

From Dewars to VIPs – One Century of Progress in Vacuum Insulation Technology

J. Fricke, ZAE Bayern, Am Hubland, 97074 Würzburg
fricke@zae.uni-wuerzburg.de

1 The thermos trademark

James Dewar, professor at Cambridge, had liquefied most gases and even solidified hydrogen towards the end of the nineteenth century. In the course of this work he invented the vacuum flask. The original vessel of 1892 was made of glass and was uncoated. When he wanted to switch to metal flasks, he realized, that adsorbed gases at the metal surface spoiled the vacuum. Only by integrating charcoal into the flask and cooling the system, he could get the required low gas pressure. He also found, that by painting the inner surfaces of the flask silvery, thermal radiation could be reduced.

His flask was not manufactured for domestic or commercial use until 1904, when two German glass blowers founded Thermos GmbH. The Thermos trademark was sold to three independent companies in the United States, Canada and England in 1907, who developed it into a widely sought after product. Just a year ago “Thermos” celebrated its 100th anniversary [Thermos 1904].

2 Early R&D on nano-materials

Due to their shape, cylindrical or spherical vacuum containers are load-bearing – they support the atmospheric pressure of 1 bar or 10^5 N/m^2 , which corresponds to a weight of 10 tons per m^2 . Contrariwise flat hollow container would collapse under this load, if not a supporting kernel were inserted between the container walls. The thermal conductivity of the evacuated kernel should be very small and insensitive against a leakage-induced pressure increase.

As we know today, nano-structured insulants are most suited in this respect: they are finely divided with a fractal-like build-up; they thus interrupt the solid pathways for the heat flow innumerable often, which leads to a small solid thermal conductivity; they have very small pores and thus suppress the gaseous thermal conduction already under a technical vacuum (instead of a high vacuum, which is required in Thermos flasks); and they can easily be mixed with infrared opacifiers, absorbing and scattering powders, in order to reduce radiative thermal transport.

The first nano-structured insulants were made by S.Kistler at Stanford University/Cal. in the 1930s. He succeeded in drying waterglass-derived silica gels without structural collapse by using the supercritical extraction route [Kistler 1932]. His highly porous, transparent or translucent materials, which he called aerogels, had surprisingly small thermal conductivities (Fig.1): in air values as low as $0.020 \text{ W/(m}\cdot\text{K)}$ were recorded; for his finest granular aerogels he measured conductivity values of about $0.004 \text{ W/(m}\cdot\text{K)}$ under a technical vacuum (gas pressure $< 1 \text{ mbar}$) and without any mechanical load; if an external load of 1 bar was applied he determined an increase of about 0.001 to $0.002 \text{ W/(m}\cdot\text{K)}$. In his monolithic aerogels gaseous conduction was suppressed already for gas pressures $< 10 \text{ mbar}$, which gave him already at that time a hint on the sub-micron-sized pores. Kistler was familiar with the importance of the ratio of the molecular mean free path and the pore size, the so called Knudsen

number. However, he obviously didn't consider radiative thermal transport at all, as no information was given with respect to boundary temperatures or plate emissivities. With Kistler's help aerogels were industrially produced at Monsanto and sold under the name Santogel for about two decades. Santogel – in ground form - was used as a pourable insulation, as an additive and thixotropic agent in cosmetics and toothpaste. By Johns-Manville Santogel was mixed with asbestos fibers and bonded with an organic resin. This block-like insulation "Min-K" was intended for use in the nuclear and aerospace industry.

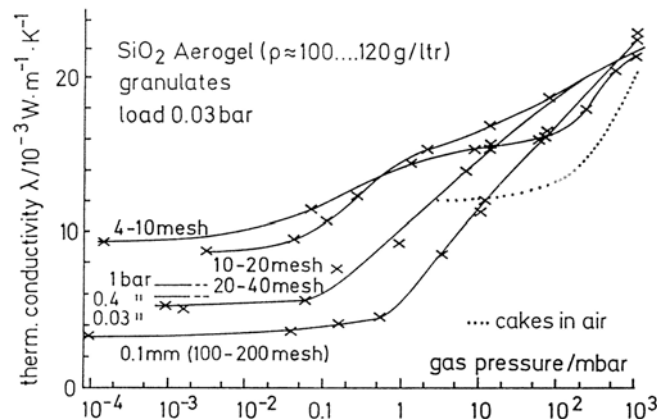


Figure 1: Thermal conductivity of monolithic (...) and powdery silica aerogels of different grain size (—) as a function of gas (air) pressure; the smaller the mesh-number, the larger is the grain size; the average temperatures within the aerogel samples were 33 to 36°C [Kistler 1934].

The aerogel production ceased, when pyrogenic or fumed silica became available at lower costs. This new type of silica was invented in 1942, when Harry Kloepper, a chemist at Degussa, burned an organic precursor in a hydrogen flame. From the high-temperature hydrolysis and condensation processes nano-structured silica particles were obtained. Starting in 1944 this material was sold by Degussa under the brand name Aerosil®. In the following decades other companies around the world joined this route, rendering pyrogenic (or fumed) silica powders a widely sold product, with applications as filler material, thixotropic agent and insulant. Despite large R&D activities on aerogels in the 1980s and 1990s by BASF [Herrmann 1995] and Hoechst [Hoechst 1997], aerogels could never again make it against fumed silica. Perhaps translucent applications of silica aerogels, which are now manufactured by Cabot [Cabot 2005] and sold as Nanogel®, will prevail.

Parallel to the development in nano-material synthesis progress was made in thermophysics of insulants. Early contributions for the successful development of the present VIP-technology came from M.G. Kaganer in the Soviet Union [Kaganer 1969]. Kaganer measured the thermal conductivity of fibrous and powdery materials as a function of gas pressure, of external load and of temperature. He interpreted his data by using a linear superposition of gaseous, solid and radiative conductivity. He derived power laws for the dependence of the solid conductivity on the external load. He also extracted characteristic pore sizes for powder fills (Fig.2) using the equation

$$\lambda = \lambda_{\text{evac}} + \lambda_{\text{GO}} / (1 + 2\beta \cdot \text{Kn}), \quad (1)$$

with λ = total thermal conductivity, λ_{evac} = conductivity of the evacuated specimen (i.e. the sum of radiative conductivity λ_R and solid conductivity λ_S), λ_{GO} = gaseous conductivity of still air, $\beta = 1.6$ for air and Kn the Knudsen number (ratio of molecular mean free path and pore width). Kaganer showed furthermore, that the radiative thermal conductivity varies with the third power of a mean temperature. He applied this finding also to silica aerogels (Fig.3) and pointed out, that data extrapolation $T \rightarrow 0$ in a $\lambda(T^3)$ -plot gives an intercept with the abscissa, representing the solid conductivity. (As we shall see

later, this gives reliable results only, if the temperature dependence of the solid conductivity and the extinction are weak.)

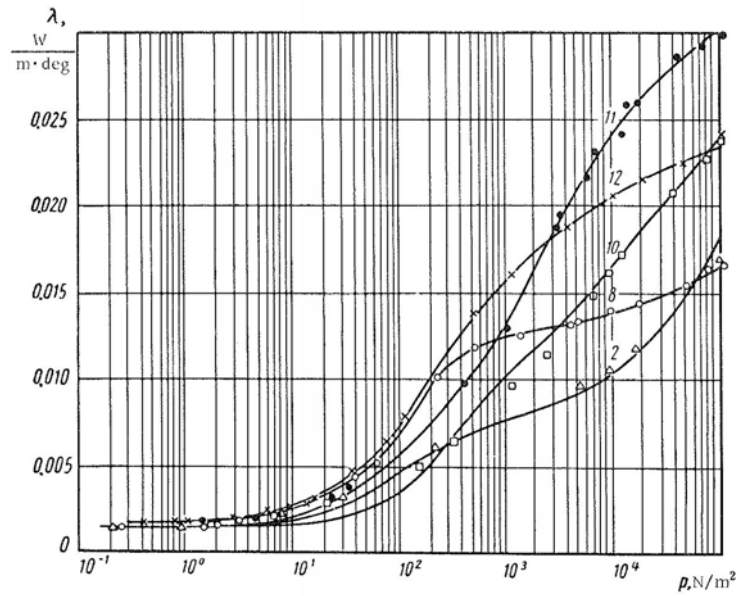


Figure 2: Thermal conductivity of various porous silica powders of different grain size and nano-structure as a function of gas (air) pressure; for example from curve 2 Kaganer derived an intra-grain (nanopore) size of 220 nm and an inter-grain size of 130 μm by making use of equ.1. Boundary temperatures were 293 and 90 K [Kaganer 1969].

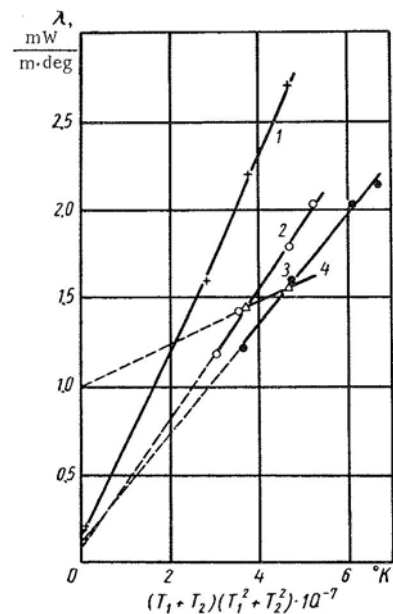


Figure 3: Kaganer showed, that the thermal conductivity of various evacuated aerogel samples varied with the third power of temperature; the data thus fall on a straight line in a $\lambda(T^3)$ -plot [Kaganer 1969]

Kaganer also showed in his measurement (Fig.4), that the thermal conductivity λ_{evac} of evacuated insulants varies with the density ρ according to

$$\lambda_{\text{evac}} = C_1/\rho + C_2 \cdot \rho. \quad (2)$$

The first term describes the dependence of the radiative transport on the density, the second the variation of the solid conduction with ρ . C_1 and C_2 are constants, which depend on the kind of material used, its infrared-optical and structural properties and the temperature.

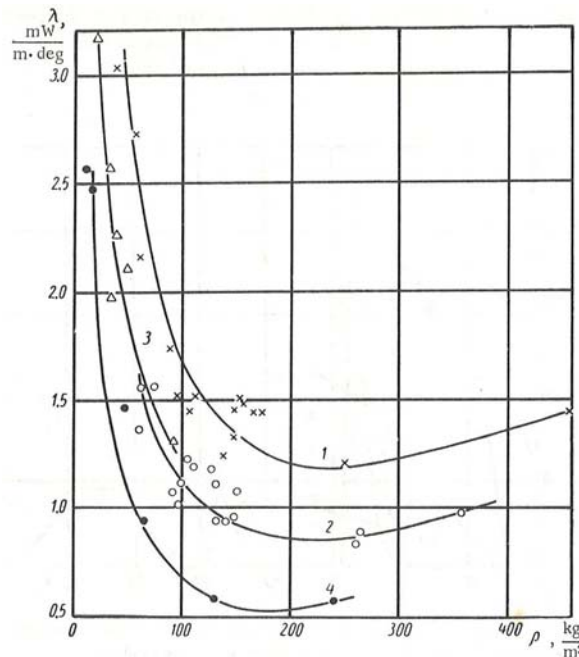


Figure 4: Variation of the thermal conductivity of various evacuated samples with density; the boundary temperatures were 293 and 90 K; no information was given with respect to the applied external load ; 1 = aerogel, 2 = perlite (expanded ebonite), 3 = mipora (an urea-formaldehyde resin), 4 = glass wool. The conductivity passes through a minimum for densities around 200 kg/m³ [Kaganer 1969].

He stated with respect to equ.2: “It is a mistake to reduce the bulk density of materials used in evacuated powder insulations to a minimum, as is sometimes done.”

3 Progress in VIP-technology

To our knowledge powder-filled vacuum insulation panels (VIPs) were first patented by L’Aire Liquide [Gervais 1979]. In the 1980s Brown Boverie & Cie (BBC) in Heidelberg developed rectangular evacuated casings, filled with powders and fiber mats for the insulation of the sodium-sulphur high temperature battery [Fischer 1978, Caps 1983].

In the beginning of the 1990s Degussa in Hanau manufactured VIPs for application in refrigerators [Reuter 1993]. These VIPs had a filling of precipitated silica ($\rho \approx 200 \text{ kg/m}^3$), which fared favourably compared to perlite (see Fig.5). The envelope consisted of a deep-drawn high-barrier plastic envelope as bottom and a flat Al-lined film (Al-thickness 12 μm) as top. The VIPs had a thermal conductivity of 0.006 to 0.007 W/(m·K) at 1 mbar and a life expectancy of 15 years ($\lambda \leq 0.008 \text{ W/(m·K)}$). Maximal dimensions were 80x60x2.5 cm³. The tolerance of the precipitated silica kernel against a moderate pressure increase was already remarkably high (Fig.5).

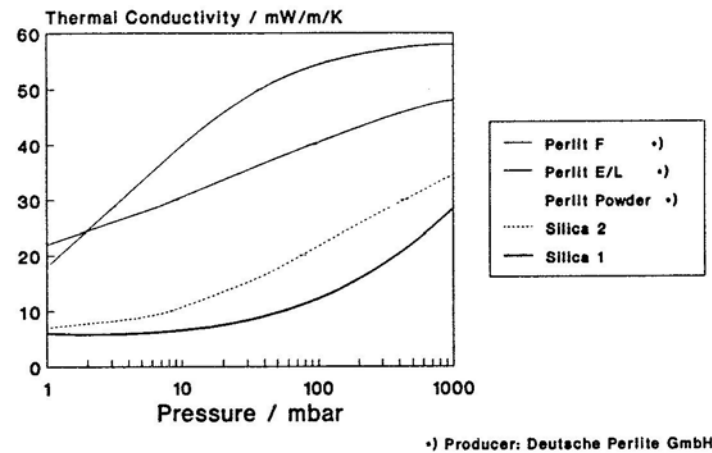


Figure 5: Degussa's comparison of thermal conductivity of different filler materials [Reuter 1993]

At the same time Owens Corning began to produce fiber-filled VIPs ("Aura"- panels) with a kernel density of about 240 kg/m^3 . The envelopes consisted of electron-beam welded sheet steel with a thickness of only $75 \text{ }\mu\text{m}$ [McGrath 1993]. Owens Corning mentioned a center R-value of 50 per inch (which corresponds to a thermal conductivity of about $0.002 \text{ W/(m}\cdot\text{K)}$).

At MBB not only VIPs with a $100 \text{ }\mu\text{m}$ sheet steel casing and a diatomite fill ($\rho \approx 400 \text{ kg/m}^3$) were developed, but also tests with a vacuum-insulated pipe for district heating performed [Schilf 1993]. The thermal conductivity of the diatomite kernel was given as 0.005 to $0.010 \text{ W/(m}\cdot\text{K)}$ for external loads up to 40 bar and gas pressures of 0.01 mbar.

In 1994 ICI introduced its open celled PU-foam based VIP (VACPAC™) and tried to promote its application in refrigerators and freezers. The kernel had a density of about 60 kg/m^3 , a cell size of about $100 \text{ }\mu\text{m}$ and a thermal conductivity of 0.005 to $0.007 \text{ W/(m}\cdot\text{K)}$ at 0.01 mbar [Hamilton 1999]. In order to maintain its low conductivity over the years, i.e. to keep the gas pressure below 1 mbar, a getter had to be used.

The INSTILL vacuum insulation core was developed by Dow Chemical [Pendergast 1999]. It consisted of an extruded open celled PS-foam of density 80 to 140 kg/m^3 with a thermal conductivity of 0.005 to $0.006 \text{ W/(m}\cdot\text{K)}$ at 0.1 mbar. The cell size was 10 to $30 \text{ }\mu\text{m}$.

For applications in cars BMW and Längerer&Reich developed a latent heat storage device with vacuum insulation [Blüher 1991]. As filling silica-aerogels were employed.

Most VIPs today are manufactured with a fumed silica kernel and are sealed into a high-barrier laminate. For quality control an integrated thermosensor is essential.

4 Acquired thermophysics know-how

During the decades after Kaganer's book appeared numerous experiments with well defined external load, small temperature spread across the specimen and selected boundary emissivity were performed. The thermophysics community had developed an excellent understanding of the thermal transport in VIPs, which allows one to optimize the kernels with respect to the total conductivity λ and/or its components:

$$\lambda = \lambda_G + \lambda_S + \lambda_R + \lambda_C. \quad (3)$$

The coupling term λ_c is negligible for foams. Contrariwise it can be considerable at elevated gas pressures, e.g. 0.020 to 0.030 W/(m·K) for powders consisting of hard grains. The coupling term becomes noticeable, when – upon increase of gas pressure - the contact resistances between the grains are thermally shorted by the gas molecules. The variation of the gas conductivity λ_G with the gas pressure p_G in equ.1 can be rewritten

$$\lambda_G = \lambda_{G0}/(1 + p_{1/2}/p_G). \quad (4)$$

$p_{1/2}$ is the gas pressure, at which the gaseous thermal conductivity is equal to $\lambda_{G0}/2$. For air we get

$$p_{1/2}/\text{mbar} \approx 230/(\Phi/\mu\text{m}). \quad (5)$$

From this equation and Fig.6 we recognize, that for nanostructured materials with $\Phi \approx 200$ nm one gets $p_{1/2} \approx 1000$ mbar. If the gas pressure is reduced to below 10 mbar, the gaseous conductivity becomes negligible. For coarse materials with $\Phi \approx 20$ μm the gaseous conductivity is fully developed at 1 bar and evacuation to about 0.1 mbar is required, in order to suppress gaseous conduction.

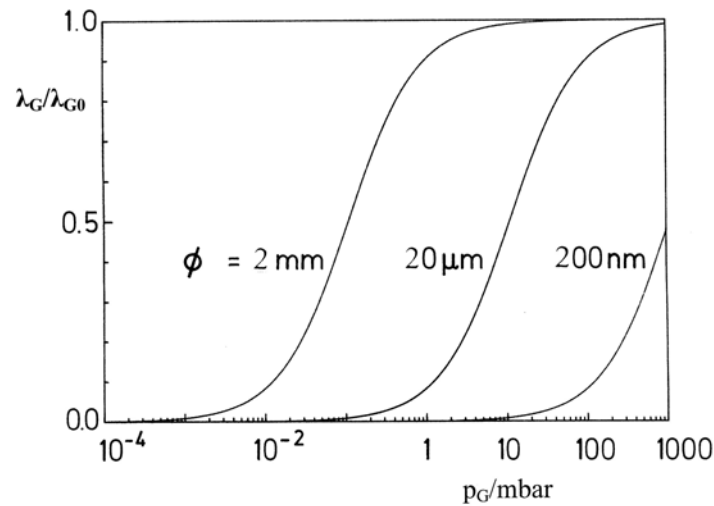


Figure 6: Variation of the relative thermal conductivity as a function of air pressure with the pore diameter as a parameter

The solid conductivity λ_s is the smaller, the more thermal resistances are built into the insulating material, i.e. the finer structured the material is. Nano-materials are superior in this respect, as they resemble fractals, which interrupt the heat flow on the nm-level, while perlite and diatomite consist of rather coarse, well conducting grains. The solid conductivity scales with density ρ of the material:

$$\lambda_s \sim \rho^\alpha, \quad (6)$$

with $\alpha \approx 1$ for foams and $\alpha \approx 1.5 \dots 2$ for materials as aerogels or fumed silica. As fumed silica is amorphous, its solid conductivity increases only slightly with temperature at ambient conditions. As for vitreous silica one gets $\Delta\lambda_s/(\Delta T \cdot \lambda_s) \approx 10^{-3}/\text{K}$. The solid conductivity of insulants also depends on the external pressure load onto the material; a quantitative description is difficult, as most materials show a hysteresis behaviour. Typical values for pressure loaded fibers are $\lambda_s \approx 0.001 \dots 0.003$ W/(m·K), for powders $\lambda_s \approx 0.003 \dots 0.010$ W/(m·K) and for pressure sustaining foams $\lambda_s \approx 0.005 \dots 0.007$ W/(m·K).

In order to reduce the radiative thermal transport at a given temperature, absorbing and scattering particles have to be integrated into the silica, which is a weak absorber in the near infrared. A suitable opacifier is SiC. Quantitatively the radiative thermal conductivity [Fricke 1993] within an optically thick specimen is described by

$$\lambda_R = \frac{16n^2 \cdot \sigma \cdot T_r^3}{3E(T_r)}. \quad (7)$$

Here n is the index of refraction, which can be approximated by $n \approx 1$ for low density silica. $\sigma = 5.67 \cdot 10^{-8} \text{ W/(m}^2 \cdot \text{K}^4)$ is the Stefan-Boltzmann constant and T_r is an average temperature within the insulant:

$$T_r = (T_1 + T_2) \cdot (T_1^2 + T_2^2) / 4. \quad (8)$$

T_1 and T_2 are the temperatures of the VIP surfaces. $E(T_r)$ is the extinction coefficient of the insulating material, which is the reciprocal of the mean free path l_{ph} of the thermal photons and is correlated with the density ρ and the mass specific extinction $e(T_r)$ as follows

$$E(T_r) = e(T_r) \cdot \rho = 1/l_{ph}. \quad (9)$$

For opacified silica kernels one has $l_{ph} \approx 100 \text{ } \mu\text{m}$, which means, that VIPs with a thickness of 2 cm are infrared-optically thick, thus the radiative transfer is a diffusive process (while it would be ballistic for optically thin media). $e(T_r)$ can be calculated from the spectral mass specific extinction $e(\lambda)$, which is derived from infrared-optical extinction measurements within the wavelength range $\lambda = 2 \dots 40 \text{ } \mu\text{m}$ (see fig.7). By properly averaging $e(\lambda)$ over the diffusing thermal spectrum at T_r ("Rosseland" average), $e(T_r)$ is obtained (fig.8).

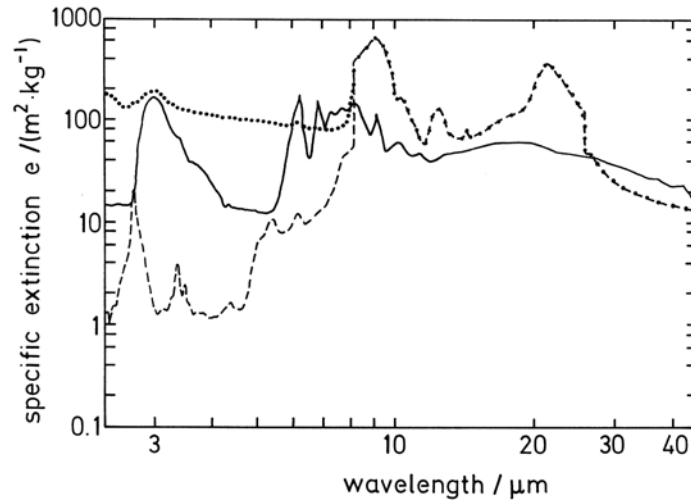


Figure 7: Spectral mass specific extinction versus wavelength for pure silica (– –), organic resorcinol formaldehyde aerogel (—) and for opacified silica with 5% carbon black (...). Note the small extinction of pure silica below 8 μm . [Lu 1992].

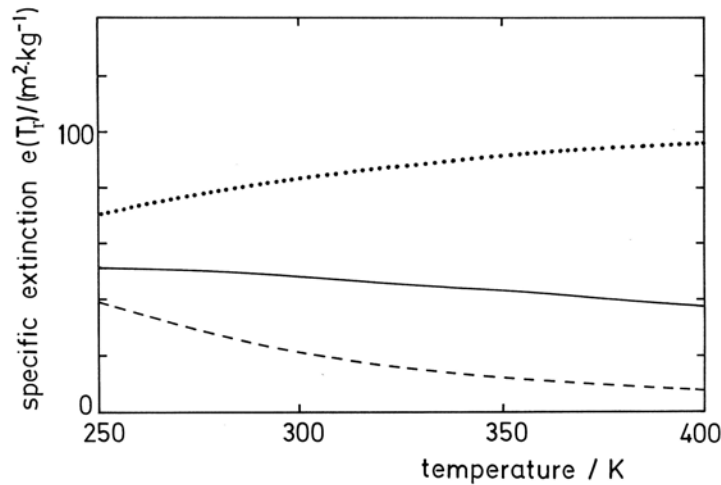


Figure 8: Mass specific extinction versus temperature of the materials in Fig. 7 [Lu 1992]

According to equation 7 the radiative conductivity of an opacified silica kernel at $T_R = 300$ K, with a mass specific extinction $e \approx 50 \dots 60 \text{ m}^2/\text{kg}$ and a density $\rho \approx 150 \text{ kg/m}^3$ is $\lambda_R \approx 0.001 \text{ W/(m}\cdot\text{K)}$. We also recognize, that λ_R is proportional to the third power of T_R , if (and only if) the temperature dependence of e can be neglected. If also the temperature dependence of λ_S is weak, one then can plot

$$\lambda_{\text{evac}} = \lambda_S + \lambda_R \quad (10)$$

in a $\lambda(T_R^3)$ – diagram and use Kaganer’s interpretation to separate λ_S and λ_R (see Fig.3).

To wrap up the details in this section (see also Fig.9), one can expect total thermal conductivities of about 0.004 to $0.005 \text{ W/(m}\cdot\text{K)}$ for dried and evacuated opacified fumed silica kernels at 300 K, with contributions of 0.003 to $0.004 \text{ W/(m}\cdot\text{K)}$ from solid conduction and $0.001 \text{ W/(m}\cdot\text{K)}$ from radiative transport. These values are nearly optimal, if one also considers the fact, that the $p_{1/2}$ -pressure for fumed silica with about 1 bar is large in comparison to $p_{1/2}$ of other insulants.

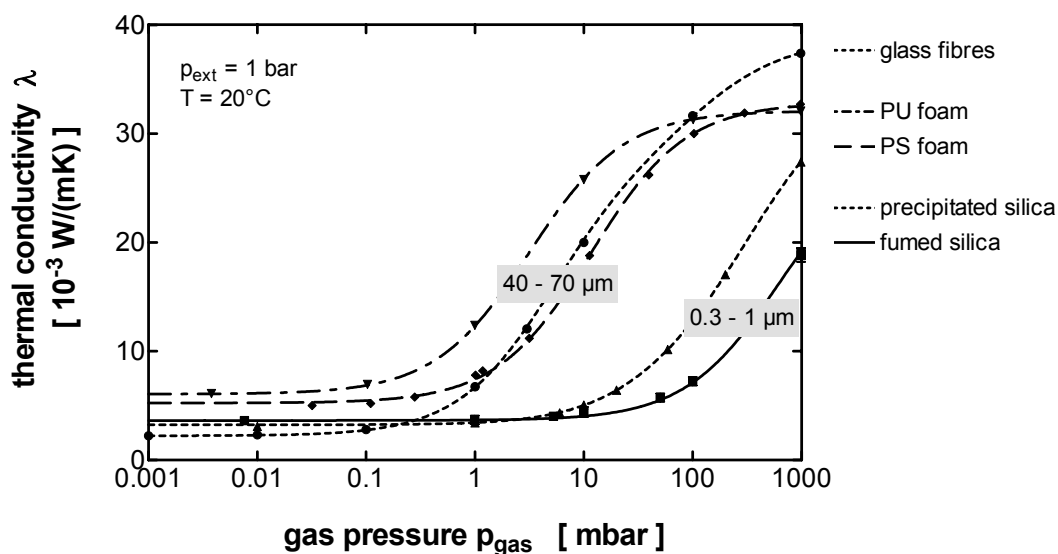


Figure 9: Thermal conductivity of fibers, powders and foams as a function of gas (air) pressure [Heinemann 2002]

5 Lessons to heed

Most VIPs today are manufactured with a fumed silica kernel with $\rho \approx 180 \text{ kg/m}^3$, in which an opacifier (SiC) and a fiber component are integrated. The kernel is sealed into a PE-coated Al-foil or a high-barrier laminate (Fig.10). As the former causes considerable thermal bridging at the perimeter of the VIP, the latter is to be preferred, especially for small VIPs. PE-coated Al-foils and the best available laminates limit air infusion to less than 1 mbar/year, if the sealing is correctly performed and if the barrier is not breached in a point defect. This can be checked by integration of a thermosensor [Caps 2002] into the VIP and by at least two, possibly three pressure checks, one after production, the second about 2 or 3 weeks later and the third before the VIPs are covered with plaster. The foil lift-off method seems too difficult to handle for on-site checks (who would transport a large vacuum chamber to a building site?). In order not to discredit VIP-technology for the long-term application in buildings (where service lifetime of about 50 years are required) a stringent quality control, which is most easily realized with an integrated sensor, is essential.

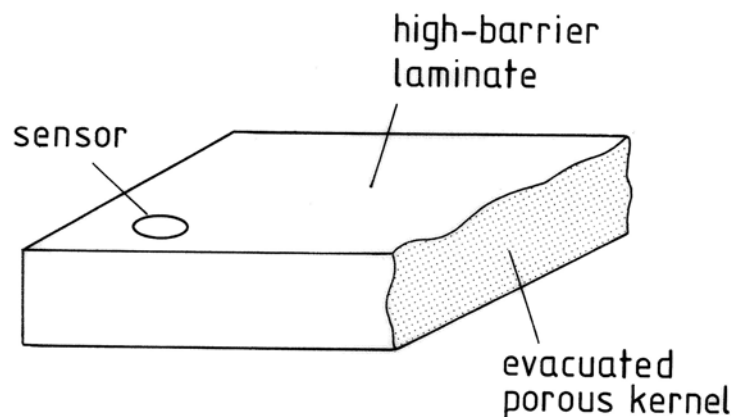


Figure 10: Construction of a VIP; the nano-structured kernel is sealed into an PE-coated Al-foil or a high-barrier laminate; for quality control a thermosensor is essential.

6 References

[Blüher, 1991] P.Blüher, Latentwärmespeicher erhöht den Fahrkomfort und die Fahrsicherheit, ATZ Automobiltechnische Zeitschrift **93**, Heft 10 (1991).

[Cabot 2005] www.cabot-corp.com —> aerogels.

[Caps 1983] R.Caps, J.Fricke, H.Reis, Improving the Extinction Properties of an Evacuated High-Temperature Powder Insulation, High Temperatures – High Pressures **15**, 225 – 232 (1983).

[Caps 2002] J. R. Caps, Vorrichtung und Verfahren zur Messung des Gasdruckes in evakuierten Dämmplatten, Patentschrift DE 10215213C1.

[Fischer 1978] W.Fischer, W.Haar, Die Natrium/Schwefel-Batterie, Physik in unserer Zeit **9**, 184 – 191 (1978).

[Fricke 1993] J.Fricke, Materials Research for the Optimization of Thermal Insulation, High Temperatures – High Pressures **25**, 379 – 390 (1993).

[Hamilton 1999] A.J.Hamilton, An Evaluation of the Practical Application and Use of VACPAC™ Panel Technology, VUOTO **XXVIII**, 27 – 30 (1999).

[Heinemann 2002] Daten U. Heinemann, ZAE Bayern.

[Herrmann 1995] G.Herrmann, R.Iden, M.Mielke, F.Teich, B.Ziegler, On the Way to Commercial Production of Silica Aerogels, Non-Cryst. Solids **186**, 380 – 387 (1995).

[Hoechst 1997] Innovative Heat Insulation with Aerogels, Hoechst AG, Frankfurt VF1255-1-2e/0507(014), in: Future Special Science 2 (1997).

Kaganer 1969] M.G.Kaganer, Thermal Insulation in Cryogenic Engineering, Israel Program for ScientificTranslations, Jerusalem (1969).

[Kistler 1932] S.S.Kistler, Coherent Expanded Aerogels, J.Phys.Chem. **34**, 52 – 64 (1932)

[Kistler 1934] S.S.Kistler and A.G.Caldwell, Thermal Conductivity of Silica Aerogels, Industrial and Engineering. Chemistry **26**, 658 – 662 (1934).

[Lu 1992] X.Lu, M.C.Arduini-Schuster, J.Kuhn, O.Nilsson, J.Fricke, R.W.Pekala, Thermal Conductivity of Monolithic Organic Aerogels, Science **225**, 971 – 972 (1992).

[McGrath 1993] R.McGrath, Owens Corning, at: 1993 Non-Fluorocarbon Insulation, Refrigeration and Air-Conditioning Technology Workshop, Sept. 1993, Wiesbaden.

[Pendergast 1999] P.Pendergast, B.Malone, Characterization and Commercialization of INSTILL Vacuum Insulation Core, a Unique Polystyrene Vacuum Insulation Filler From the Dow Chemical Company, VUOTO **XXVIII**, 77 – 81 (1999).

[Reuter 1993] R. Reuter, G. Sextl, Degussa AG, Hanau, Vacuum Insulation Panels (VIPs), at: 1993 Non-Fluorocarbon Insulation, Refrigeration and Air-Conditioning Technology Workshop, Sept. 1993, Wiesbaden.

[Schilf 1993] L.Schilf, MBB, The MBB-Vacuum Super Insulation (VSI), *ibid*.

[Thermos 1904] www.thermos.com.