THERMAL CONDUCTIVITY OF CERTAIN ADSORPTION MATERIALS AT THE TEMPERATURES 10-200°K

A. I. Raigorodskii, R. G. Amamchyan,
and I. I. Gil'man

UDC 621.592.3.045:536.24

Experimental results on the thermal conductivity of silica gels, including metallized gels, at cryogenic temperatures are presented.

The prospects for reducing the temperature level of two- or three-stage cryogenic helium machines (CHM) are related to the use of checkers of low-temperature CHM regenerators from gas-containing, particularly, adsorption materials [1]. The specific heat of such materials, based on silica gel for example, is determined by the specific heat of the adsorbed gas (helium) and is sufficiently high. However, in order to use the specific heat of adsorption checkers efficiently in the working cycle of a CHM (for $n \approx 1500$ rpm), it is necessary to assure sufficient thermal diffusivity of the checker element. It has been established that the thermal conductivity of the adsorbent material should not be less than 0.5 W/m·deg [2].

The purpose of this work is to clarify to what degree different adsorbents satisfy the requirement relative to thermal conductivity.

The thermal conductivity and diffusivity are the least studied of the properties of adsorbents. Data available in the literature [3, 4] characterize the thermal conductivity of a layer of bulk checker but not the thermal conductivity of the adsorbent material of interest to us.

An investigation of the thermal conductivity of elements of a CHM checker is fraught with considerable difficulties. These elements are particles with porous structure; the particle size does not exceed 0.3 mm. Hence, the thermal conductivity of pressed specimens, with properties similar to the checker elements, is measured. The specimens are fabricated in the form of disks 15 mm in diameter and 1.5-4 mm high by pressing powders with a 15- to 60-μ particle size at a pressure on the order of 17 kbar. It turns out that broadening of the specimen occurs 10-15 days after the pressing under the effect of internal stresses (the aftereffect phenomenon) and stratification. However, it has been established that the specimens are not spoiled upon executing the measurements directly after the pressing, and if the temperature drop over the specimen does not exceed 10-20° during its cooling, the specimen is maintained for 20-25 cooling and heating cycles.

The thermal conductivity of specimens of adsorption materials was measured by the method of monotonic nonsymmetric heating [5] by using a λ-calorimeter. The calorimeter (Fig. 1) consists of the calorimetric cell 1, a helium 2 and nitrogen 3 bath, a nitrogen shield 4, a vacuum housing 5, as well as an evacuation vacuum station and a set of thermometer instruments (not shown in the figure). The nitrogen and helium baths of 3.2-and 0.8-liter capacity were hooked to the cover of the vacuum housing 6 by thin-walled stainless steel tubes 7 (for pouring in the coolants and removing their vapors) and are connected to the bellows 8 (for mechanical and thermal decoupling). Both baths are protected from thermal radiation by metallized polyethylene terephthalate film with glass fog seals.

The calorimetric cell 1 contains a heat receiver 9, the test specimen 10, the shield 11, and a polished copper plate 12 soldered to the upper cover of the helium bath.

To diminish the heat influx to the heat receiver and the specimen and the contact thermal resistivities, all the cell components were covered by a thin gallium film and were soldered together. In addition, the thermocouple wire was put in thermal contact with the nitrogen and helium baths and the shield 11 of the calorimetric cell.

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 33, No. 3, pp. 449-454, September, 1977. Original article submitted July 13, 1976.

0022-0841/77/3303-1050$07.50

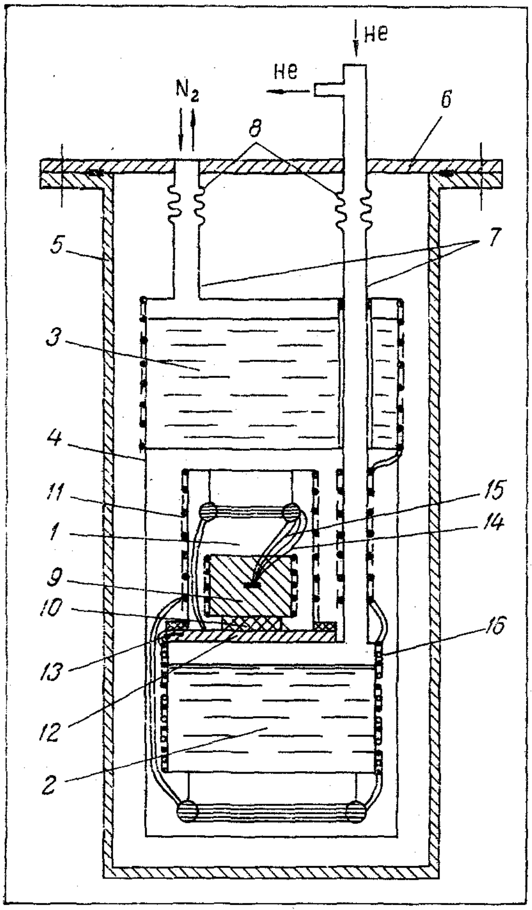

Fig. 1. Diagram of the experimental set-up.

The thermal conductivity of the specimens investigated varied considerably in the 10-200°K temperature range. Hence, to maintain the operating parameters of the experiments within definite limits (approximately a 2 to 6° temperature drop over the specimen, around a 0.02 deg/sec heating rate) a set of heat receivers was required. Copper MI was used as heat-receiver material in conducting investigations in the 80-300°K range. Two heat receivers of different mass were fabricated from it and were used depending on the thermal conductivity of the material under investigation. Mercury was used as a heat receiver in conducting tests in the 4-80°K band. Two heat receivers in the form of thin-walled copper containers covered on the inside by a thin film of lacquer and filled with mercury were also fabricated for these experiments.

Monotonic heating of the specimens was accomplished by a smooth change in the current intensity flowing through the electrical heater 16 glued to the helium bath. The rate of change of the current intensity was first estimated by means of the approximate values of the specimen thermal conductivity and was refined during repeated experiments with the same specimen. The criterion for the correctness of the selection of the rate mentioned is monotonicity of the heating in the whole range of temperature variation.

The rate of heating the heat receiver was around 0.02 deg/sec in the majority of tests at 10-50°K, and the temperature drop over the specimen was about 4°. After the specimen had been set in the cell and the vacuum cavity of the cryostat had been evacuated, the λ-calorimeter was cooled by filling the baths 2 and 3 with liquid nitrogen and helium. Then a vacuum higher than 10^{-5} torr was maintained in the vacuum space of the calorimeter by using a cryosorption pump for a long time. After complete cooling of the calorimetric cell, the readings of all the temperature sensors were compared with the temperature measured by the pressure of the saturated helium vapors in the bath.

The temperature of the heat receiver 9 and the temperature drop over the specimen 10 were measured during the experiments. Thermocouples 14 and 15 (Cu + Fe/Cu electrode material) were used as sensors. The temperature of the plate 12 was simultaneously checked by using a GaAs resistance thermometer 13 (P-type, 2 wire). The temperature of the heat re-

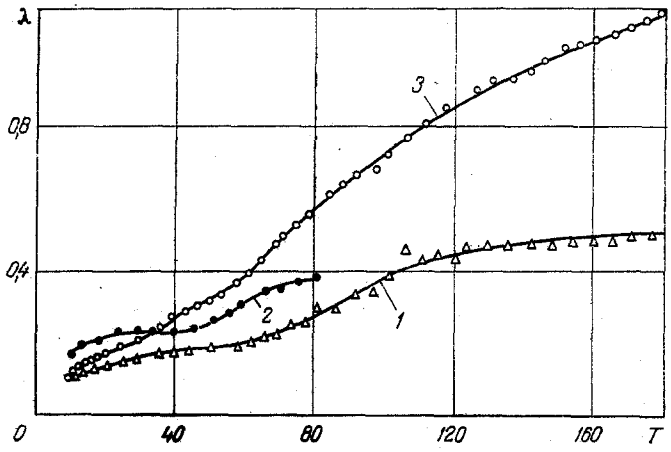

Fig. 2. Thermal conductivity of nonmetallized silica gels: 1) coarse porosity silica gel; 2) fine-pore; and 3) hydrogen form of silica gel, λ, W/m·deg; T, °K.

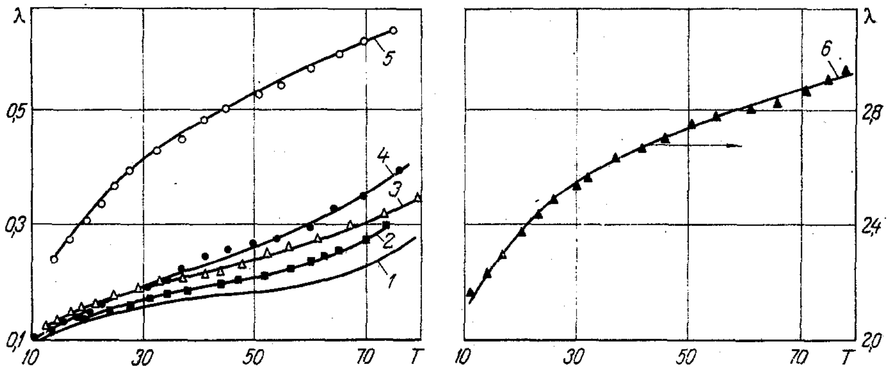

Fig. 3. Thermal conductivity of metal-containing adsorbents and coarse-pore silicagels: 1) coarse-pore silicagel; 2) coppered; 3) leaded; 4) silvered; 5) palladiumized; 6) silvery formof silicagel.

ceiver and the temperature drop over the specimen were measured every 50–100 sec for 10–80°K and every 100–600 sec for 80–200°K, depending on the heating rate.

Standard specimens, stainless steel, polytetrafluoroethylene, and fused quartz (monolithic and pressed specimens), whose thermal conductivity has been studied adequately [4, 6–8], were also investigated, in addition to the adsorbents, in order to verify the method and the apparatus. The results of measuring the thermal conductivity of the standard specimens turned out to be in good agreement (to ±5% accuracy) with data in the literature. The thermal conductivity of the pressed fused quartz specimens with porosity within the 15–25% range is correspondingly 10–20% less than the thermal conductivity of the monolithic specimen. It can be expected that the true value of the thermal conductivity of adsorption material will differ considerably less for silica gels with a disperse structure from the thermal conductivity determined by using the pressed specimens. Therefore, the measurement method used and the apparatus developed permit obtaining sufficiently reliable results on the thermal conductivity of adsorption materials.

The results of measuring the thermal conductivity λ of different adsorbent specimens (Figs. 2 and 3) indicate the weak and monotonic nature of the temperature dependence of the thermal conductivity, which corresponds to a phonon mechanism of heat transfer in dielectric, glassy materials [9]:

$$\lambda \sim CU\Lambda_{\mathrm{p}}. \qquad (1)$$

The specific heat C varies with temperature according to a cubic law in the temperature range considerably below the Debye value T_D. The phonon mean free path at temperatures below 100°K grows substantially with the drop in temperature:

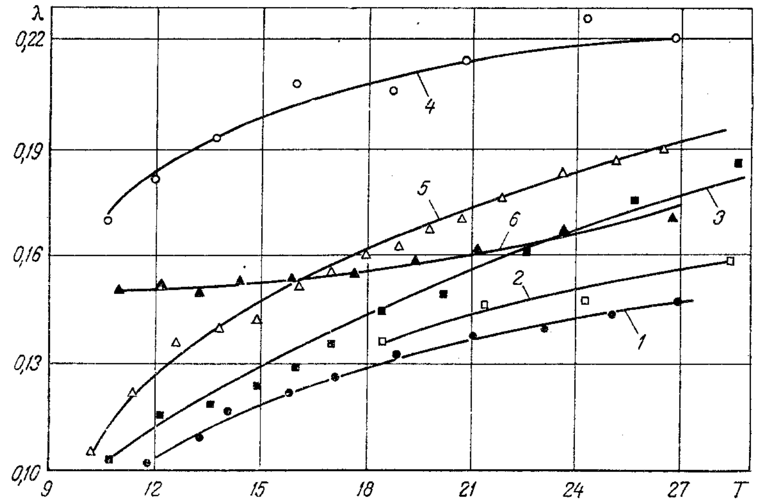

Fig. 4. Thermal conductivity of fused quartz and adsorption materials with different specific surface in the 10-30°K band: 1) coarse-pore silica gel; 2) coppered; 3) silvered; 4) fine-pore; 5) hydrogen form of silica gel; 6) fused quartz.

$$\Lambda_p \sim T^{-2}, \tag{2}$$

and the velocity of phonon propagation U varies slightly with temperature. Therefore, at low temperatures the phonon thermal conductivity depends linearly on the temperature in a first approximation:

$$\lambda \sim T^3T^{-2} \sim T. \tag{3}$$

It should be mentioned that the thermal conductivity of specimens with a highly porous silica gel structure is close to the thermal conductivity of fused quartz. Let us note that the thermal conductivity of fine-pore silica gel is noticeably higher than the thermal conductivity of coarse-pore and metallized specimens of coarse-pore silica gel, and it is even higher than the thermal conductivity of a monolithic fused quartz specimen for T < 50°K (Fig. 4). The growth of the thermal conductivity of specimens with the increase in the specific surface of the adsorbent is apparently determined by the following.

As is known [10], for T << T_D the specific heat of a porous body is higher by

$$_\Delta C \sim T^2 \tag{4}$$

than for a monolithic body, which is related to the increase in the internal energy of the porous body, and this contribution of "surface" specific heat grows with the increase in the specific surface. Therefore, the thermal conductivity should also be higher in conformity with (1).

The thermal conductivity of the coppered, silvered, and leaded silica gels is somewhat higher than for the initial nonmetallized coarse-pore silica gel specimen; this difference increases noticeably for T > 20°K (Fig. 3). The palladiumized silica gel of all the specimens, obtained by metal-coating coarse-pore silica gel, is characterized by the greatest thermal conductivity. The differences in the thermal conductivities of metallized specimens are apparently explained mainly by certain features of the technology for inserting metals into the adsorbent pores. The relatively high thermal conductivity of the palladiumized silica gel indicates that the metal in the sorbent pores is distributed more uniformly. A continuous metal film has apparently not been obtained successfully using the method of metallizing an adsorbent by soaking it in a salt solution and reducing the salt to a metal. Liberation of the metal probably occurs at separate active centers of the adsorbent surface, and, hence, the contribution of the conduction electrons to the total thermal conductivity of the adsorbent turns out to be comparatively small.

A substantially higher thermal conductivity is detected in the silvery form of silica gel (Fig. 3) out of all the adsorbents investigated, obtained by cation substitution of silver for hydrogen during synthesis of the hydrogen form of silica gel [11]. The film of silver cations in the pores of the silvery form of silica gel is apparently sufficiently homogeneous and continuous. Computations show that a silver content of about 20% corresponds to a monolayer.

The weak temperature dependence of the thermal conductivity as well as the influence of the dimensional effect on the thermal conductivity [12] indicate that the electronic mechanism of heat transfer in metal-containing specimens is made difficult. This is confirmed by the results of measuring the electrical conductivity which show that the introduction of the metal only changes the electrical resistivity insignificantly.

An adsorbent, the silvery form of silica gel, whose conductivity greatly exceeds 0.5 W/m·deg, the minimum needed for effective operation of the checker of a CHM regenerator, has been selected as a result of the investigation of a number of silica gel specimens. This adsorbent can also be used in other cryogenic apparatus, for instance, in the production of high-speed cryosorption pumps.

The authors are grateful to I. E. Neimark, I. B. Slinyakov, and L. P. Finn for providing the specimens of the silvery form of silica gel.

NOTATION

λ, thermal conductivity, W/m·deg; T, temperature, °K.

LITERATURE CITED

1. USA Patent No. 3262277 (1965).
2. V. G. Pron'ko, R. G. Amamchyan, I. I. Gil'man, and A. I. Raigorodskii, On the Heat Accumulating Capacity of Adsorption Checkers of Cryogenic Machine Regenerators [in Russian], XM-6, No. 2, Ékspress-Informatsiya, Tsintikhimneftemash (1976).
3. M. G. Kaganer, Thermal Insulation in Low-Temperature Engineering [in Russian], Mashinostroenie, Moscow (1966).
4. L. L. Vasil'ev and Yu. E. Fraiman, Thermophysical Properties of Poor Heat Conductors [in Russian], Nauka i Tekhnika, Minsk (1967).
5. É. S. Platunov, Thermophysical Measurements in the Monotonic Regime [in Russian], Énergiya, Leningrad (1973).
6. L. A. Novitskii and I. G. Kozhevnikov, Thermophysical Properties of Material at Low Temperatures [in Russian], Mashinostroenie, Moscow (1975).
7. R. Berman, Proc. Phys. Soc., 65, Pt. 12, No. 396A, 1029 (1952).
8. R. L. Powell, W. M. Rogers, and D. O. Coffin, J. Nat. Bur. Stand., 59, No. 5, 349 (1957).
9. R. G. Klemens, Proc. Roy. Soc., A208, 108 (1951).
10. A. I. Shal'nikov (editor), Low Temperature Physics [in Russian], Moscow (1959).
11. Author's Certificate No. 218831, Byull. Otkrytiya, Isobreteniya, Promysh. Obratztsy, Tovarn. Znaki, No. 18 (1968).
12. M. H. Francombe and R. W. Hoffman (editors), Physics of Thin Films, Vol. 6, Academic Press (1971).