and HCl in solution. The results agreed very well with the values calculated by Equation 5 (Table IV). The calculated results are nearly identical with those calculated by the equations in Table III.

The heats of solution of CO_2 in the various solutions were calculated by Equation 1 from the values of α at 20° and 30° C., assuming a relatively constant value of ΔH in that range. The results are listed in Table V.

Table III. Linear Solubility Relationships

$C = 0$ to 0.1 molal

Solution	CO_2 Solubility Equation
As_2O_3	$S = S_0(1 - 0.41C)$
As_2O_5	$S = S_0(1 - 0.29C)$
HCl	$S = S_0(1 - 0.04C)$

Table IV. Values Calculated by Equation 5

Molality			Temp., ° C.	α	
As_2O_3	As_2O_5	HCl		Calcd.	Found
0.0329	0.0273	. . .	20	0.859	0.864
. . .	. . .	. . .	25	0.743	0.744
. . .	. . .	. . .	30	0.651	0.649
0.0465	0.0159	0.0625	20	0.855	0.854
. . .	. . .	. . .	25	0.739	0.732
. . .	. . .	. . .	30	0.648	0.650
0.0305	0.0307	0.1271	30	0.648	0.653

Table V. Calculated Values of $\Delta H_{sol.}$ CO_2

Solution	ΔH, Cal./Mole
Water	−4900
0.1113 molal As_2O_3	−4892
0.133 molal As_2O_5	−4822
0.637 molal HCl	−4890

DISCUSSION

The plots of the absorption coefficients *vs.* concentration of the acid species (Figures 2 and 3) at different temperatures have approximately equal slopes and can be represented by the same general equation (Table III) within experimental error. This would indicate that there is no appreciable change in the heat of solution of CO_2 per mole within the concentration ranges used. This fact is further illustrated by the data in Table V, where the calculated values of the heats of solution are equal within experimental error. Therefore, the authors concluded that the heat of solution of CO_2 per mole in any of the solutions generally encountered in calorimetric work ($< 0.1M$ As_2O_3) can be considered equal to that in pure water. The maximum error introduced by this assumption, calculated from the data in Table V and assuming the use of 20 ml. of a 0.1 molal As_2O_3 solution in the bomb, would be on the order of 0.2 calorie.

The change in solubility of CO_2 in solutions of up to 0.1 molal As_2O_3 is rather significant. The decrease in the amount of CO_2 dissolved in the bomb solution from that in pure water may be more than 5%. With 20 ml. of solution in the bomb, this would amount to an error of about 0.9 calorie. Therefore, it may be advantageous to compute the correction for the solubility of CO_2 in the final bomb solution considering the salting-out effect of the various species present. This calculation should also take into account the usual correction for the fugacity of CO_2 in the presence of oxygen.

LITERATURE CITED

(1) Barber, C.R., Handley, R., Herington, E.F.G., *Brit. J. Appl. Phys.* **5**, 41–4 (January 1954).
(2) Bohr, Chr., *Wied. Ann.* **68**, 504 (1899).
(3) Geffcken, Gustav, *Z. Physik. Chem.* **49**, 257 (1904).
(4) Glasstone, Samuel, "Text-book of Physical Chemistry," p. 689, Van Nostrand, New York, 1940.
(5) Markham, A.E., Kobe, K.A., *J. Am. Chem. Soc.* **63**, 1165–6 (1941).
(6) Reilly, J., Rae. W.N., "Physico-chemical Methods," Vol. **III**, p. 147, Van Nostrand, New York, 1948.

RECEIVED for review September 15, 1967. Accepted October 24, 1967. Work was funded under the Foundational Research Program of the Director of Naval Laboratories and the Thermochemical Studies Program, Task Assignment RMMP-22-153/286-1/R001-06-01.

Thermal Conductivity of Fibrous Silica

EDMUND J. ROLINSKI
Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433
THOMAS L. SWEENEY
The Ohio State University, Columbus, Ohio 43310

The thermal conductivity of fibrous-silica high temperature insulation, commercially available as Dynaquartz, was measured in air, argon, and under high vacuum from 735° to 2860° R. mean temperature.

CRYSTALLINE fibrous-silica insulation, commercially available as Dynaquartz (*5*), has properties which make it a promising material for high temperature use. These are: a low density of 6.2 pounds per cubic foot (p.c.f.); good dimensional stability with less than 1.0% shrinkage after several hours at 3060° R.; maximum rated temperature of 3210° R.; and chemical stability characterized by low volability and low reactivity (*5, 7, 8, 11*).

The material used in this investigation was 99+% crystalline silica in randomly oriented fibrous form. The range of observed fiber diameter was 3.3 to 6 microns. The true density of the fibers was determined to be 2.17 grams per cc. The void volume fraction was 0.954. Figure 1 is a photomicrograph of the fibrous silica sample.

The thermal conductivity of fibrous silica insulation, obtained with a guarded hot plate apparatus, is reported.

Figure 1. Photomicrograph of fibrous silica surface

Fibers are 3.3 to 6 microns in diameter

Previous measurements have been made with a radial heat flow apparatus (*4*, *6*) or by using a transient calorimetric technique (*9*).

EXPERIMENTAL DESCRIPTION

The thermal conductivity measurements reported here were made with the guarded hot plate instrument that has been described elsewhere (*10*). The sample size was 12 × 12 × ½ inches. One sample was used on each side of the heater. The top sample was modified to support the loads applied to it by the apparatus (*7*). For tests conducted in the air, the temperatures of the hot and cold surfaces were monitored by using platinum *vs.* platinum–10% rhodium thermocouples. For the argon atmosphere and vacuum experiments Chromel-Alumel thermocouples were used on the cold surface only. Thermocouples were placed on the corner and side guard sections for measuring imbalance of the main and guard

Table I. Thermal Conductivity of Fibrous Silica—6.2 Pounds per Cubic Foot

$k, \frac{\text{B.t.u.-Inch}}{\text{Hr.-Sq. Ft.-}^\circ\text{R.}}$	T, ° R. mean	ΔT, ° R.	Imbalance, R.
AIR[a]			
0.606	1421.6	409.1	4.0
0.614	1433.6	406.9	7.3
0.614	1435.0	409.5	6.9
0.764	1716.0	466.6	9.9
0.760	1719.5	451.9	6.7
0.752	1722.2	454.9	8.1
0.750	1725.9	455.9	7.8
1.074	2208.7	425.1	7.5
1.083	2230.6	419.9	4.9
1.101	2246.7	411.8	9.0
1.195	2338.5	378.3	8.7
1.160	2339.3	388.7	2.7
1.250	2342.7	365.2	8.0
1.210	2343.9	376.4	14.4
1.298	2346.8	361.7	7.3
1.255	2346.8	373.0	13.3
1.222	2364.7	373.0	16.0
1.151	2371.3	393.9	0.0
1.338	2607.9	343.9	17.4
1.292	2609.8	363.7	18.0
1.298	2615.4	347.0	16.0
1.258	2618.8	362.7	10.3
1.724	2847.7	373.3	15.8
1.657	2866.2	353.6	18.3
1.622	2867.6	360.8	15.7
1.564	2881.0	362.7	10.7
1.623	2881.5	350.3	7.6
1.639	2886.0	355.3	5.0
1.596	2886.2	364.3	12.3
ARGON[b]			
0.372	726.7	145.5	1.0
0.347	731.0	156.0	1.2
0.341	733.1	158.9	0.9
0.321	737.0	162.0	1.7
0.340	737.3	159.6	1.2
0.385	778.5	179.1	11.4
0.401	797.7	192.1	11.1
0.394	804.4	192.9	10.4
0.531	1225.0	372.6	15.0
0.532	1226.3	369.3	16.2
0.530	1227.0	369.9	15.9
0.528	1227.1	370.9	15.6
0.608	1705.2	444.8	7.4
0.615	1715.7	429.1	4.1
0.612	1717.2	431.9	5.5
0.611	1717.3	444.6	10.8
0.605	1717.9	430.4	5.6
0.610	1719.1	431.7	4.7
0.612	1719.4	433.3	5.2
0.876	2047.8	386.6	0.8
0.857	2057.1	393.3	12.1
0.869	2063.1	388.6	10.9
0.873	2069.9	383.9	11.1
0.880	2084.9	364.2	10.0
1.200	2372.9	331.2	4.5
1.205	2378.3	334.3	12.1
1.182	2391.1	339.7	10.9
1.155	2405.6	351.8	4.5
VACUUM, PRESSURE $<10^{-4}$ TORR[c]			
0.154	927.2	216.1	1.4
0.150	930.4	222.3	2.0
0.187	1268.6	358.6	9.5
0.189	1268.7	356.9	7.9
0.187	1269.6	360.2	8.2
0.186	1269.9	360.1	9.8
0.187	1269.9	360.1	7.5
0.281	1740.8	351.6	3.6
0.278	1742.5	350.5	2.1
0.273	1745.5	345.4	1.9
0.287	1747.0	340.5	0.2
0.292	1753.1	336.8	1.3
0.308	1754.8	316.7	1.2
0.363	1959.8	335.9	11.1
0.418	2106.6	333.6	10.6
0.457	2119.7	333.8	10.1
0.392	2148.1	342.3	15.0
0.407	2166.2	331.4	6.4
0.395	2169.5	333.5	5.8
0.449	2359.2	343.5	15.0
0.435	2373.5	333.6	4.5
0.561	2514.7	334.1	2.9
0.575	2522.7	345.8	9.9
0.581	2531.5	318.0	9.9
0.583	2476.7	322.3	9.1
0.555	2487.4	340.9	8.1

[a] Least square equations: $k = -1.059 + 1.897(10^{-3})T - 6.956(10^{-7})T^2 + 1.250(10^{-10})T^3$. $E_{\max} = 0.135$ at 2847.7° R. $E_{\text{rms}} = 0.056$. $k = 5.422(10^{-1}) + 4.645(10^{-11})T^3$. $E_{\max} = 0.155$ at 2346.8° R. $E_{\text{rms}} = 0.068$. [b] Least square equations: $k = -4.479(10^{-1}) + 1.859(10^{-3})T - 1.290(10^{-6})T^2 + 3.350(10^{-10})T^3$. $E_{\max} = 0.068$ at 2405.6° R. $E_{\text{rms}} = 0.027$. $k = 3.459(10^{-1}) + 6.021(10^{-11})T^3$. $E_{\max} = 0.075$ at 1226.3° R. $E_{\text{rms}} = 0.040$. [c] Least square equations: $k = 8.623(10^{-2}) + 5.081(10^{-5})T - 5.535(10^{-9})T^2 + 2.409(10^{-11})T^3$. $E_{\max} = 0.063$ at 2373.5° R. $E_{\text{rms}} = 0.023$. $k = 1.377(10^{-1}) + 2.696(10^{-11})T^3$. $E_{\max} = 0.063$ at 2373.5° R. $E_{\text{rms}} = 0.023$.

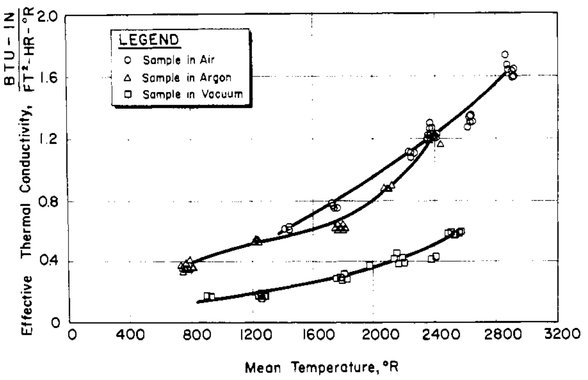

Figure 2. Effective thermal conductivity of fibrous silica in air, in argon, and vacuum vs. temperature

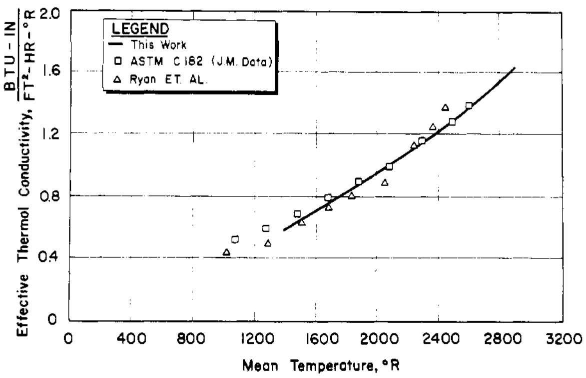

Figure 3. Effective thermal conductivity of fibrous silica in air vs. temperature

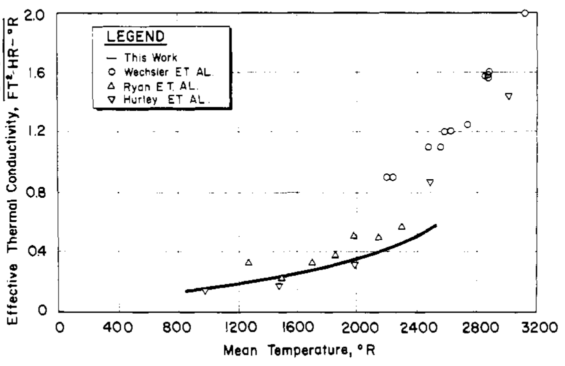

Figure 4. Effective thermal conductivity of fibrous silica in vacuum vs. temperature

heaters. New thermocouples were used for each run. The procedure was in accordance with ASTM Specification C-177-63 (*1*), except for two deviations that were necessary above 1660° R. mean temperature. Because of the large temperature gradient through the sample, the temperature difference between the main and guard heaters exceeded, in some runs, 0.75% of the temperature difference across the sample. Also, it was not possible to maintain the apparent thermal conductivity to within 1% for long periods of time.

EXPERIMENTAL RESULTS

The thermal conductivity of 6.2 p.c.f. fibrous silica was measured in air from 1460° to about 2860° R. mean temperature, in argon from 735° to about 2410° R. mean temperature, and in vacuum of less than 10^{-4} torr from 910° to about 2460° R. mean temperature. The experimental data are tabulated in Table I and are plotted in Figure 2.

Two least-square equations were determined for each data set. The first is a simple power series in temperature including all terms of a cubic. The first equation is plotted for each data set in Figure 2. The other equation is a cubic in temperature with the linear and quadratic terms suppressed. This latter equation is useful in interpreting the radiative contribution to the thermal conductivity (*7, 8*).

Maximum deviation and root mean square deviation from the least-square equations are indicated below the tables of data. The tabulated values show the mean temperature, the temperature difference across a ½-inch thick sample, and the imbalance between the side guard and main heater temperatures. The imbalance was usually within 5% of the specimen ΔT, but some values were as high as 7%. The total maximum error due to uncertainties in the measurements is estimated to be ± 14% and the usual error in the thermal conductivity measurements is estimated to be about ± 10% (*7*). Imbalance errors were estimated using the method of Woodside and Wilson (*12, 13*) for guarded hot plate apparatus.

The consistency between the air and vacuum data up to approximately 2500° R. mean temperature was verified using a correction for the conductivity of air to the measurements in an air environment. If the conductivity of air multiplied by the void volume is subtracted from the conductivity value obtained in air, the results are within the scatter of data obtained in a vacuum. The consistency between the argon and vacuum data up to approximately 2500° R. mean temperature was also verified. In Figure 3, the thermal conductivity data obtained in air are compared with those (*5, 9*) obtained using a radial heat apparatus and a transient calorimetric technique. The results are in good agreement.

The thermal conductivity measurements in vacuum are compared with other measurements (*4, 9, 11*) in Figure 4. Most of the data show good agreement up to about 2200° R. mean temperature. The disagreement above 2200° R. in the vacuum measurements is qualitatively attributed to the following (*8*):

> Imbalance between the main and guard heater in the case of the guarded hot plate where radiation interchange between the heaters is possible at higher temperatures.
>
> Temperature gradients in the samples which were different. The effect of temperature gradients at constant average temperature underscores the influence of radiation heat transfer at temperatures above 2000° R. (*2*) for fibrous insulating materials.
>
> Contact resistance between the fibers and heater. An attempt was made to measure true sample temperature in the guarded hot plate work.
>
> Sample fiber orientation. This may differ between radial heat flow samples and guarded hot plate samples.

LITERATURE CITED

(1) American Society for Testing Materials, Designation C177-63, "Standard Method of Test for Thermal Conductivity of Materials by means of Guarded Hot Plate," ASTM Standards on Thermal Insulating Materials sponsored by ASTM Committee C-16, 3rd ed., 1963.
(2) Chen, J. C., Churchill, S. W., *A.I.Ch.E. J.* **9**, No. 1, 35-41 (1963).
(3) Haskins, J. F., Cambell, M. D., Hertz, J., Percy, J. L., "Thermophysical Properties of Plastic Materials and Composites to Liquid Hydrogen Temperatures (−423° F.), Part I," ML TDR 64-33, WPAFB, Ohio, June 1964.
(4) Hurley, J., Traiger, H., in "Lightweight Thermal Protection System Development," AFML TR 65-26, Vol. **II**, WPAFB, Ohio, June 1965.

(5) Johns-Manville Co., Bulletin No. IN-475A, New York, June 1963.
(6) Plunkett, J.D., in "Lightweight Thermal Protection System Development," ASD TDR 63-596, Vol. **III**, Materials-Existing Data and Recommended Data acquisition. WPAFB, Ohio, June 1963.
(7) Rolinski, E. J., M. Sc. thesis, Ohio State University, Columbus, Ohio, 1966.
(8) Rolinski, E. J., G. V. Purcell, Paper No. 128, Third International Heat Transfer Conference, Chicago, Ill., August 1966.
(9) Ryan, J. M., Cross, R. I., Stockham, T., in "Lightweight Thermal Protection System Development," AFML TR 65-26, Vol. **II**, WPAFB, Ohio, June 1965.
(10) Sparell, J. K., Coumou, K. G., Plunkett, J. D., "An Instrument for Measuring the Thermal Conductance of High Temperature Structural Materials," ASD TDR 63-359, WPAFB, Ohio, May 1963.
(11) Wechsler, A. E., Kritz, M., "Investigation and Development of High Temperature Insulation Systems," AFML TR 65-138, WPAFB, Ohio, June 1965.
(12) Woodside, W., Wilson, A. G., *Rev. Sci. Instr.* **28**, 1033-37 (1957).
(13) Woodside, W., Wilson, A. G., "Unbalance Errors in Guarded Hot Plate Measurements," presented at ASTM Symposium in Thermal Conductivity Measurements, Philadelphia, Pa., ASTM Special Publication 217, 1957.

RECEIVED for review November 7, 1966. Accepted December 19, 1967.

Adiabatic Compressibility of Liquid Ammonia

D. E. BOWEN[1] and J. C. THOMPSON
Physics Department, The University of Texas at Austin, Austin, Tex. 78712

Values of the adiabatic compressibility of pure liquid ammonia, derived from sound speed measurements between the freezing point and the normal boiling point are reported. The sound speed was a linear, decreasing function of the temperature. A comparison with other values is given.

VALUES for the adiabatic compressibility of pure liquid ammonia at its vapor pressure between the normal freezing and boiling points are reported. These data were obtained as a part of a detailed study of the physical properties of metal-ammonia solutions and are presented here because of the scant information available on the pure solvent in this temperature and pressure range.

The adiabatic compressibility, defined by (*4*)

$$\beta_s = -(\partial v/\partial p)_s/v \qquad (1)$$

was determined by measuring the velocity of sound, C_s, using the published values of the density (*5*), ρ, and the relation (*6*)

$$\beta_s = 1/C_s^2\rho \qquad (2)$$

The liquid ammonia was contained in a cylindrical quartz cell 2.0 cm. long and 1.6 cm. in diameter. The velocity of sound was determined by a standard time-of-flight technique using pulsed 10 MHz. compressional waves generated by crystal transducers cemented to the outside of the cell (*6*). This system was calibrated by measuring the velocity in liquids with a well known velocity. The quartz sound cell was placed in a system in which the temperature was regulated to within ±0.1° K. between 200° and 240° K. The temperature was measured by copper-constantan thermocouples, calibrated in liquid N_2(~77° K.) and liquid NH_3(~240°) with interpolations from NBS tables (*3*), placed next to the sample cell. Ammonia, 99.95% pure NH_3 (Matheson Co.), was further purified by preparing a sodium-ammonia solution and allowing the solution to stand for at least 12 hours. The ammonia was then distilled from this solution into the previously evacuated (less than 10^{-3} torr) cell.

With the time-of-flight technique, it is possible to determine the sound velocity to within one part in 10^3 (*9*); however with the present system this was not possible owing to the temperature fluctuations; thus, for these experiments, the velocity as a function of the temperature was determined to about one part in 10^2. The determination of the velocity requires two inputs: the length of the cell; and the time between pulse and echo. As the cell was a modified optical absorption cell, its length could be determined in terms of known absorbances of standard solutions. The authors also made measurements of the sound speed in well known systems such as water, acetone, and methanol and obtained agreement to 3+ significant figures at room temperature. The length was 1.986 ± 0.009 cm. with a 95% confidence level. Time measurements were made using the delayed sweep of a Tektronix 555 oscilloscope. The manufacturer states the precision of the time base to be one part in 10^4 (on the scale used) with an accuracy of 0.2%. Thus a precision of better than one part in 10^3 is attainable if the pulse initiation point can be determined with arbitrarily high precision. In the present apparatus, the measurement of the time between the original pulse and the first echo was limited by the width of the oscilloscope trace to a precision of one part in 10^3. Each datum reported is the average of four to 10 independent measurements of the time interval. Thus, the quoted over-all precision in C_s is reached.

The velocity was measured as the temperature of the system was changed between 194° and 240° K. All data were taken within 4 cm. of Hg of the vapor pressure. The experimental values of C_s are given in Table I and are plotted in Figure 1. Values of C_s obtained by Maybury and Coulter (*7, 8*) are also shown in Figure 1. There is considerable scatter in the data of Maybury and Coulter when compared with the present data.

The sound velocity data were fitted by a straight line in the form

$$C_s = C_0 - C_1T \qquad (3)$$

where, by a least squares analysis (*1*), the values of C_0 and C_1 were determined to be

$$C_0 = 3209 \pm 3.6 \text{ meters per second}$$

$$C_1 = 6.19 \pm 0.05 \text{ meters per second degree}$$

The density data of Cragoe and Harper (*5*) are shown in Figure 2. They have determined the density of one part in 10^4. The present authors have chosen to fit this

---

[1] Present address: Physics Department, The University of Texas at El Paso, El Paso, Tex. 79999