

Friction Effects and Pressure Calibration in a Piston-Cylinder Apparatus at High Pressure and Temperature

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The pressure of a piston-cylinder apparatus was calibrated at a temperature of 1100°C. The calibration is based on the quartz-coesite phase transition. Pressure losses are considerable and a correction of -11% at 1100°C and 35 kb is indicated for a compression run with talc as the pressure-transmitting medium. This correction was evaluated by comparing results obtained with talc and silver chloride pressure-transmitting mediums.

INTRODUCTION

In recent years increasing use of piston-cylinder apparatus at high pressure and temperature has been made in phase-equilibrium studies. It has been shown that hydrostatic pressure conditions are more closely attained in this type of apparatus than in an anvil apparatus [Boyd and England, 1960a]. However, there are uncertainties as to the pressure loss due to friction between the piston and the walls of the pressure vessel and due to friction and other possible effects inherent in the talc pressure-transmitting medium. We have investigated the magnitude of pressure losses in the piston-cylinder apparatus at high temperature by using two different pressure-transmitting mediums. Talc is normally used, but it has a substantial shear strength. Silver chloride was chosen as the pressure medium for comparison with talc because of its much lower shear strength.

Early estimates of the magnitude of pressure losses were based on calibrations using the bismuth and thallium transitions at room temperature [Boyd and England, 1960b]. They used silver chloride and talc pressure-transmitting mediums and determined the correction needed to account for pressure loss in the talc medium, assuming that silver chloride has a negligible strength. They concluded that a friction correction of -13% is needed at room temperature. They attributed the pressure loss to the shear strength of talc, and, since this will decrease with increasing temperature, they suggested that at high temperatures the friction

correction would be closer to $-8 \pm 5\%$ [Boyd and England, 1960a; Boyd, 1962]. In later work Boyd and England [1963] considered that at high temperatures the shear strength of talc is very low, and they no longer applied a friction correction.

Kitahara and Kennedy [1964], in their study of the quartz-coesite transition, applied a friction correction of -12% at 17.1 kb, -8% at 30 kb, and -7% at 41 kb for a compression cycle. They estimated this correction from a study of the melting point of mercury at different pressures [Klement *et al.*, 1963]. Their friction correction was determined at any specific pressure as half the difference between the compression and decompression strokes. They assumed that the pressure loss on a compression run was the sum of the piston-cylinder friction and friction in the talc.

Newton [1965], in work at pressures of 4 to 8 kb and temperatures of 640 to 860°C and using a piston-cylinder apparatus similar in design to Kennedy's apparatus, applied a pressure correction of -1.5 kb over the 4- to 8-kb pressure range; this represents a -37% to -19% correction. It was determined using the LiCl melting curve at about 700°C as the calibration point.

EXPERIMENTAL METHOD

The quartz-coesite phase transition at 1100°C has been chosen as the calibration point, since a considerable amount of high-pressure work in this laboratory has been done in the neighborhood of this temperature. Also, experience showed that when the sample temperature

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was 1100°C at pressures greater than 30 kb, there was no significant melting of the silver chloride pressure medium. Some minor melting in the immediate vicinity of the 'hot spot' may have occurred. The nearness of the temperature to the melting point of the silver chloride would also reduce its strength and so improve it as a pressure-transmitting medium. Silver chloride pressure cells were made by melting the silver chloride, pouring it into a mold, and then machining it to the required dimensions (Figure 1c).

The quartz-coesite transition is rapid at 1100°C if some moisture is present, so that run times of an hour length are adequate. A great deal of work has been done recently on establishing the quartz-coesite curve with piston-cylinder and other apparatus, and adequate results are available for comparison.

The apparatus used is based on the design of Boyd and England [1960b], and the experimental procedure is similar to that described by Boyd and England [1960a, b] and by Ringwood and Green [1964]. Temperature is measured with a Pt|Pt-10Rh thermocouple. Temperature calibration of a normal assembly with

talc as the pressure medium showed that the temperature gradient in the space normally occupied by the specimen capsule is less than 5°C. In a normal run, once thermal equilibrium is reached, the temperature varies by approximately 5°C on either side of the control point. Hence temperatures are believed to have a precision better than $\pm 10^\circ\text{C}$. Oil pressure applied to the ram is measured with a Heise gage with a precision of better than 0.1%. The nominal pressure on the sample (i.e., assuming perfect transmission of applied pressure) is computed from the measured oil pressure, using the known cross-sectional areas of the piston and hydraulic ram.

The starting materials consisted of very finely ground mixes of either (1) 94% quartz, 4% coesite, and 2% silicic acid or (2) 90% coesite, 5% quartz, and 5% silicic acid. The coesite used in these mixes was prepared from silicic acid subjected to a temperature of $900 \pm 60^\circ\text{C}$ and a pressure of 40 kb for 2½ hours. The first mix was used for most of the runs. A run was considered to be in the quartz field when the coesite had demonstrably disappeared and in the coesite field when the amount of coesite increased measurably. A few runs on the second mix demonstrated reversibility of the reaction.

Approximately 10 to 20 mg of undried sample was sealed in a platinum tube of wall thickness 0.015 cm. Three different ways of achieving the pressure-temperature conditions of a run were used:

1. Single-stage compression. The pressure was raised to the required value, then the temperature increased to 1100°C. This method resulted in final inward piston movement when used with talc (Figure 1a) and talc + boron nitride pressure mediums (Figure 1b). It was intended also to use it for the silver chloride + boron nitride pressure medium (Figure 1c), but when the temperature was increased, expansion of the assembly resulted in a pressure excess of 1 to 1½ kb, so that in actual fact the run was over-pressed and pressure had to be released. Thus, with the silver chloride, the single-stage application of pressure and temperature resulted in a decompression run.

2. Double-stage compression. The pressure was increased to about 2 kb below the required value. The temperature was then raised to

TABLE 1. Resu

Starting Material*	Type of Pressure Cell	
Q	T	One-s
Q	T	One-s
Q	T	One-s
Q	T + BN ₂	One-s
Q	T + BN ₂	One-s
Q	T + BN ₂	One-s
Q	T + BN ₂	One-s
Q	T + BN ₂	One-s
Q	AgCl + BN ₂	One-s
Q	AgCl + BN ₂	One-s
Q	AgCl + BN ₂	One-s
Q	AgCl + BN ₂	One-s
Q	T + BN ₂	Two-s
Q	T + BN ₂	Two-s
Q	AgCl + BN ₂	Two-s
Q	AgCl + BN ₂	Two-s
Q	AgCl + BN ₂	Two-s
Q	AgCl + BN ₂	Two-s
Q	T + BN ₂	Two-s
Q	T + BN ₂	Two-s
Q	T + BN ₂	Two-s
Q	T + BN ₂	Two-s
Q	AgCl + BN ₂	Two-s
Q	AgCl + BN ₂	Two-s
Q	AgCl + BN ₂	Two-s
Q	AgCl + BN ₂	Two-s
C	AgCl + BN ₂	Two-s
C	AgCl + BN ₂	Two-s

Q signifies mix composed of 94% quartz, 4% coesite, and 2% silicic acid.
C signifies mix composed of 90% coesite, 5% quartz, and 5% silicic acid.

1050°C, followed by final adjustment to the required value, and was completed with final adjustment to 1100°C.

3. Double-stage decompression first applied was about 5 kb below the required value and then the temperature was increased to 1050°C. Release of pressure to the required value followed and final temperature was increased to 1100°C.

In this way the quartz-coesite transition was approached from the quartz stability field (two-stage compression) or from the coesite stability field (two-stage decompression). The conclusion of a run the sample was examined by switching off the power to the sample and the relative amounts of quartz and coesite were estimated.

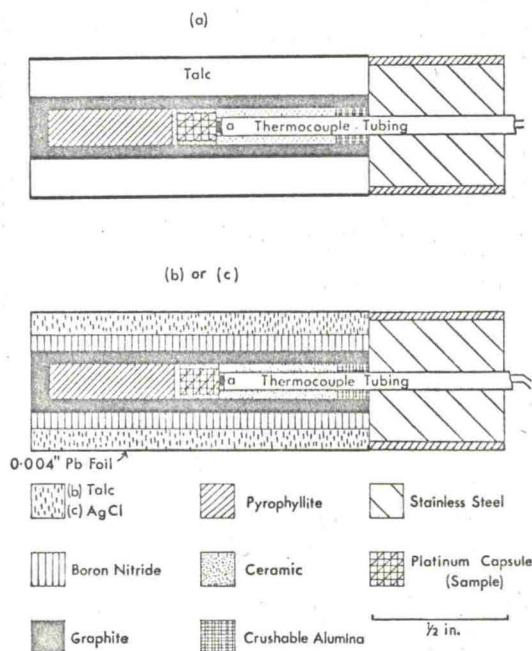


Fig. 1. Detail of types of pressure cells used in the calibration. Thermocouple junction, in contact with sample capsule.

TABLE 1. Results of Runs on the Quartz-Coesite Transition at 1100°C

Starting Material*	Type of Pressure Cell	Run Procedure	Nominal Pressure, kb	Time, min	Results
Q	T	One-stage compression	35	60	Quartz + trace coesite (<<4%)
Q	T	One-stage compression	35.5	60	Quartz
Q	T	One-stage compression	36	60	Quartz + almost equal coesite
Q	T + BN ₂	One-stage compression	35	60	Quartz
Q	T + BN ₂	One-stage compression	35.5	60	Quartz
Q	T + BN ₂	One-stage compression	36	60	Coesite + 50% quartz
C	T + BN ₂	One-stage compression	35	60	Quartz
C	T + BN ₂	One-stage compression	36	60	Coesite + trace quartz
Q	AgCl + BN ₂	One-stage decompression	35	60	Coesite
Q	AgCl + BN ₂	One-stage decompression	33	60	Coesite
Q	AgCl + BN ₂	One-stage decompression	31	60	Coesite + 60% quartz
Q	AgCl + BN ₂	One-stage decompression	30	60	Quartz
Q	T + BN ₂	Two-stage compression	35	60	Quartz
Q	T + BN ₂	Two-stage compression	36	60	Coesite + 60% quartz
Q	AgCl + BN ₂	Two-stage compression	31	60	Quartz
Q	AgCl + BN ₂	Two-stage compression	32	60	Quartz
Q	AgCl + BN ₂	Two-stage compression	33	15	Coesite + 70% quartz
Q	AgCl + BN ₂	Two-stage compression	34	50	Coesite
Q	T + BN ₂	Two-stage decompression	30	60	Quartz
Q	T + BN ₂	Two-stage decompression	32	60	Quartz
Q	T + BN ₂	Two-stage decompression	33	60	Quartz + trace coesite (4%)
Q	T + BN ₂	Two-stage decompression	34	60	Coesite + 60% quartz
Q	AgCl + BN ₂	Two-stage decompression	30	60	Quartz
Q	AgCl + BN ₂	Two-stage decompression	31	60	Quartz + trace coesite (<4%)
Q	AgCl + BN ₂	Two-stage decompression	32	60	Coesite
C	AgCl + BN ₂	Two-stage decompression	30.5	60	Quartz + 10% coesite
C	AgCl + BN ₂	Two-stage decompression	31.5	55	Coesite

Q signifies mix composed of 94% quartz, 4% coesite, and 2% silicic acid.

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compression. The pressure required value, then the tem- d to 1100°C. This method ward piston movement when figure 1a) and talc + boron ediums (Figure 1b). It was se it for the silver chloride + ure medium (Figure 1c), but, ture was increased, expansion sulted in a pressure excess of at in actual fact the run was pressure had to be released. ver chloride, the single-stage essage and temperature re- ession run.

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1050°C, followed by final adjustment of pressure to the required value, and the procedure was completed with final adjustment of temperature to 1100°C.

3. Double-stage decompression. The pressure first applied was about 5 kb above the required value and then the temperature was increased to 1050°C. Release of pressure to the required value followed and finally the temperature was increased to 1100°C.

In this way the quartz-coesite equilibrium was approached from the quartz stability field (two-stage compression) or from the coesite stability field (two-stage decompression). At the conclusion of a run the sample was quenched by switching off the power to the furnace. The sample was then examined by optical and X-ray means, and the relative amounts of quartz and coesite were estimated.

RESULTS

The conditions and results of the runs are summarized in Table 1 and Figure 2. There is no difference between the results obtained using talc or talc + boron nitride as the pressure medium. Also there is no significant difference between single-stage and two-stage compression runs.

The quartz-coesite transition at 1100°C occurs at a nominal pressure of 35.5 kb in a two-stage compression run with a talc + boron nitride pressure medium and at 33.0 kb in a two-stage decompression run with the same pressure medium. Thus the difference in the pressure of the quartz-coesite transition between the two-stage compression and decompression runs is 2.5 kb. This is attributed to friction between the piston and the walls of

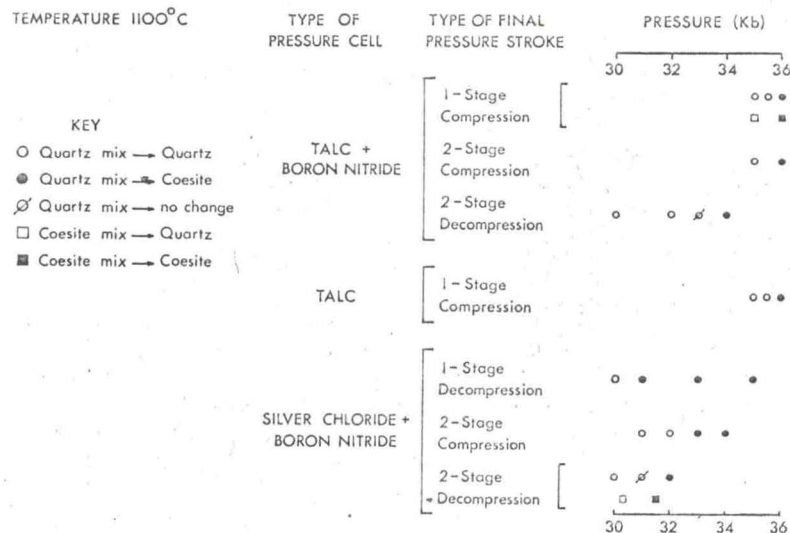


Fig. 2. Results of high-pressure runs on the quartz-coesite transition at 1100°C using different pressure cells.

the pressure vessel and to friction within the talc and boron nitride. It represents a -4% pressure correction to a two-stage compression run, and the quartz-coesite transition at 1100°C, using this correction, is placed at 34.3 kb.

With the silver chloride + boron nitride pressure medium for a two-stage compression run, the quartz-coesite transition at 1100°C occurs at a nominal pressure of 32.5 kb; in a two-stage decompression run it occurs at 31 kb. Thus the difference in pressure between compression and decompression results for the quartz-coesite transition is 1.5 kb. This is attributed to piston friction and to friction within the boron nitride, since friction losses in the silver chloride are considered to be negligible, and it represents a -2% friction correction to a two-stage compression run. The quartz-coesite transition at 1100°C, using this correction, is placed at 31.8 kb.

There remains a discrepancy of 2.5 kb between the results obtained using talc and silver chloride pressure mediums, even after corrections for friction losses have been made. To bring these results into agreement, a further correction of -7% is needed for a two-stage compression run with talc + boron nitride as the pressure medium.

DISCUSSION

This work indicates that at 35 kb and 1100°C a total pressure correction of -11% is needed on a two-stage compression run, and this correction appears to consist of two components. The first of these is an irreversible component being characterized by hysteresis; it is attributed to frictional losses between the piston and cylinder and in the talc + boron nitride pressure medium. This correction amounts to -4%. The second component of pressure loss is re-

versible (i.e., it is not steresis) and is attributed to the distribution of stress in the experimental work established of this component as a distribution of stress in likely to occur even in there is no irreversible piston friction. It is probably caused by differences in strengths and compressive components of the pressure medium. For example, the talc and silver chloride have substantially greater strength than graphite furnace and its especially since the graphite furnace is hotter than most of the other pressure cells. In boron nitride cylinders. Friction on the end of the pressure vessel at the base of the pressure vessel is the same as the actual pressure in the middle of the sample in the middle of the pressure vessel. This effect that causes the discrepancy between the results for the silver chloride and talc cell with significant strength.

In Table 2 a comparison is made of the results of previous workers with the results of this work. Good agreement is seen between England's early, corrected results and those from their design. We agree with their conclusion that the strength of the pressure medium increases with increasing temperature but that a pressure correction is therefore no longer required at higher temperatures. It probably remains essentially constant at the run temperature because of the small volume of the talc column in the vicinity of the hot spot, which is affected by changes in run temperature. It is shown that, as well as an increase in pressure loss, there is also a decrease in pressure loss due to the appreciable pressure cell.

The difference between the results of this work and Kennedy's apparatus were due to variations in design and to the different time factors used in the experiments used to determine the pressure correction. Kennedy and co-

TABLE 2. Quartz-Coesite Transition at 1100°C as Determined in Piston-Cylinder Apparatus

	Boyd and England [1960a]	Kitahara and Kennedy [1964]	Khitarov [1964]	This Work
Corrected pressure, kb	32.3	32.8	31.8	31.8
Uncorrected pressure, kb	35	35.3		35.5

versible (i.e., it is not characterized by hysteresis) and is attributed to nonuniform distribution of stress in the pressure cell. This experimental work establishes the magnitude of this component as -7% . This nonuniform distribution of stress in the pressure cell is likely to occur even in the ideal case where there is no irreversible pressure loss due to wall friction. It is probably caused by the differences in strengths and compressibilities of the various components of the pressure cell (Figure 1). For example, the talc and boron nitride will have substantially greater strength than the graphite furnace and its internal components, especially since the graphite cylinder is much hotter than most of the volume of the talc and boron nitride cylinders. Hence the mean pressure on the end of the piston in contact with the base of the pressure cell is not necessarily the same as the actual pressure exerted on the sample in the middle of the pressure cell. It is this effect that causes the discrepancy between the results for the silver chloride pressure cell with negligible strength and the talc pressure cell with significant strength.

In Table 2 a comparison is given between the results of previous workers and the present results. Good agreement is obtained with Boyd and England's early, corrected results. This is to be expected because our apparatus is built from their design. We agree with their suggestion [Boyd and England, 1963] that the shear strength of the pressure medium decreases with increasing temperature but do not agree with their conclusion that a pressure correction is therefore no longer required. The pressure loss probably remains essentially independent of the run temperature because only a very small volume of the talc column, in the immediate vicinity of the hot spot, will be markedly affected by changes in run temperature. We have shown that, as well as an irreversible frictional pressure loss, there is also a reversible pressure loss due to the appreciable strength of the pressure cell.

The difference between the pressure correction for our piston-cylinder apparatus and Kennedy's apparatus we attribute to slight variations in design and dimensions and also to the different time factor involved in the experiments used to determine the pressure correction. Kennedy and co-workers used short-

time melting experiments in their calibration. In our work, calibration experiments lasted an hour.

Good agreement with our corrected results and the Russian work is apparent (Table 2). We understand that the Russian apparatus is a two-piston-cylinder type, a piston entering each end of the cylinder. The friction and non-uniform distribution of pressure would probably be substantially smaller in such an apparatus than in the single-piston apparatus which we used.

CONCLUSION

Comparing our work at 1100°C and at pressures near 35 kb (pressure correction -11%) with Boyd and England's work at room temperature and in the approximate pressure range 20 to 40 kb (pressure correction -13%) [Boyd and England, 1960b] suggests that in the temperature range 0 to 1100°C a pressure correction of -11% on compression runs yields absolute pressures that are correct to within $\pm 2\%$ in the pressure range 20 to 40 kb. Since the effect of temperature on pressure loss appears to be comparatively small, the -11% pressure correction is probably applicable at temperatures well above 1100°C , but the uncertainty may be somewhat greater. Although Kennedy and co-workers worked under somewhat different physical conditions, their pressure correction is approximately comparable with our results in the same pressure range. Considering the results of all three investigations mentioned above, we believe that after applying a -10% pressure correction to a compression run at pressures greater than 15 kb we can expect an accuracy of $\pm 3\%$.

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PRESSURE (Kb)

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tion at 1100°C using dif-

a discrepancy of 2.5 kb be obtained using talc and silver mediums, even after corrections have been made. To bring into agreement, a further 7% is needed for a two-stage with talc + boron nitride as medium.

DISCUSSION

It is noted that at 35 kb and 1100°C a pressure correction of -11% is needed after a compression run, and this correction consists of two components. One is an irreversible component caused by hysteresis; it is attributed to pressure losses between the piston and the talc + boron nitride pressure cell. The correction amounts to -4% . The reversible component of pressure loss is re-

Determined

Khitarov [1964]	-This Work
31.3	31.8 35.5

- to 50 kilobars and temperatures up to 1750°C, *J. Geophys. Res.*, *65*, 741-748, 1960b.
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Glassy Spherules

Most students of cosmic magnetic opaque particles are tallied, partly because of their size and partly because it is difficult to identify silicate particles from terrestrial rocks [Wright *et al.*, 1963; Hodges, 1964]. However, we could hypothesize that some of the cosmic dust particles that are similar in composition to those found in the

In the precipitate of magnetic opaque particles collected on December 20, 1964, near Santa Fe, New Mexico, glassy spherules were found under a binocular microscope. One of the typical spherules is shown in Figure 1. In shape it is roughly spherical with a tail-like protrusion on one side. The face is bright, clear, and smooth. No fissures are observed on the surface. The transparent body with no internal structure. Its refractive index is 1.505. Its chemical composition is (in weight percent): Al₂O₃, 12.5; FeO (total), 3.0; Na₂O, 1.5; K₂O, 2.5. As the spherule is small, it was analyzed by X-ray fluorescence method using the electron



Fig. 1. The typical 'teardrop' spherule.