THE THERMAL AND ELECTRICAL CONDUCTIVITY OF FUSED QUARTZ AS A FUNCTION OF TEMPERATURE

By Herman E. Seemann

Abstract

Thermal conductivity of fused quartz.—The thermal conductivity as a function of the temperature has been determined for clear fused quartz by the radial flow method from 235°K to 1225°K. The specimen was in the form of a hollow cylinder closed hemispherically at one end. Energy to maintain a steady temperature gradient was supplied by means of an electrically heated filament mounted axially inside the specimen. Thermal contact with the specimen was made with mercury inside and outside at the lower temperatures and with the tin-lead eutectic at the higher temperatures. Inside and outside temperatures were obtained with thermocouples. A guard ring scheme was used to prevent heat loss or gain at the open end of the cylinder and correction was made for the heat flow through the hemispherical end cap. The results may be represented by the linear equation: $K=3.83\times10^{-6}T+0.00163$. An abrupt change in the thermal conductivity was noted in the vicinity of 1140°K which is attributed to heat treatment i.e. annealing or partial crystallization.

Electrical conductivity of fused quartz.—An attempt was made to measure the specific electrical resistance as a function of the temperature by the same method at the same time. The results were not conclusive because of the small number of data taken but there is every reason to believe that the *method* would be entirely successful for the determination of both quantities. The specific resistance was measured for a small piece of the original specimen. C. C. Bidwell's modification of Königsberger's formula was verified i.e. $\rho=A\epsilon\,(Q/\mathrm{RT}+a\mathrm{T})$ $\rho=\mathrm{A}\epsilon^{\,(Q/Rt+aT)}$. The results indicate the presence of both electrolytic and delectiric polarization. Certain peculiarities in the polarization were noted at about 1140°K as well as a general change in the resistance-temperature curve due to heat treatment. The interpolated results are as follows:

Temperature:	550°K	750°K	950°K	1150°K
Specific Resistance:	4.46×10^{9}	2.09×10^{7}	1.35×10^{6}	2.69×10^{5}

Introduction

Work has been done on the dependence on temperature of the thermal conductivities of some non-metallic substances by C. C. Bidwell[1] and by A. Eucken.[2] The present investigation was undertaken with a view to extending this field. Eucken worked in the temperature range from about -250°C to $+100$°C. One of the materials which he studied was fused quartz. Since this is a simple chemical compound (SiO_2) and is highly refractory, it seemed that it would be of interest to measure its thermal conductivity through a large temperature range. Furthermore, quartz is a good electrical insulator so that whatever theory might be evolved to account for its thermal conductivity would not need to take into account the heat transfer by free electrons.

Since the determination of the surface temperatures is so important it was deemed desirable to have a molten metal in contact with the specimen

[1] C. C. Bidwell. Phys. Rev. **10,** 756 (1917).

[2] A. Eucken Ann. d. Physik **34,** 185 (1911) and Verh. der D. Phys. Gesell. **13,** 829 (1911).

and measure its temperature as near the interface as possible. The specimen was in the form of a hollow cylinder closed hemispherically at one end.[3] It was obtained from the General Electric Company and was quite clear and practically bubble free. There must have been some strains in the specimen before it was used as there were four or five small cracks in it at the start. These did not extend through the wall. The specimen was therefore rapidly heated in an electric furnace to an estimated temperature of 800°C to see whether the cracks would cause further trouble but they did not grow perceptibly. However, several large patches of milky white quartz appeared on the outside. The surface was ground to remove these and make it uniform. Grinding was not necessary for the inside as mere traces of the white showed and the irregularities were slight. It is thought that this white quartz was tridymite which formed rapidly on the surface because of some surface impurity's acting as a flux. The quantities measured to determine the thermal conductivity were: the dimensions of the specimen, the power supplied to the filament and the temperature inside and outside when a steady state was attained.

Apparatus and Procedure

Thermocouples were used for all temperature measurements and especial care was taken to get the difference in readings of the two couples for the same temperature during the calibration.

Fig. 1 is a scale drawing in section which shows the arrangement of the apparatus used for measuring the thermal conductivity in the temperature range from −38°C to + 85°C.[4] The water bath was kept circulating by a pump. The temperature could be varied and controlled by an electric heater. For a temperature of −38°C the apparatus was placed in a large Dewar flask supplied with a slush of carbon dioxide snow and gasoline. The temperature drop from the outside of the specimen to the slush was such that the mercury outside the specimen was frozen while that inside was molten. Inside the specimen a heavy copper rod *C* was used in conjunction with the mercury bath. There was about half a millimeter clearance between the copper rod and the specimen and this space contained mercury. The copper was used because of its high thermal conductivity and because it served as a convenient holder for the heater filament *H* and the copper thermocouple protecting tube *T*. The latter made a snug fit in a groove milled in the copper bar. The thermocouple itself was of No. 28 double cotton covered copper-Advance wire and the junction was swedged into the side of the tube tip so as to be turned toward the surface of the specimen. Thus the tip was not more than a half millimeter from the surface, with mercury intervening. The outside thermocouple tube tip was made similarly and the tube wired to the outside of the specimen. The heater *H* consisted of a No. 22 Chromel wire in a

[3] The radial flow method seems to have been first suggested by C. Niven, Proc. Roy. Soc. **76**, 34 (1905).

[4] It is dangerous to use mercury in the open as high as 85°C because of its toxic vapor but the laboratory was well ventilated and no ill effects were noticed.

porcelain tube. Potential leads of the same material were welded to the current carrying filament at P. The wires above this point were threaded through four-hole porcelain tubing while those below were in two-hole tubing. This unit fitted snugly in a glazed porcelain tube which was wrapped with one layer of cotton tape to make a snug fit in the hole in the copper rod.

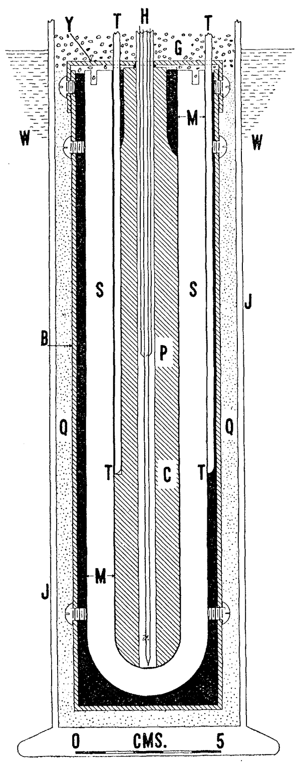

Fig. 1. Apparatus for low temperature measurements. S, specimen; T, thermocouple; P, potential terminals; C, copper bar; M, mercury; Q, sand; J, glass jar; H, heater; Y, yoke; G, ground cork; B, brass cup; W, water bath.

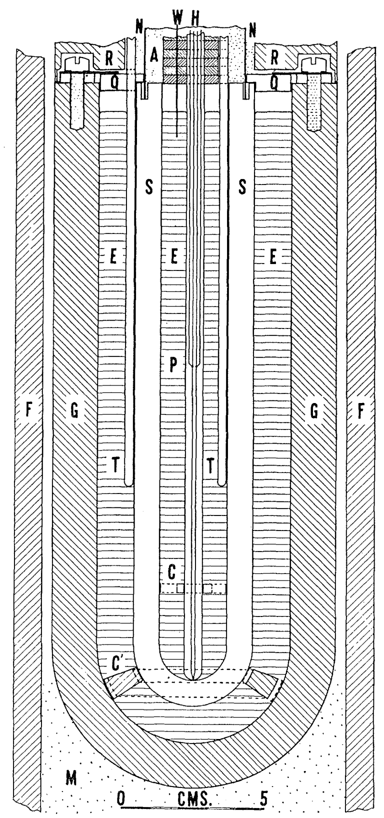

Fig. 2. Apparatus for high temperature measurements. S, specimen; E, alloy; P, potential terminals; T, thermocouple; C-C', centering rings; G, graphite cup; F, furnace wall; M, magnesium oxide; Q, quartz ring; A, Alundum cement; N, nickel cylinder; W, wire; H, heater.

Since the potential leads were taken from P, only the region below this point could be strictly considered as the specimen while the part above served as a thermal guard ring, as it was supplied with the same power per unit length as the lower part. Heat gains or losses not accounted for would thus disturb the radial flow more at the top than at the bottom. The current was measured with an ammeter and the potential difference with a voltmeter.

Fig. 2 shows in section the apparatus for the high temperature work. The thermocouple protecting tubes in this case were translucent fused quartz tubes with half millimeter walls. They were placed 180° apart so as to minimize their interference with the heat flow. The inside thermocouple tube was held in place by two small rings of strip molybdenum which pressed outward forcing it against the specimen. The outside tube was introduced into the metal bath after the apparatus was in the furnace.

A thermal guard ring was considered essential to this type of experiment when carried out in a furnace. This was to distribute the heat radially immediately above the specimen to similate the flow *in* the specimen. Iron discs were mounted on the heater tube and extended about 4.5 cm above the

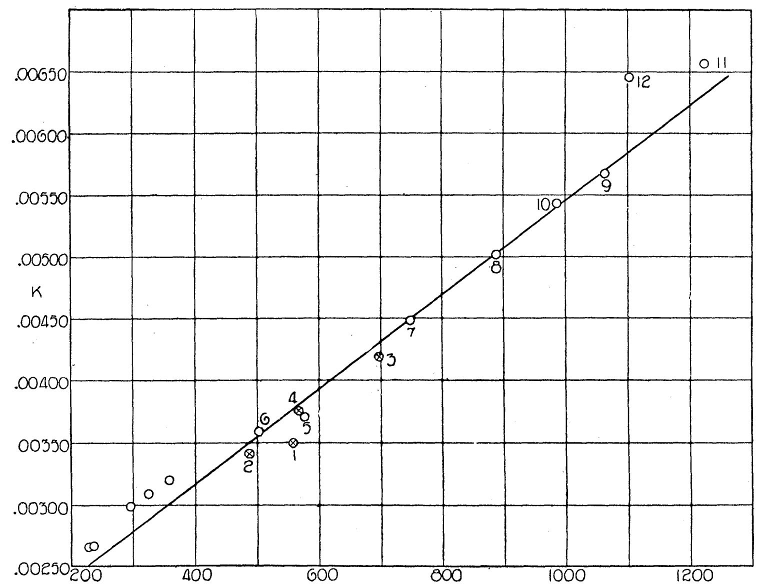

Fig. 3. Curve showing the variation of thermal conductivity with absolute temperature.

specimen. There was thus a good thermal path radially from the heater but a very poor one longitudinally. The dotted region A is the Alundum cement which similates the specimen. R is a graphite ring making poor contact with the lower parts. Another graphite ring resting on this one made the heights of the iron discs and graphite the same. W is a tungsten wire to make electrical connection to the inside of the specimen for electrical conductivity measurements. N is a cylinder of sheet nickel resting in a groove in the fused quartz and extending to the outside of the furnace. It was grounded so as to by-pass leakage currents.

Results

Fig. 3 is a graph of the results on the thermal conductivity K of fused quartz plotted against the absolute temperature. The data below 400°K were taken with the apparatus of Fig. 1. The two low points do not fall on the straight line determined by the other three. This may be due to the difficulty in stirring the slush of carbon dioxide snow and gasoline effectively, or it may be real. Eucken's data show a slight concavity toward the temperature axis in this region but also a concavity upward between 273°K and 373°K. His value at 373° is, however, in doubt. The results here given are about 15 percent lower than those of Eucken and 19 percent higher than those of Barratt.[5] There are more data corroborative of the three upper points but they were omitted for the sake of clarity. Plotted to a much larger scale, there is no systematic deviation from a straight line apparent in this region.

The rest of the datum points are numbered in the order in which they were taken according to the method of Fig. 2. The crossed circles numbered 1, 2, 3, and 4 represent the first run and, being erratic, the apparatus was taken apart to locate the defect. None was definitely found, but Alundum cement was substituted for the powdered magnesium oxide originally in the guard ring and the apparatus reassembled.

If air bubbles were caught at the interface of the metal bath and the specimen, thus increasing the apparent thermal resistance, and if these were being driven off by progressive heating it is easy to account for the lack of consistency in the data of this first run.

There is a slight indication of this on points 5 and 6 of the final run but this source of error was undoubtedly removed at a relatively low temperature. Points 7, 8, 9 and 10 show no systematic deviation from a straight line. Points 11 and 12 are interesting because at about 1143°K fused quartz begins to change to the crystalline form known as tridymite.[6] The furnace was maintained at temperatures in this region for about 24 hours. Long times were, of course, necessary in order to permit the system to settle to a steady state. The total time for the run from point 5 to point 12 was about 72 hours and was continuous. Work done at the Bureau of Standards[7] on the thermal expansion of fused quartz shows that the specimens did not quite return to their original lengths on cooling to room temperature after they had been subjected to temperatures above 1000°C. This seems to give considerable weight to the idea that there is a real change in the structure of fused quartz which affects its thermal conductivity. A fact which may or may not be significant is that Eucken's data on the thermal conductivity of quartz crystal when extrapolated to 1223°K give a value of 0.007 cal./cm. deg. sec. parallel to the optic axis and 0.004 cal./cm. deg. sec. perpendicular to the optic axis; values which are above and below those here given. Rock crystal quartz and tridymite are, of course, different in crystal structure and this comparison may not be justified but the question raised is, Do all forms of SiO_2 have the same thermal conductivity above 1143°K? It is to be noted that Eucken found that the thermal conductivity of crystalline quartz de-

[5] T. Barratt Proc. Phys. Soc. London **27,** 81 (1914–15).

[6] C. N. Fenner Amer. Jour. Sci. **36,** 331 (1913).

[7] W. Souder and P. Hidnert Sci. Papers B. S. No. 524 (1926)

creases with rise in temperature so that $1/K$ plotted against the temperature is practically a straight line.

After this run the apparatus was allowed to cool and the metal bath to freeze. It was later raised to a moderate temperature to get a check point but unfortunately the heater filament burned out. The apparatus was taken apart and it was then discovered that the specimen had broken into a number of pieces which seemed to have actually separated from one another only when all external constraint was removed. The inside thermocouple tube and the fused quartz heater filament tube were also broken into small pieces. The most logical explanation of this seems to be along two lines: first, the quartz was weakened because of the high temperature heat treatment and so could not stand the strains due to differential expansion between it and the metal when the apparatus was raised from room temperature to the eutectic melting point and second, the metal had come into very intimate contact with the quartz. When some of it was pulled from the broken pieces, in some cases quartz came off with the metal. It was comparatively easy to remove the metal from the specimen after earlier unsuccessful attempts to assemble the apparatus when the temperature had not been high. The specimen and tubes certainly did not break during the run on which the data were taken because a stiff wire was thrust into the inside thermocouple tube to feel for possible cracks before introducing the thermocouple itself. The break must have occurred during the frozen state prior to attempting a check point or when the apparatus was heated to take it apart. Points 11 and 12 could not have been due to the cracking of the specimen as this would have been accompanied by an apparent decrease in the conductivity.

The data were computed from the formula[9]

$$W=\left\{\frac{4.19\cdot 2\pi r_1 r_2}{r_2-r_1}+\frac{4.19\cdot 2\pi L}{\log_\epsilon r_2/r_1}\right\}K(T_2-T_1)$$

where W is the watts input on the filament below the potential terminals, 4.19 the number of joules in a calorie, r_1 the inside radius of the specimen, r_2 the outside radius, L the length of the cylindrical part below the potential terminals, K the thermal conductivity and T_2-T_1 the temperature difference between thermocouples. The inside radius was computed by weighing the mercury required to fill the specimen, measuring its depth and taking the density of mercury into account. The outside radius is the mean of several measurements taken with calipers. In the above formula the first term of the sum accounts for the flow through the hemispherical end and the second through the cylinder.

The power supplied to the filament was of the order of 10 watts: 5 amperes, with 2 volts between the potential terminals. It was measured to better than 1 percent and fluctuations were negligible. The power was supplied by a 55 volt circuit, with suitable resistance, from a 110 volt direct current generator.

[9] See for example Preston's "Theory of Heat" or Ingersoll and Zobel's "Mathematical Theory of Heat Conduction."

The temperature difference maintained between the inside and outside of the specimen was of the order of 10°C. Since the thermoelectric power of copper against constantan is about 40 microvolts per degree and readings could be estimated to the nearest microvolt, the error in temperature measurement for one reading may have amounted to 0.5 percent. This applies to the apparatus of Fig. 1. Although mercury is only five times as good a conductor as fused quartz the error due to the distance of the tip of the couple from the surface must have been very small as the outside one touched the surface and the inside one protruded a little from the copper rod. Readings were taken for a period of fifteen to thirty minutes as this was found ample for reproducible results.

The error in reading temperature differences at the higher temperatures with the noble metal couples would be about 2 percent since the thermoelectric power is 10 microvolts per degree. At very high temperatures it was not possible to attain the steady state in the strict sense as there were temperature difference fluctuations amounting to 3 percent and occasionally even more. These were probably due to circulation in the metal bath. Accordingly, readings were taken for more than an hour and averaged for a datum.

If the thermal conductivity of the tin-lead eutectic is assumed to be the mean of the values of the components it is from ten to twenty times as good a conductor as fused quartz, depending on the temperature of the latter. Thus with the thermocouples themselves about 1.5 mm from the surface the computed values of the thermal conductivity are about 3 percent low. This is in a direction to account for part of the discrepancy between the high and low temperature work. The absolute accuracy of the results is estimated as ± 5 percent and the precision as ± 1 percent No correction could be made for the energy transfer through the specimen by radiation because of the lack of data on the emissivity of the surfaces and the absorption of fused quartz in the infrared as a function of its temperature. A separation between the energy transfer due to conduction and radiation could be effected if several different power inputs were used at the same average specimen temperature. The equation $K = 3.83 \times 10^{-6} T + 0.00163$ expresses the relation between the thermal conductivity of fused quartz and the absolute temperature. Compton's assumption[10] of the linear increase in thermal conductivity with tempeiature for amorphous materials on the basis of Eucken's work is further justified by these results.

Electrical Conductivity

Fig. 4 is a diagrammatic sketch of the apparatus used for measuring the electrical resistance of the specimen. Considering R_1 as a source of electromotive force e, the equation $e/R_M = E_2/R_s$ applies to this circuit, neglecting small resistances. It is to be noted that the guard ring effectively by-passes leakage currents back to the battery by way of the ground without influencing the galvanometer. Insulators as well as a piece of copper foil

[10] A. H. Compton Phys. Rev. 7, 341 (1916).

between the glass tubes containing the thermocouple cold junctions were also grounded for the same purpose. The connection to the inside of the specimen was made with a wire entering the metal bath (Fig. 2) and the outside connection was made to the graphite cup. The advantages of this method are that it is a null method so that the sensitivity of the galvanometer need not be accurately known and the potential applied to the specimen may be kept at a definite known value over a wide range of values of its resistance.

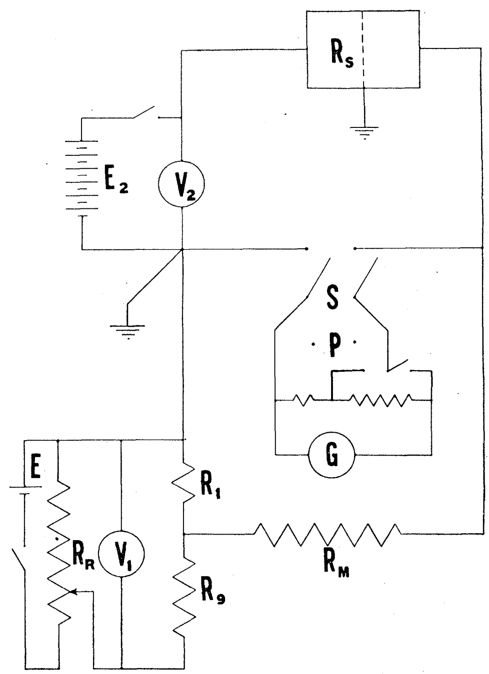

Fig. 4. Circuit for measuring resistance. R_S, specimen; E_2, battery; V_2, voltmeter; S, switch; P, potentiometer terminals; G, galvanometer; E_1, dry cell; R_R, slide rheostat; V_1, voltmeter; R_1, 1 ohm; R_9 9, 99 or 999 ohms; R_M, megohm box.

Results

The results of the measurements on the resistance of fused quartz are given in Fig. 5. The logarithm to the base 10 of the specific resistance ρ is plotted against the reciprocal of the absolute temperature. The upper curve is from data due to Horton[11] included for comparison. The large double circles are all the data that were obtained when the apparatus of Fig. 2 was in use. One of the leads burned out before the entire run for the thermal conductivity was completed so but few data were obtained. The results are erratic but no check could be made by this method because of the failure of the specimen, already discussed. Accordingly, a piece of the original specimen was ground into a shape of practically square cross section (0.674×0.686 cm) and 3.7 cm long. Fine nickel wire was wrapped around both ends in notches and the

[11] F. Horton Phil. Mag. **11**, 505 (1906)

short free ends inserted in small holes ground in the ends. These nickel terminals were secured near the notches and in the holes with Alundum cement, which is a much better conductor than fused quartz. This scheme of connections made a close approximation to metallic plate terminals on the ends of a specimen about 3.3 cm long. The nickel leads were threaded through porcelain tubes which were wired to the sheet nickel lining of a small electric resistance furnace. This lining was grounded and was equivalent to grounding the insulation, as well as giving protection against possible leakage currents from the furnace winding. Baffle plates were introduced above and below the specimen, and a thermocouple, used in the earlier work, protruded into this space to determine the temperature.

The apparatus just described was used in taking all the remaining data. The small open circles represent data taken with a potential of 68 volts applied to the specimen all the time and always in the same direction. The curve was drawn on the basis of these results. The crossed circles were

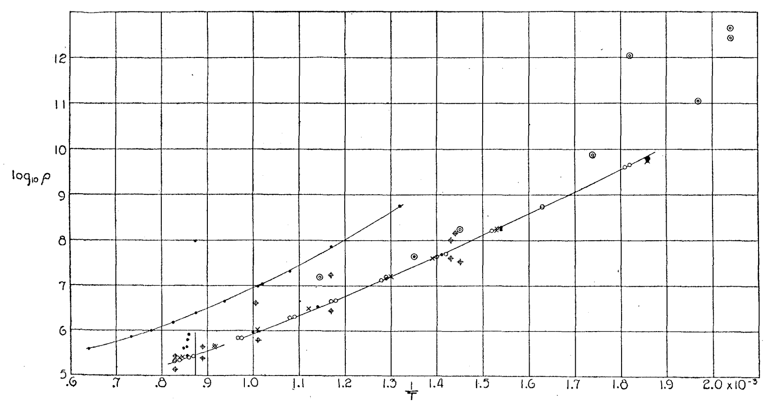

Fig. 5. Curve showing the variation of the logarithm of the specific resistance with the reciprocal of the absolute temperature.

obtained when a potential of 1.45 volts was applied. This voltage was on "direct" to get a reading, then reversed and another reading taken as soon as a balance could be obtained (within 2 minutes). This scheme meant that the potential was on "direct" for from 15 to 30 minutes, a reading taken, then a "reverse" reading taken quickly and the potential changed to "direct" for a period of time for the next reading, and so on. The points above the curve are due to "direct" readings and those below to "reverse." It is interesting to note that below 1000°–1100°K the difference between "direct" and "reverse" readings is definitely greater than at higher temperatures. The short vertical line on Fig. 5 is drawn at 1143°K, the temperature previously noted as a transformation temperature for fused quartz. Other data were also taken in the same manner with a potential of 68 volts applied. The difference effect was small (around 10 percent) at low temperatures but increased to about the same values as in the case just cited, above the 1100°K region. These results have been omitted from the graph to avoid confusion in reading it. The solid black circles represent data taken with a potential of 68 volts applied to the specimen. "Direct" and "reverse" readings were obtained and from 10 to 20 minutes allowed before every reading so as to have steady conditions, i.e., eliminate the difference between "direct" and "reverse" readings. Above 1143°K an hour was not a sufficient time for the potential to be applied in one direction to obtain the same reading that had been obtained in the opposite direction. These results do not lend themselves readily to a simple interpretation but the manner in which the resistance depends upon the time during which the potential has been applied in a given direction and also upon the absolute value of this potential points toward the existence of both dielectric and electrolytic polarization. The difference effect is greatest with small potentials applied. A small constant electrolytic e.m.f. would make large percentage errors in resistance measurements made with low potentials and small errors with large potentials. The variation of resistance with time is characteristic of dielectric polarization. Probably

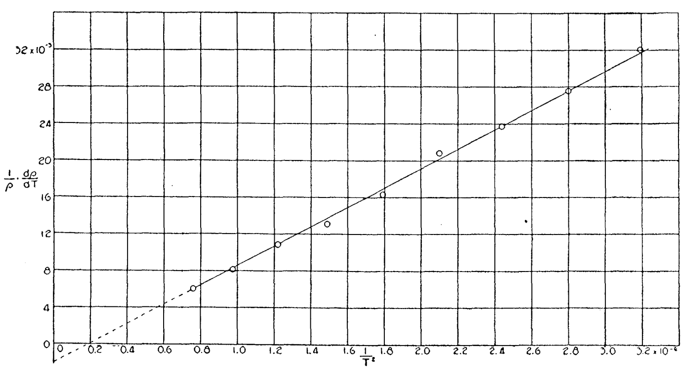

Fig. 6. Verification of the resistance formula calling for a linear relation between $-d\rho/\rho dT$ and $1/T^2$.

both types of e.m.f. depend upon the temperature and the vicinity of 1143°K is particularly significant.

To see whether or not heat treatment had any effect on fused quartz with respect to this property or any other, the furnace was maintained at a temperature a little above 1143°K for 18 hours with no potential applied. Another run was then taken (indicated by the crosses) in a manner similar to the previous one but the peculiar effect above 1143°K was not observed. It is interesting to note, however, that a curve drawn with the crosses as a basis would be slightly above the one given at high temperatures and slightly below at the lower temperatures, indicating a heat treatment effect. This change of slope means that Q decreases with heat treatment. (See below for significance of Q.) The effect was small but there seemed to be no experimental difficulties to invalidate the results.

The curve of Fig. 6 was plotted from interpolated data taken from the curve of Fig. 5 because of the convenient relations obtainable from C. C.

Bidwell's[12] modification of Königsberger's formula for the resistance-temperature relation of poorly conducting substances. This formula is: $\rho = A\epsilon^{(Q/R+aT)}$. It may be written:

$$\log_{10}\rho = 0.434(Q/RT+aT)+\log_{10}A$$

The curve of Fig. 5 shows that a is an appreciable quantity, as this curve is not a straight line. By differentiation the second equation becomes $-d\rho/\rho dT = Q/RT^2 - a$ so that the straight line obtained in Fig. 6 is a verification of the first equation. a has the value of $+2\times10^{-3}$ and Q/R is 1.05×10^4. Since R, the gas constant, is 1.98, i.e., $8.3\times10^7/4.2\times10^7$, Q is found to be 2.08×10^4 calories per gram atom of the metallic element in the oxide. Q is the heat required to liberate one electron from each atom in a gram-atom. Königsberger gives 2×10^4 for this quantity.

The following are results interpolated from the curve drawn:

Temperature (degrees absolute):	550	750	950	1150
Specific Resistance (ohms/cm³):	4.46×10^9	2.09×10^7	1.35×10^6	2.69×10^5

Acknowledgment is gratefully made of the kindly and helpful suggestions of Professor E. Merritt and Professor C. C. Bidwell in the course of this work. The problem was suggested by Professor Bidwell.

Rockefeller Hall,
Cornell University,
May, 1927.

[12] C. C. Bidwell Phys. Rev. **8,** 12 (1916).

It was not until the present investigation was nearing completion that the recent work on the thermal conductivity of fused quartz by G. W. C. Kaye and W. F. Higgins was noticed. This is outlined in Science Abstracts "A" No. 352 p. 299. The original paper is in Roy. Soc. Proc. 113. p. 335, Dec. 1, 1926. They obtained a straight line relation between the conductivity and temperature with a value of .00330 c.g.s. units at 333°K and .00364 at 513°K. The absolute values agree well with the data of Fig. 3 but the rate of increase of the conductivity is only about one half that obtained in this work. The fact that the results here given are for a temperature range of about 1000° and involved two different arrangements gives weight to the larger value of the slope although the thermal history of a specimen of fused quartz may be a very important factor in determining any property as a function of temperature.