# DENSITIES OF MOLTEN ROCKS AND MINERALS.*

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ABSTRACT. Density and thermal expansion have been determined for liquid synthetic diopside and akermanite and for natural bytownite and diabase by measuring the loss of weight of a platinum ball when submerged in the fused minerals. The results for diabase are compared with those of other observers. No determinations have been made heretofore upon the pure minerals. Rough values of the surface tensions are included.

## INTRODUCTION.

RELIABLE values for the density of rocks and minerals at temperatures above their melting points would be useful in a variety of geophysical and geochemical problems. The few measurements which have been published are not in satisfactory agreement. Two methods have been used: the first, adopted by Barus[1] and by Wolarowitsch and Leontjewa,[2] consists in the observation of the changes in level of the surface of molten material contained in a narrow platinum tube. Although the legitimate application of this method would seem to be restricted to the determination of the density and thermal expansion of molten material, it was utilized by Barus in a pioneer attempt to find directly the difference in density between vitreous diabase and crystalline diabase. The second method, adopted by Day, Sosman, and Hostetter,[3] consists in determining the buoyancy, as a function of temperature, of a given mass of material submerged in a bath of liquid tin or silver, whose expansion is already known. This method is applicable to the crystalline as well as the vitreous state, and yielded, among other important results, the change in volume of a sample of Palisades diabase on passing from the crystalline to the molten condition. The change in specific volume on melting was found to be significantly greater than the difference in specific volumes of glassy and crystalline Palisades diabase at room temperature (9.9 per cent at 1200° C., 7.2 per cent at room temperature); and there is no reason for supposing that other materials may not show still greater differences.

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A third method has been adopted for the work which is to be described below: the density and thermal expansion of certain molten silicates are determined from the loss of weight of a platinum mass of known volume when submerged in the liquid of unknown density. The use of this method is necessarily restricted to melts of relatively low viscosity; it gives no information concerning the crystalline state. The thermal expansion of the crystalline minerals from which these melts were made have been given[4] up to 1000° C.; short extrapolation of these data leads to fairly reliable estimates of the densities of the crystals at the melting point, and of the change in volume on melting.

The selection of material for this work was guided by the following considerations: the melt should have a viscosity not exceeding $10^3$ in the accessible temperature interval (less than 1550° C.); the melt should not react chemically with platinum nor with the air; the material should have a definite, known composition. These conditions excluded iron-bearing compounds, feldspars with more than 30 per cent albite, and minerals melting at temperatures above 1550° C. Pure synthetic diopside and akermanite were specially prepared for this work through the kindness of Dr. J. F. Schairer of the Geophysical Laboratory. A very pure natural bytownite was obtained from the collection of the Department of Mineralogy of Harvard University. For the purpose of comparison with the work of other experimenters, a sample of diabase from Vinal Haven, Maine, was also included, although it did not satisfy the requirement of chemical stability given above. Attempts were also made to measure more siliceous materials; but they failed because their high viscosity prevented the elimination of all bubbles. Improvements in technique may permit future measurements with other important minerals.

### *Apparatus and Procedure.*

The necessary volume of the platinum bob determined the size of the balance, crucible, and furnace, which, with a thermocouple, made up the rest of the apparatus. Because of the high surface tension of molten glasses, it was decided that a volume of about 1 cm.$^3$ would be the minimum that could give accurate results. The bob actually used had a weight of about 19 grams, with a volume of 0.88 cm.$^3$ at room temperature. It had the shape of a short cylinder with hemispherical ends; a

platinum suspension wire was welded to a small projection at the top. With this volume, a 50-gram analytical balance proved amply sensitive. In order to avoid excessive viscous damping, a 40-cm.$^3$ platinum crucible was used to hold the glass. The height and diameter of this crucible were 42 mm., leaving a reasonably large clear space about the bob when it was centered in the melt. The problem of heating so large a crucible to over 1500° C. by means of a platinum-wound furnace presented certain difficulties; the method of construction finally evolved may be of some interest.

The original furnace was of conventional design, with an inner tubular core of alundum, 6.2 cm. in diameter, wound externally with a platinum-rhodium alloy, and a concentric outer core, 14 cm. in diameter, wound with nichrome. This type of furnace failed repeatedly by melting of one or both windings before the crucible reached 1500° C.

A satisfactory furnace was finally constructed with windings on the inside of hemispherical shells. The inner shell, with an internal radius of 3 cm., carried 24 feet of No. 22 wire. To make the shells, the wire was wound between small brads driven into hemispherical wooden forms; and then covered with alundum cement. After a day, the nails could be safely removed, and after five days, the form was taken out. Except for 12-mm. holes at the top and bottom for the introduction of the bob and thermocouple, the crucible was completely surrounded by the heating element; the temperature in the crucible was uniform to within 1° C. The outer core was made in the same way, with a radius of 10 cm. A larger hole was left in the upper hemisphere, through which the upper half of the inner core and the crucible could be removed. When the furnace and charge were assembled, this space was filled with refractory material except for a tubular opening, 12 mm. in diameter, running vertically upward from the crucible. Powdered magnesia filled the space between the cores, and also to about 5 cm. beyond the outer core. Outside of this was rock wool, to fill the remaining space in a large galvanized can. With this arrangement, the power consumption at 1530° C. was about 400 watts for the inner winding, plus 450 watts for the outer winding. This furnace ran continuously for several days at temperatures above 1530° C., and for weeks above 1450° C.

The temperature was measured with a LeChatelier thermocouple, whose hot junction was in contact with the bottom of

the crucible. Couples were calibrated at the melting points of the synthetic minerals (diopside, 1391°, akermanite, 1458°).

The bob and its supporting wire were let down through the opening in the top of the furnace; vertical adjustments were accomplished by means of a turnbuckle, while horizontal adjustments could be made by moving the balance. The suspended system was shielded from air currents by a wooden casing around the wire, nearly closed at the bottom, and reaching almost to the furnace. The weight on the suspension wire, with the bob immersed in the melt, was still about 17 grams. At the higher temperatures, a wire 0.627 mm. in diameter was required, smaller wires proving too weak. With a wire of this size, an appreciable correction is required for the effect of surface tension. This effect was determined by measuring the pull exerted by the glass on plain wires, without bob, when their ends just touched the surface of the melt. The forces on wires of from 0.56 to 2.0 mm. in circumference ran from 16 to 60 mg.; the correction to the measurement of the density of the glass amounted to about 2 per cent, and was known with an accuracy of perhaps 5 per cent of itself.

The sensitivity of the weighing with the bob submerged in a melt depended primarily upon the viscosity of the glass. Thus with materials of low viscosity, such as NaCl and $B_2O_3$, which were used as reference materials, weighings could be made to 0.1 mg., corresponding to about 0.01 per cent on the density. With very viscous melts, such as feldspars, the motion of the balance became impractically slow. Melts of high viscosity cannot, moreover, readily be freed of air-bubbles, whose presence evidently reduces the value of the results. Thus, while readings could be obtained with such materials as obsidian and labradorite, these readings depended upon the length of time of heating and were not considered reliable. The presence of bubbles could usually be detected without difficulty by examination of a small sample brought up on a wire probe. The principal criterion for the present purpose was reproducibility of results on heating and cooling. A clear correlation existed between the presence of visible bubbles and failure to obtain repeatable results. It is not claimed that all gas was eliminated from the melts, but the amount that remained must have been relatively insensitive to changes of temperature or have had little effect upon the density.

The reported densities and thermal expansions depend upon

the thermal expansion of platinum; this was taken from Jaeger,[5] in the form,

$$V_t = V_o\ (1 + 0.26604 \times 10^{-4} t + 0.3972 \times 10^{-8}\ t^2)$$

where t is the centigrade temperature. Holborn and Day[6] give results in close agreement with Jaeger's. The change of volume of the bob is thus about 3 per cent between 0° and 1000°. Aside from small corrections, the density of the glass is computed from the expression

$$\delta_G = (M - m_t)/V_t,$$

where M is the mass of the bob, m its apparent mass when submerged in the glass, at the temperature t, $V_t$ the volume of the bob, as computed above. The volume $V_o$ was found by weighing the bob in air and in water or toluene. No operations other than weighing are required.

## *Results.*

In order to have a few results for materials that have already been studied with some precision, runs were made with NaCl and with $B_2O_3$. The density of NaCl at two temperatures, with the comparable measurements of other observers, are shown in Table 1. The present values fall closest to those of Hanlein, whose work is the most recent.

TABLE 1.

Density of NaCl. (gm./cm.$^3$).

| Observer | Temperature 900° C. | 1100° C. |
|---|---|---|
| Borneman and Sauerwald[7] | 1.527 | 1.422 |
| Hanlein[8] | 1.499 | 1.392 |
| Jaeger[9] | 1.487 | 1.361 |
| Dane | 1.495 | 1.400 |

The salt used in the present work was Mallinckrodt's Analytical grade, stated to contain less than 0.027 per cent total impurity. While this is not equal in purity to the material used by the other investigators, it seems unlikely that the large differences are to be accounted for in this way.

For $B_2O_3$, the density at 1000° C. is 1.516; Wolarowitsch and Leontjewa[10] give 1.447, with a curve of specific volume very

nearly parallel with the present one, which is shown in Fig. 1. Differences in residual water content perhaps account for the lack of agreement.

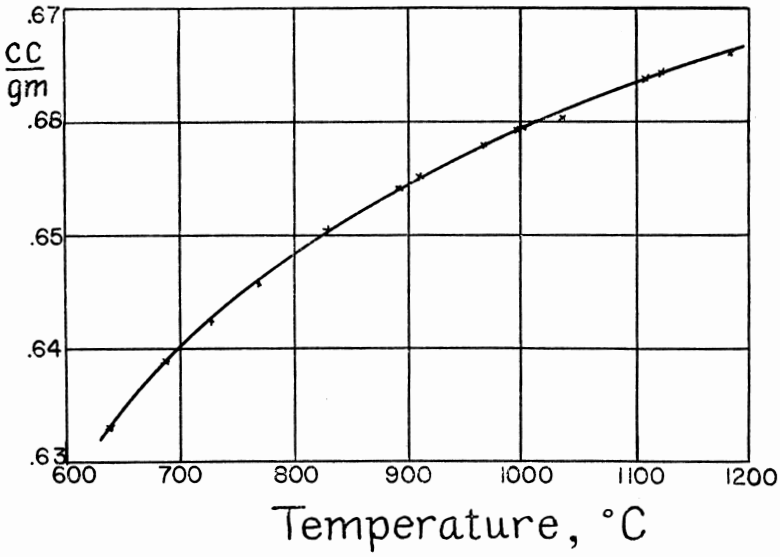


FIG. 1. Specific Volume of Boric Anhydride. Cubic centimeters per gram.

The new results for the minerals are shown in Table 2, together with certain values obtained by combining these measurements with data on the thermal expansion of the crystalline materials.

The differences in density were computed as the density of the crystal minus that of the glass, divided by the density of the crystal. The akermanite is unusual in that the density of the glass appears to be greater than that of the crystal, at 20°. Unfortunately, its expansion in the crystalline state has not been measured to high temperatures. The diabase has no definite melting point; 1250° is merely the temperature at which the density is given. The expansion of this rock in the crystalline state was computed from the weighted average of its constituents, the expansions of which have been measured by Kozu. The result agrees well with the measured value for the Palisades diabase.

From room temperature to the melting point, the vitreous Vinal Haven diabase shows a somewhat smaller expansion than

TABLE 2.

High Temperature Densities of Minerals.

| | Diabase Vinal Haven | Diopside Synthetic | Akermanite Synthetic | Bytownite Norway $Ab_{30}An_{70}$ |
|---|---|---|---|---|
| Density of crystal, 20° C. | 2.969 | 3.265 | 2.94 | 2.71 |
| Density of glass, 20° C. | 2.78 | 2.846 | 2.95 | 2.61 |
| Difference of density at 20°, per cent | 6.5 | 12.9 | —0.4 | 3.7 |
| Melting point, °C. | (1250) | 1391 | 1458 | 1480 |
| Computed density of the crystal at M. P. | 2.89 | 3.14 | | 2.63 |
| Density of glass at M. P. | 2.64 | 2.671 | 2.724 | 2.519 |
| Decrease of density on melting, per cent | 8.6 | 14.9 | | 4.2 |
| Volumetric thermal expansion of the glass at M. P. | $38 \times 10^{-6}$ | $64 \times 10^{-6}$ | $56 \times 10^{-6}$ | $56 \times 10^{-6}$ |
| Surface tension of glass in dynes per cm. | 345 | 280 | 360 | 220 |

the Palisades diabase of Day, Sosman, and Hostetter. Above 1250° the difference is much greater. However, in their text, Day, Sosman and Hostetter make a downward correction of the high temperature density, because of the formation of CO by reaction of the graphite crucible on the iron minerals of the rock. It is probable that their expansion is also too high, as this gas would form more and more rapidly with increasing temperature. The present result is in good agreement with that of Barus, viz., $44 \times 10^{-6}$, for a similar diabase. Wolarowitsch and Leontjewa obtained a comparable figure for the expansion of a basalt glass of nearly the same composition as the Vinal Haven diabase. However, their values for some diabase glasses are very much higher. As is shown in Table 3, the composition of their diabases is rather different from that of the Vinal Haven and Palisades rocks. However, it seems doubtful if this difference is great enough to account for variations in expansion between 38 and $300 \times 10^{-6}$.

TABLE 3.

Composition of Diabases.

| | Vinal Haven diabase | Palisades diabase 1 | Palisades diabase 2 | Olonetz diabase | Transcaucasian basalt |
|---|---|---|---|---|---|
| $SiO_2$ ..... | 48.24 | 50.4 | 51.46 | 51.63 | 49.03 |
| $TiO_2$ ..... | .82 | | | 1.98 | .57 |
| $Al_2O_3$ ..... | 18.12 | 15.6 | 13.98 | 12.96 | 19.25 |
| $Fe_2O_3$ ..... | 1.25 | 3.65 | 2.66 | 4.01 | 1.46 |
| FeO ..... | 6.70 | 6.30 | 8.92 | 11.97 | 7.68 |
| MgO ..... | 9.41 | 6.08 | 7.49 | 4.56 | 8.84 |
| CaO ..... | 11.84 | 10.41 | 10.49 | 8.54 | 9.61 |
| $Na_2O$ .... | 2.56 | 2.57 | – | 2.75 | .84 |
| $K_2O$ ..... | .26 | .62 | 4.75 | 1.34 | .38 |
| $H_2O$ ..... | .66 | 2.69 | | | .75 |

Figure 2 shows the specific volume at high temperature for various rock and mineral glasses. All the materials studied here show straight-line relations between volume and temperature over the interval measured. The irregularities associated with change of state found by other investigators do not show up, because the present glasses were all heated well above the melting point to remove bubbles before measurements were started. All these glasses supercooled enough so that no crystallization was observed in the interval studied; but all except the feldspar crystallized completely within the next hundred degrees if allowed to cool with the furnace.

The change of density or of specific volume on melting are quantities that play an important rôle in theories of the thermal history of the earth. For single-component systems, the rate of change of melting point with pressure is given by Clapeyron's equation,

$$\Delta T/\Delta P = T\Delta V/L$$

where $\Delta T$ is the change of melting temperature produced by a change of pressure $\Delta P$, T is the absolute melting temperature, L the latent heat per gram, and $\Delta V$ the change of specific volume on melting. This formula has been applied to the present materials, with the results shown in Table 4. The figures for albite, included for comparison, are taken from Goranson[11].

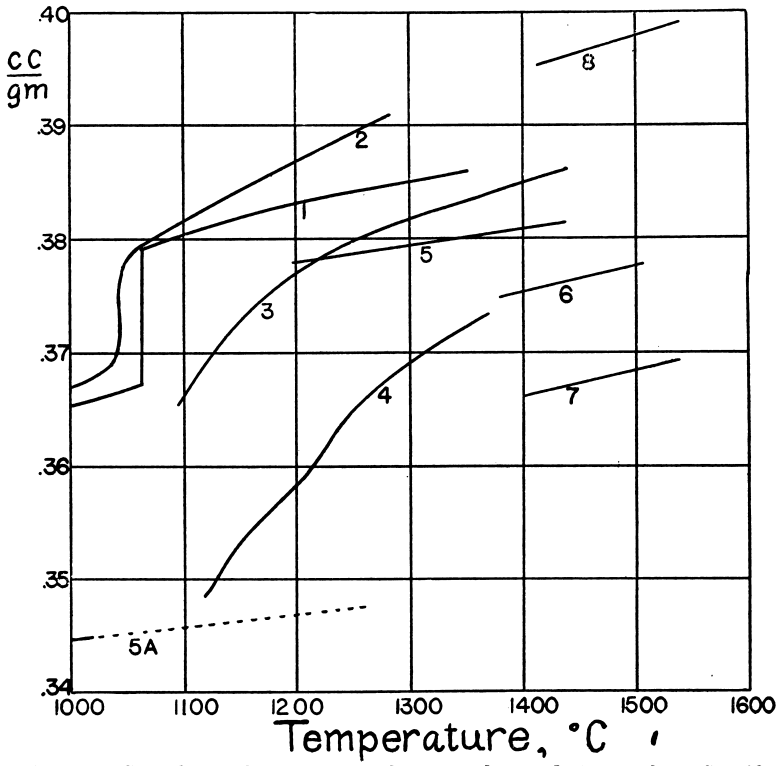


FIG. 2. Specific Volumes of Molten Rocks and Minerals. Specific Volumes in cubic centimeters per gram of: 1, Barus diabase; 2, Palisades diabase; 3, Transcaucasian basalt; 4, Olonetz diabase; 5, Vinal Haven diabase; 5A, crystalline Vinal Haven diabase; 6, Diopside; 7, Akermanite; 8, Plagioclase ($Ab_{30}An_{70}$).

TABLE 4.

Effect of Pressure on Melting Point.

| Material | T °abs. | L kg.cm./gm. | ΔV cm.³/gm. | ΔT/ΔP °C. per 1000 kg./cm.² | ΔT/Δx °C. per km. |
|---|---|---|---|---|---|
| Diopside ..... | 1664 | 4390 | 0.056 | 21.2 | 5.9 |
| Bytownite ..... | 1753 | 3770 | .017 | 7.9 | 2.2 |
| Diabase ..... | 1523 | 4260 | .033 | 11.6 | 3.3 |
| Albite ..... | 1388 | 2070 | .039 | 26 | 7.3 |

In its simple form, Clapeyron's equation is strictly valid only for the diopside and albite; it probably gives an approximately correct result for the bytownite. Its application to such a complex system as diabase is of questionable value; T is a

somewhat arbitrary temperature, here taken as 1250° C.; $\Delta V$ and L refer to an interval of temperature of at least 100°. The computed $\Delta T/\Delta P$ is, however, not unreasonable, falling between the values for diopside and for bytownite.

In the last column of Table 4 are given values for the rate of increase of melting temperature with "depth" in a layer of material having a density of 2.8, the pressure at depth x being supposed to equal the weight of the column of this material x km. deep. The use of such values to define the change of melting point with depth in the primitive magma, or even the present crust, would be difficult to justify. Goranson has shown that in the presence of water, the initial change of melting temperature of albite with pressure is at the rate, not of +26° per 1000 kg./cm.,$^2$ but of −402° per 1000 kg./cm.$^2$ As the pressure increases, the absolute value of the rate of decrease of melting temperature with pressure decreases; it is likely that $\Delta T/\Delta P$ eventually becomes positive, but there seem to be few, if any, natural circumstances where the use of the coefficients determined for the "dry" minerals is appropriate.

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