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PRELIMINARY EXPERIMENTS ON PHASE TRANSITION OF ADSORBED GASES ON POROUS GLASS

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ABSTRACT

The normal fusion point of argon (83.9 K) is between the boiling points of liquid nitrogen (77.5 K) and liquid oxygen (90.2 K). Krypton at 90.2 K is below its fusion point (115.9 K). The isotherms of argon on porous glass are compared to those of nitrogen and krypton. No change in the shape of the hysteresis was observed: the adsorbate obviously kept the liquid state as a result of triple point decrease in the mesopore system. Temperature dependent effects were found only in the kinetics of ad- and desorption.

INTRODUCTION

The phase of an adsorbed layer on a solid can differ from the respective bulk phase at similar temperatures, also this is the case in the higher layers as a result of long ranging surface forces. Therefore, it is better to speak of mobile or localized

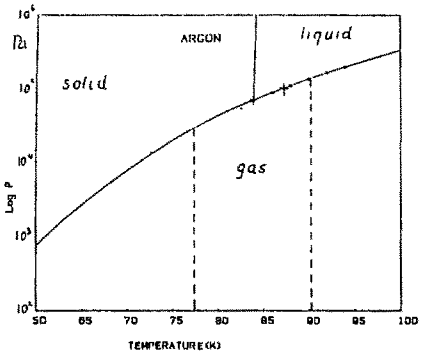

Fig. 1. Phase diagram of argon. Dashed lines: Isotherms at 77 K and 90 K (see Figs. 3+4).

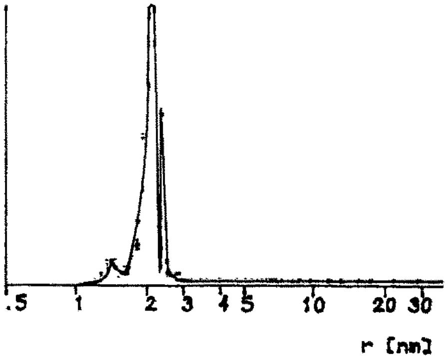

Fig. 2b. Pore width distribution of the nitrogen isotherm (Fig. 2a).

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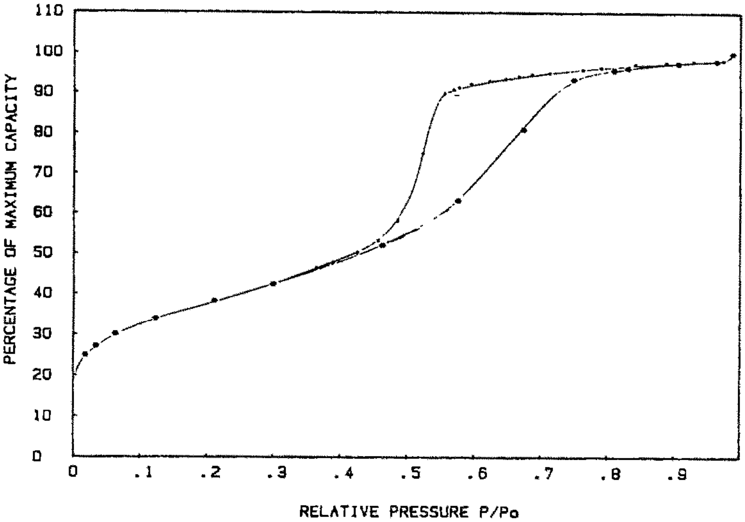

Fig. 2a. Nitrogen isotherm at 77.5 K on Vycor glass.

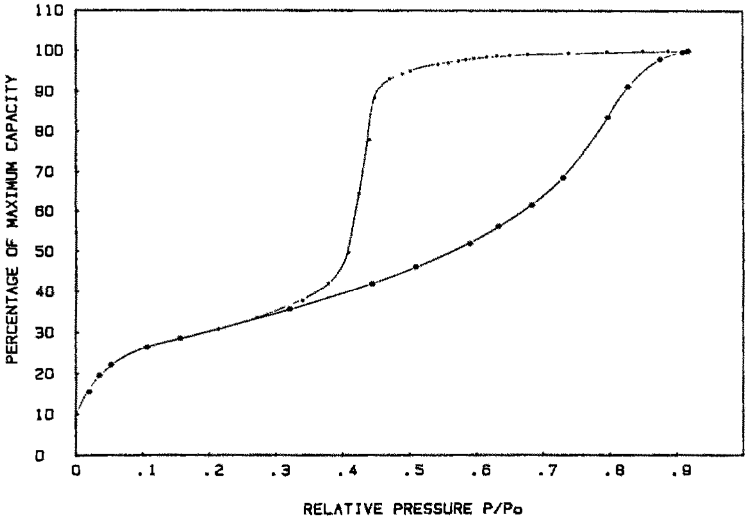

Fig. 3. Krypton isotherm at 90.2 K on Vycor glass.

layers, rather than of liquid and solid sorbate. Critical parameters e.g. triple point, melting and boiling points are shifted towards lower values depending on the chemical nature and the geometry of the adsorbent. In the presence of mesopores this effect is rather large (refs. 1,2). Around the completion of the

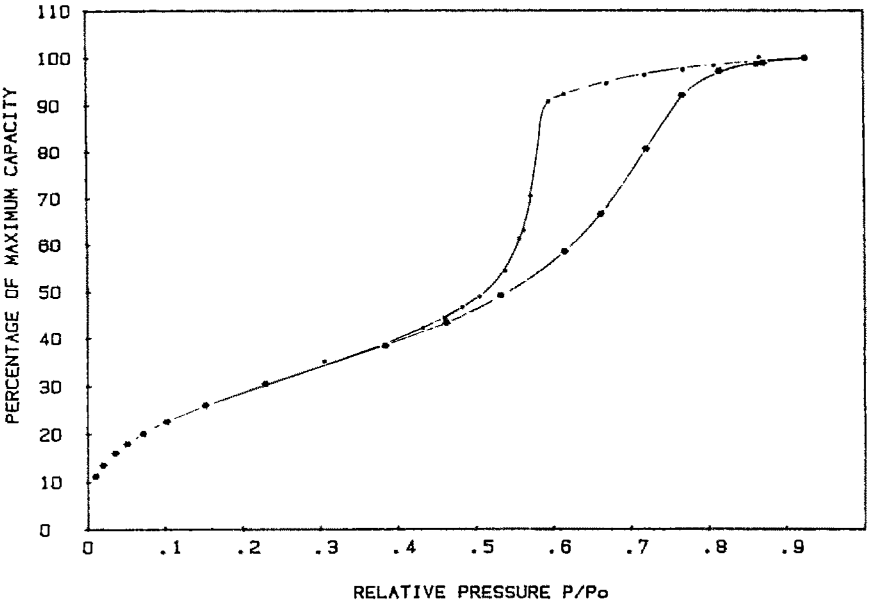

Fig. 4. Argon isotherm on Vycor glass at 90.2 K.

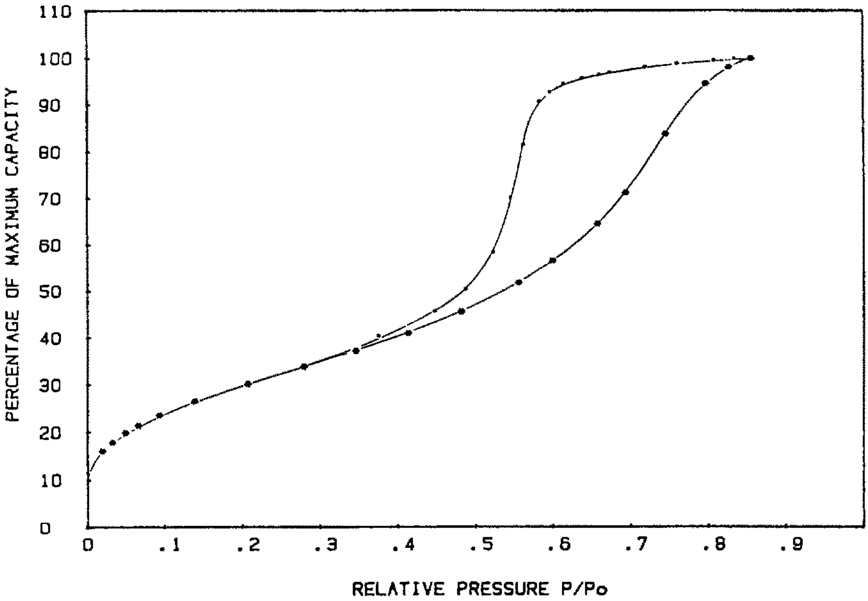

Fig. 5. Argon isotherm at 77.5 K on Vycor glass.

argon and nitrogen monolayer, at 77 K on graphite, a phase change was observed (refs. 3,4). Others found such effects at various adsorbents and number of layers at far lower temperatures (refs. 5-6).

In order to examine phase transition in pores, we measured sorption isotherms with different inert gases at liquid nitrogen and liquid oxygen temperatures, using a well defined, highly mesoporous glass. In the monolayer and submonolayer region, phase transitions should have manifested themselves stepwise in the isotherms. In the multilayer region we expected to find **noticeable** differences in the shape of isotherms and the hysteresis loops, and furthermore in the adsorption and desorption kinetics.

EXPERIMENTAL

The measuring apparatus consists of two microbalances developed by Gast, a turbomolecular vacuum pump, a gas supply with electric controlled needle valves, both to the inlet and to the pump. Low pressure was measured using a heat conductivity instrument and above 1.5 mbar a piezoelectric manometer. Samples were thermostatted using liquid nitrogen and oxygen, respectively, in Dewar vessels one meter in length, the level of the liquid being controlled manually. The apparatus is described in detail by Straube, also the calculation routines were developed by him (refs. 5,6).

As adsorbent, we used Vycor glass which we had investigated earlier. The highly porous glass includes pores in a restricted mesopore range and with a most frequent pore width of 2 nm. We measured nitrogen, argon and krypton isotherms. The experiments with argon are shown in the normal phase diagram (Fig. 1).

EXPERIMENTAL RESULTS

The nitrogen isotherm at 77 K and the respective pore size distribution are shown in Figs. 2 a + b and the numerical results in Tab. 1. The argon isotherms at 90 K and 77 K and the krypton isotherm at 90 K are depicted in Figs. 3 - 5. One determination failed because of the generation of a argon-"icicle" 50 mm in

TABLE 1

Specific surface area and pore parameters of a Vycor glass.

specific surface area		specific pore volume		most frequent pore radius	
method	m^2/g	method	ml/g	method	nm
Kaganer	188	Gurwitsch	.228	adsorption	1.76
2 parameter BET	201			desorption	2.15
3 parameter BET	189			Pierce	2.17
cumulative	208				

length and up to 10 mm in diameter on the counterweight's suspension wire.

The shape of the isotherms and of the hysteresis loop coincide in principle: All isotherms correspond to the type H2 of the IUPAC classification. 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). In all cases the boiling and fusion temperature of the normal bulk phase could be taken. Differences were found in the kinetics of adsorption and desorption: These reactions took place far more slowly with argon at 77 K and krypton at 90 K. Furthermore, we observed, after the exponential increase, a gradual linear increase of the adsorbed mass (Fig. 6). Equilibrium was reached after 1 to 3 hours, whereas with nitrogen at 77 K and argon at 90 K after 10 min to 1 h.

DISCUSSION

We didn't observe steps in the isotherm near monolayer completion and also no change in the shape of the isotherm due to temperature. Thus, we can presume, that, the adsorbate is mobile even far below the fusion temperature and able to form a meniscus. On the other hand, there could be a melting reaction included in the adsorption/desorption process. Obviously, the ad-

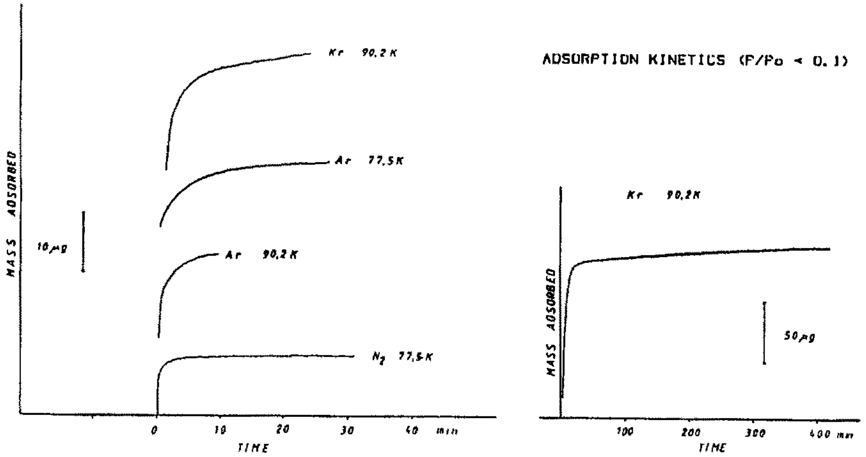

Fig. 6. Adsorption kinetics

sorbate resists serving as a solidifying nucleus. This result matches Eyraud's theory of condensation in pores (refs. 1,2). We doubt whether the adsorbate can be regarded as a supercooled liquid, because there was no visible relationship to the corresponding boiling points. Furthermore, the slow adsorption and desorption process is not predictable in the case of liquid sorbates. Also questions arise about the slow linear increase of the kinetic curves.

REFERENCES

1 C. Eyraud, M. Betemps, J.F. Quinson, F. Chatelut, M. Brun, B. Rasneur, Bull. Soc. Chim. France (1984) no. 9-10, I-237-I-244.
2 C. Eyraud: Thermoporométrie. Ecole d'Eté Cadarache, 3-7.9.1984
3 Y. Grillet, F. Rouquerol, J. Rouquerol, J. Colloid Interface Sci. 70 (1979) 239-244.
4 J. Rouquerol, F. Rouquerol, Y. Grillet, M. Triaca, Thermochimica Acta, this volume.
5 A. D. Migone, Z. R. Li, M. H. W. Chan, Phys.Rev.Lett. 53 (1984) 8, 810-813.
6 J.L. Seguin, J. Suzanne, M. Bienfait, J.G. Dash, J.A. Venables, Phys. Rev. Lett. 51 (1983) 2, 122-125.
7 B. Straube, Thermochimica Acta, this volume.
8 B. Straube: Kritische Untersuchung und Standardisierung physikalisch chemischer Meßmethoden zur Ermittlung der spezifischen Oberfläche und Porenverteilung von Adsorbentien. Dissertation Mainz 1985.