, all condensates seem to be liquid. However, the 95 % confidence regions (± 0.02) cover all previous liquid and solid values. Therefore, we are not able to decide whether the condensates are in liquid or solid phase.

TABLE 2

Specific pore volume of Vycor glass 7930 calculated using Gurwitch's rule

condensate	temperature	density liquid	density solid	ads. mass at saturation	pore volume liquid	pore volume solid
	K	kg m^{-3}		mg/mg	ml g^{-1}	
nitrogen	77.5	807		0.1872 ±.0002	0.232 ±.02 0.228 ±.02	
argon	90.2	1410		0.3091 ±.0002	0.214 ±.02	
argon	77.5	1418	1623	0.3054 ±.0002	0.215 ±.02	0.188 ±.02
krypton	90.2	2451	2826	0.5650 ±.0002	0.231 ±.02	0.200 ±.02

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