

THERMAL ANALYSIS OF QUARTZ AND ITS USE IN CALIBRATION IN THERMAL ANALYSIS STUDIES*

GEORGE T. FAUST, *U. S. Geological Survey, Washington, D. C.*

ABSTRACT

The character of the thermal analysis diagram of quartz is interpreted in terms of the latent heat of inversion from the low to high form of quartz and of the change in heat capacity (specific heat) accompanying the polymorphic transformation.

The sharpness of the thermal peak accompanying the inversion of quartz from the low to the high temperature form and its reproducibility make it an ideal means of calibrating thermal analysis apparatus.

The use of the inversion of quartz from the low to the high temperature form is here proposed as a fixed point for calibrating the temperature-thermocouple in thermal analysis apparatus. A series of thermal analysis diagrams are given in this paper for quartz of various grain sizes and of different paragenetic histories.

APPARATUS

The differential thermal analysis apparatus in use in the Section of Geochemistry and Petrology of the U. S. Geological Survey is similar to the one developed by Hendricks and Nelson (1939) at the Department of Agriculture. This apparatus is of the dynamic type, that is, the temperature of the furnace and of the sample being studied is continuously changed. In this study the temperature was changed at the rate of 15° C. per minute. The temperature of the reaction chamber in the furnace is measured by means of a chromel:alumel thermocouple. The magnitude of the thermal effects such as inversion, dissociation or other reactions is measured by means of a platinum:platinum 90 per cent-rhodium 10 per cent differential thermocouple.

The reaction chamber is a nickel block containing three holes, two of which are of equal size and volume and adjacent to one another. These holes, or cells, are filled respectively with a thermally neutral substance, fused alumina, and the unknown sample to be tested. The two junctions of the differential thermocouple are centered in these cells. The third hole is perpendicular to the aforementioned cells and approximately between them. It is of smaller size. The hot-junction of the chromel:alumel thermocouple is inserted here.

The thermocouple used to measure the temperature of the reaction chamber was originally calibrated by the following indirect method. The deflection of a galvanometer is directly proportional to the electromotive force impressed across its terminals. The magnitude of the potential dif-

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ference developed by a chromel:alumel thermocouple as given by Roeser, Dahl and Gowens (1935) is 0.60 millivolts at 15° C. and 41.31 millivolts at 1,000° C. Accordingly, various potential differences ranging from 0.60 millivolts to 41.31 millivolts were impressed across the terminals of the galvanometer and the corresponding deflection of the galvanometer was recorded optically on photographic paper. A chart was then constructed relating the deflection of the galvanometer to the millivoltage across its terminals. The substitution of temperatures for the equivalent millivolts of chromel:alumel thermocouples gives a deflection-temperature graph.

The above calibration assumes that all chromel:alumel thermocouples develop and reproduce the same potential difference at the same temperature. According to Roeser, Dahl and Gowens (1935) the manufacturers guarantee that these thermocouples will give values within the following limits, $\pm 5^\circ$ F. (3° C.) in the range 32° to 660° F. and to $\pm \frac{3}{4}$ per cent between 660° and 2,300° F. The thermocouples tested by Roeser, Dahl and Gowens fell within these limits. Within the limits of accuracy of routine thermal analysis, especially where the minerals are of the same type, the above assumptions are acceptable. In more precise work, or for those minerals which give off corrosive vapors, frequent calibration is necessary.

The direct method of using the inversion temperature of quartz as proposed here is simple, reproducible and requires no special electrical equipment as is used in the indirect calibration. Moreover, each thermocouple may be calibrated and recalibrated whenever desired.

The use of the inversion of quartz as a base point on the thermometric scale was advocated by Bates and Phelps (1927) of the National Bureau of Standards, who state on page 315:

Specimens of quartz from sources widely distributed geographically were studied and the temperature at which the inversion starts on heating found to be identical (573.3° C.). This is found to be a fixed and definite temperature occurring with great sharpness and suitable for a new type of base point on the thermometric scale, as well as for the standardization and checking of thermocouples in the average physical laboratory.

The observations of many workers, using various techniques, agree in the constancy of the inversion temperature. A single observation on one sample, by Fenner (1913), gave a lower inversion temperature. This material is of questionable homogeneity and Fenner assumes that the low result is probably due to solid solution. This indicates that when clear quartz crystals, from localities known to yield pure specimens, are used there need be little concern over this anomalous result.

THERMAL ANALYSIS OF QUARTZ

Some typical quartz thermal analysis patterns are given in Fig. 1. Thermal-analysis curves show that up to the inversion point of quartz

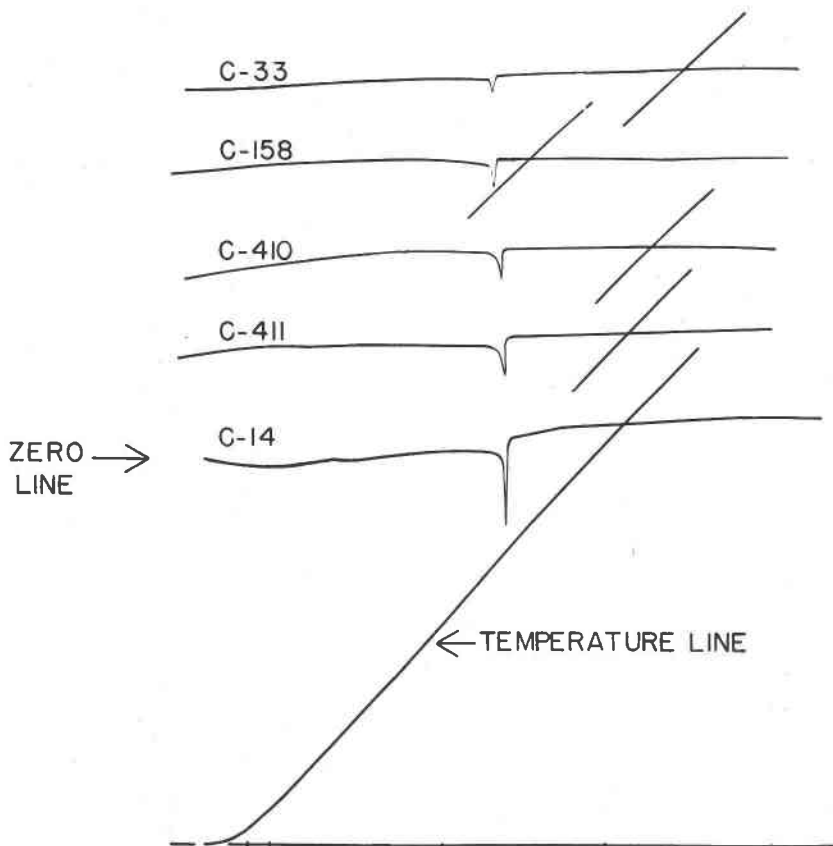


FIG. 1. Typical Thermal Analysis Curves of Quartz.

- C-33 Quartz, var:—rock crystal, Hot Springs, Arkansas, 0.53 grams, —58 mesh, 600 ohms resistance with differential thermocouple.
- C-158 Same as above, except sample weight 0.49 grams, 600 ohms resistance.
- C-410 Quartz crystals, Valles Mountain, New Mexico. These crystals are pseudomorphs after high quartz. These crystals were taken through the high-low inversion three times before the curve was made. Sample weight 0.60 grams; crystals, 2 mm. in diameter, 600 ohms resistance.
- C-411 Quartz, var:—novaculite powder, Hot Springs, Arkansas, 0.62 grams, —25 microns, 600 ohms resistance.
- C-14 Quartz, var:—rock crystal, Hot Springs, Arkansas, —58 mesh, 150 ohms resistance with differential thermocouple.

the curve is essentially a straight line. After inversion is complete, the curve again becomes straight.

The height of the straight portion of the curve of high quartz is always displaced above that of low quartz. This is presumably caused by the change in the specific heat accompanying the inversion. Wietzel (1921) has measured the mean specific heat (mean heat capacity) at the inversion temperature 573° C. and found that the low modification has a mean heat capacity of 248.2×10^{-3} (in 20° -gram calories per degree centigrade) whereas the high modification of quartz has a mean heat capacity of 252.9×10^{-3} . These data were taken from Sosman's book (1927) and are values recomputed by Sosman from Wietzel's data. The difference in the mean specific heats (mean heat capacity) of the two forms of quartz is thus 4.7×10^{-3} (20° -gram calories per degree centigrade). Moser (1936) has determined the true specific heat, c_p , of quartz crystal from Brazil, and a graphical interpolation of his data indicates that the difference in true specific heat may be as much as 10×10^{-3} . Differences in the heat capacity of this magnitude produce the offset observed. After the galvanometer is deflected to the maximum, at the peak of the quartz inversion, it returns to the new "offset" zero without any overshooting. After the inversion is completed, the curve continues as a monotonous line.

The area under the curve is proportional to the heat effect accompanying the inversion of quartz. Gibson (1928) has determined the latent heat of the inversion to be 3.1 calories per gram. An attempt was made to correlate the area under the curve with the weight of the sample used in the reaction cell. Such measurements have been made for other substances and a proportionality relation between the area under the curve and the weight of the sample established. In this study, most of the thermal analysis curves were obtained using a resistance of 600 ohms in the differential thermocouple circuit. At this sensitivity the area under the curve is small and is approximately 0.18 square centimeters for a half gram sample of quartz. With such a small area, the error introduced by choosing the proper base line to close the loop is so large that a correlation between area under the curve and weight of sample could not be established by means of a number of trial measurements with a polar planimeter. An angular measurement such as that suggested by Dean (1947) gave no better agreement. Berkelhamer (1944) using a resistance of 50 ohms in the differential thermocouple circuit produced larger areas from which he obtained a "partial area under the curve" versus "weight of sample" relationship. His partial area represents about $30\% \pm$ of the total area.

CONSTANCY OF THE THERMAL CURVES OF QUARTZ

In order to detect any variation in the character of the thermal curves

of quartz two variables (grain size and thermal history) were studied.

Thermal analyses were made on samples of fairly uniform grain size and on heterogeneous mixtures. The maximum size tested was a sample of quartz crystals all of which measured about two millimeters in diameter, and the minimum size was a natural novaculite powder whose grain size was 25 microns and less. The heterogeneous mixtures of grains were prepared by grinding rock crystal to pass a 58-mesh cloth sieve. These samples all produced curves whose shape and character are fundamentally identical (see Fig. 1).

The effect of previous thermal history was investigated by analyzing specimens of different paragenetic histories and by successively running the same sample through several inversion cycles. Quartz crystals of low-temperature hydrothermal origin, low quartz paramorphs after high quartz, and novaculite gave the same pattern. Likewise, the low quartz paramorph after high quartz from Valles Mountain, New Mexico, was rerun four successive times and no significant variation was noted in the curves. Our experience with the thermal-analysis apparatus conforms with that of other investigators using different methods of studying the inversion of quartz.

METHOD OF CALIBRATING THE THERMAL ANALYSIS APPARATUS

The establishment of a base line is necessary for temperature measurement and a system commonly used with photographic recorders is to expose the sensitive paper to the direct undeviated light beams from the galvanometer mirrors. In the "drum type" camera exposures are made at four or five positions along the circumference. A line drawn through the points, so located, establishes the base line.

To illustrate the technique of calibration, a thermal record of a quartz-gibbsite mixture is used (Fig. 2). A line is drawn perpendicular to the base line and passing through the peak of the quartz inversion. The segment of the line AB is measured. Its endpoints A and B represent the position of the galvanometer beam at room temperature and at the inversion temperature of quartz, 573° C., respectively. It is necessary, therefore, to correct the measurement made above for the "cold-junction error."

The corrected measurement on the original record of Fig. 2 is 13.35 cms. This value divided into the temperature of the inversion, 573° C., yields the constant 42.95. This constant represents the value in degrees centigrade of one centimeter along the line perpendicular to the base line. Its use is illustrated in the determination of the decomposition temperature of gibbsite. A straight line is drawn perpendicular to the base line and passing through the gibbsite peak. The distance DE is measured and to it is added the correction for room temperature giving 7.35 cms. This

value multiplied by the factor given above, 42.95, gives 315° C. as the indicated temperature.

Although the relation between millivoltage and deflection of the galvanometer is a true proportionality, this is not true for the relation between temperature and deflection of the galvanometer. This lack of proportion-

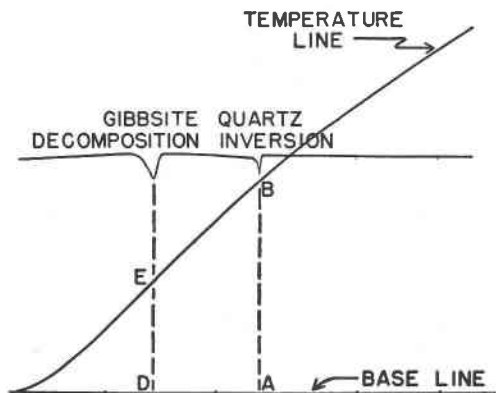


FIG. 2. Thermal analysis record of a mixture of 95% quartz and 5% gibbsite showing method of determining the temperature of the gibbsite dissociation.

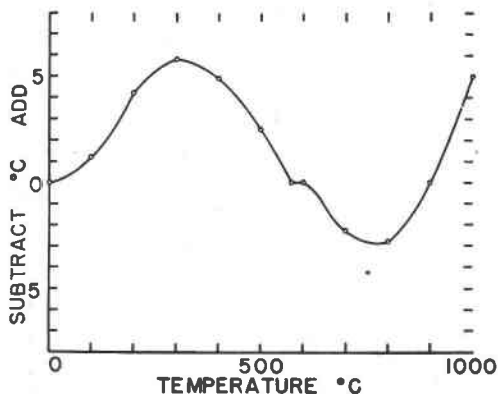


FIG. 3. Correction curve for temperatures observed with chromel: alumel thermocouple using quartz inversion temperature 573° C. as base point.

ality arises from the characteristics of the chromel: alumel thermocouple. For this thermocouple equal differences in millivoltage throughout the range of zero to 41.31 millivolts do not correspond to equal differences in temperature. To correct the indicated temperature for this difference a correction curve with its zero at 573° C., the inversion temperature of quartz, was constructed (Fig. 3). Using the millivoltage corresponding to

573° C. as the base, a true proportionality millivoltage for equal steps in temperature (100° C.) was calculated. The difference between the calculated millivoltage and the actual millivoltage gives the correction at a given temperature. The correction at 315° C. is thus 5.8° C. giving 321° C. as the temperature of the gibbsite decomposition for this particular sample.

Calibration at two additional points would be desirable for very accurate thermometry, but for most work in thermal analysis this is not required. A check on the sufficiency of the correction curve (Fig. 3) was afforded by an accidental recording of the heat effect accompanying the magnetic transition in nickel. Using the correction indicated by Fig. 3, the temperature of the transition is 353° C. which agrees very well with the accepted value of 354° C. \pm 1° C. found by Moser (1936).

OBSERVATIONS ON THE CALIBRATION OF THE THERMOCOUPLES

A selection of the data of twelve representative calibrations using quartz for the two chromel:alumel thermocouples used in the same thermal-analysis apparatus over a period of two and one-half years is given in Table 1. During this period the two thermocouples frequently became corroded at the hot junction and had to have new junctions welded together. The replacement of the old junction by a new junction always changes the value of the factor and this accounts for the difference between the runs C-410 and C-411.

The factors vary from a minimum of 40.72 to a maximum of 42.57 which represents a difference of 1.8° C. per centimeter. In Table 2, the temperature is computed for several positions on the record using the factor derived by direct calibration of the galvanometer, and the minimum and maximum values derived by calibration with quartz. The values in the table show that the difference between the selected factors increases as the temperature increases.

A study of Tables 1 and 2 shows that no great reliance can be placed on the value of the temperatures computed from the factor derived by the direct calibration of the galvanometer. Moreover, the value of the factors obtained by calibration with quartz shows that the factors change with continuous use of the thermocouple and whenever a corroded head is replaced. These results show that it is advisable to calibrate with quartz at frequent intervals. Mixtures containing quartz as a component when analyzed furnish a direct check on the calibration provided the quartz does not enter into a reaction with the other components. Since the rate of heating is so rapid, quartz rarely reacts, if at all, below 573° C.

One finds statements in the literature concerning the variation of the temperature of the peak in a nonreversible reaction and this has been

TABLE 1. CALIBRATION DATA FOR THE TEMPERATURE THERMOCOUPLES

Number of Run	Weight of Sample	Factor ° C./cm.	Resistance in series with thermocouple	Distance between base line and temperature curve	Locality
C-14		40.93	150 ohms.	14.00 cm.	Quartz-variety: rock crystal, Hot Springs, Arkansas.
C-26	0.5218 gms.	40.72	150	14.07	Same as above.
C-33	0.5329	41.67	600	13.75	Same as above.
C-60	0.5291	40.92	600	14.05	Same as above.
C-158	0.4917	40.78	600	14.10	Same as above.
C-292	0.6589	41.88	600	13.68	Same as above.
C-296	0.7528	41.67	600	13.75	Same as above.
C-320		41.10	600	13.95	Same as above.
C-401	0.6122	42.57	600	13.46	Same as above, a re-run of C-400.
C-408	0.6031	42.38	600	13.52	Quartz crystals, Valles Mountain, New Mexico, a re-run of C-407.
C-410	0.6031	42.13	600	13.60	Same as above, a re-run of C-407, 408, 409.
C-411	0.6171	41.67	600	13.75	Natural novaculite powder, Hot Springs, Arkansas.

Direct calibration of galvanometer 40.32

TABLE 2. A COMPARISON OF TEMPERATURES CALCULATED FROM THE VARIOUS FACTORS

Distance	Factor obtained by Direct Calibration of galvanometer = $F_g = 40.32^\circ \text{ C./cm.}$	Factors obtained by calibration with quartz		Difference $F_{q_2} - F_g$	Difference $F_{q_2} - F_{q_1}$
		Lowest $F_{q_1} = 40.72$	Highest $F_{q_2} = 42.57$		
5 cm.	202° C.	204° C.	213° C.	11° C.	9° C.
10	403	408	426	23	18
15	605	612	639	34	27
20	806	816	852	46	36
22	887	897	937	50	40

attributed to grain size, the presence of other materials, and rate of heating. It appears from this study that the variation in peak temperature may also arise from poor thermometry. If the variation in the peak temperature of a given reaction is studied it will be necessary to calibrate the temperature thermocouple. If the calibration is made in the nickel reaction block, only reversible processes such as the inversion of quartz should be used.

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